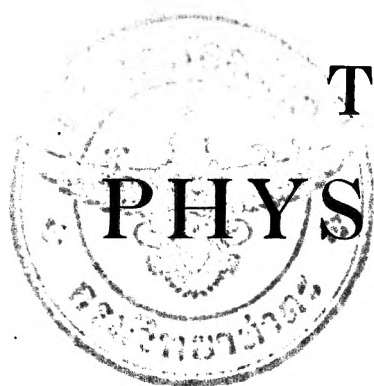




THE JOURNAL OF PHYSICAL CHEMISTRY

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ASSOCIATION BETWEEN POLYSILICIC ACID AND POLAR ORGANIC COMPOUNDS

BY R. K. ILER

Grasselli Chemicals Department, Experimental Station, E. I. du Pont de Nemours and Co., Inc.

Received June 29, 1951

The relative degree of association between polysilicic acid and various types of organic compounds in aqueous solution has been related to the structure of the organic compounds. The relative degree of association was measured by noting the solubilizing effect of the organic compounds on the precipitate obtained by mixing solutions of polysilicic acid and gelatin, other factors being held constant. In the absence of gelatin, the association of polar organic compounds with polysilicic acid is demonstrated by the fact that silica-organic complexes can be salted out of the aqueous mixture. Liquid complexes are obtained from freshly prepared solutions of polysilicic acid and polar organic compounds of low molecular weight. Solid precipitates are formed from aged solutions of the acid and organic compounds of higher molecular weight.

Since the compounds which were found to associate with polysilicic acid all contained electron-donor atoms, it was inferred that hydrogen bonds between the electron donor atoms and the silanol group might be involved. Since the degree of association is also found to be related to the potential surface energy of a number of the organic compounds, it is postulated that the formation of the complex involves oriented adsorption of the polar molecules on the surface of the polysilicic acid molecules.

No systematic study has heretofore been made of the complexes formed between soluble silicic acid and organic compounds. There have been previous indications of the existence of such complexes, such as the indefinite "adsorption compound" between silicic acid and methylene blue,¹ and the precipitate formed by adding egg albumin to silicic acid of high molecular weight as described by R. Willstätter, Heinrich Kraut and Karl Lobinger.²

In the course of tanning research in 1949, J. S. Kirk discovered that complexes were formed between silicic acid and ethers or amides, and that these could be salted out of solution as viscous oils or precipitates.³ Also, Kirk discovered that these polar organic compounds were effective in inhibiting the reaction between silicic acid and gelatin or hide substance.⁴ Since certain types of compounds, such as ethers and amides, which were found to be most effective in influencing the behavior of silicic acid, were also found by M. J.

Copley and C. S. Marvel⁵ to enter into association with molecules such as chloroform through the formation of a hydrogen bond, it was logical to suspect that the association complexes with silicic acid were likewise the results of hydrogen bonding. The association of the polar compounds with the polysilicic acid probably involves an oriented adsorption, so that the surface activity of the compound is undoubtedly an important factor. However, since most of the compounds studied are not "surface active agents" in the usual sense of the term, they will be referred to broadly as "hydrogen-bonding agents," for the sake of convenience.

General Behavior of the System Gelatin-Polysilicic Acid.—The observation that the precipitation of polysilicic acid by gelatin was inhibited by "hydrogen-bonding agents" offered a convenient point at which to begin experimentation. In preliminary qualitative tests, using a silicic acid sol prepared from sodium silicate and sulfuric acid in a standardized manner and in an aqueous medium at a constant pH of about 2.5, observations were made of the tendency of gelatin to precipitate silica with variation in age of the silica sol, pH.

(1) L. Pelet-Jolivet and N. Anderson, *Bull. soc. chim.*, [4] **5**, 510 (1911).

(2) R. Willstätter, Heinrich Kraut and Karl Lobinger, *Ber.*, **58B**, 2462 (1925); **61B**, 2280 (1928).

(3) J. S. Kirk, U. S. Patent, 2,408,654-2,408,656 (1946).

(4) J. S. Kirk, U. S. Patent, 2,276,314-2,276,315 (1942).

(5) M. J. Copley and C. S. Marvel, *J. Am. Chem. Soc.*, **62**, 3109 (1940).

concentration of electrolyte (sodium sulfate) and concentration of "hydrogen-bonding agent" (for example, acetone or diethyl "Carbitol"). Since the tendency of silicic acid to be precipitated by gelatin increased as the silicic acid polymerized, all experiments were carried out around pH 2 where polymerization is least rapid. With a sol of a given age, the precipitation characteristics were independent of pH in the range 1.5 to 3.5, and were also relatively independent of the concentrations of silicic acid and gelatin. When other factors were held constant, precipitation occurred when the concentration of salt exceeded a critical value. On the other hand, when all factors were held constant, including the concentration of salt, solubilization of the precipitate occurred (or precipitation was inhibited) when the concentration of the "hydrogen-bonding agent" exceeded a certain critical level. The coagulating effect of electrolyte was therefore offset by the solubilizing effect of the "hydrogen-bonding agent" on the gelatin-silicic acid complex.

The general behavior of the system is exemplified in Fig. 1, which shows the effects of concentration of sodium chloride, concentration of diethyl "Carbitol" (DEC) and the age of the silicic acid sol, on the formation of a gelatin-silicic acid precipitate in a system containing 0.5–2% gelatin and 1–5% SiO_2 at pH 2.5 and 27°. Each of the lines, repre-

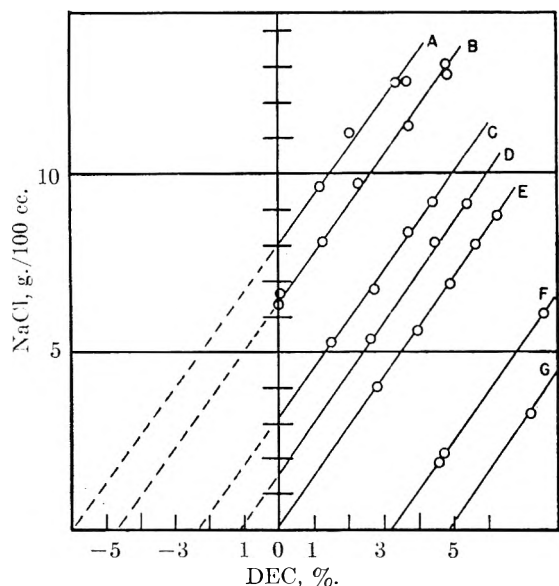


Fig. 1.—A, gelatin only, no silicic acid; B, very fresh, dilute sol; C, D, E, sols of intermediate age; F, sol becoming slightly cloudy; G, sol at very soft gel stage.

senting a particular sol, is the borderline above which a precipitate is formed. The experimental details have been described previously by R. K. Iler and P. S. Pinkney.⁶ It will be noted that gelatin alone is salted out of water when the NaCl concentration exceeds about 8 g. per 100 ml. However, when DEC is present, a higher salt concentration is required to cause precipitation as shown by Line A. Since a degraded gelatin of lower molecular weight requires a higher concentration of salt for precipitation, a standard type of gelatin was used. When silicic acid sols of increas-

ing age were also present in the system, lines B to G were obtained. An extrapolation of these lines to the DEC abscissa provided a convenient scale for characterizing the state of polymerization of the polysilicic acid.

Before discussing the effect of silicic acid in the system, the behavior of gelatin alone should be considered. The hypothesis is advanced that gelatin molecules in solution are associated with sheath of water molecules, probably held by hydrogen bonds. As salt is added, water is gradually removed from the gelatin molecules at an increasing number of points. These dehydrated sites on different molecules then associate with each other to form the cross-linked, gel network which is the precipitate. Shorter gelatin molecules of lower molecular weight thus require a greater number of crosslinks, and therefore a higher concentration of salt for coagulation. The solubilizing effect of the "hydrogen-bonding agent" is visualized as follows: When DEC, for example, is present in the system, the addition of salt brings about partial removal of water from the sheath surrounding the gelatin molecules as before, but these sites are immediately covered by adsorption of DEC molecules, so that cross-linking of gelatin molecules through hydrogen bonding at these sites is prevented.

When silicic acid is present, less salt is required to bring about precipitation. Thus, in the presence of a low molecular weight silicic acid,⁷ as represented by line, B, only 6.5% NaCl was required for precipitation as compared with 8.0% when gelatin alone was present. The gelatin thus acts as though it is of higher molecular weight. The effect of silica might be explained as follows: The polysilicic acid molecules may adsorb or otherwise hold together a number of gelatin molecules through hydrogen bonding. Furthermore, the larger polysilicic acid molecules can adsorb a larger number of gelatin molecules, and thus form a larger complex unit. However, this larger unit with the silica inside then behaves in much the same way as a single gelatin molecule of higher molecular weight, requiring less salt for precipitation. The mechanism of aggregation of the gelatin-silica complex is therefore the same as that of gelatin alone. This is borne out by the parallel slopes of the lines.

Some association between the "hydrogen-bonding agent" and silicic acid also undoubtedly occurs, since in most cases it is possible to salt out a complex of silicic acid and "hydrogen-bonding agent" even in the absence of gelatin by saturating the solution with sodium chloride.⁶ Some association of the "hydrogen-bonding agent" directly with the silicic acid, in competition with gelatin, is therefore likely.

Method of Comparing "Hydrogen-Bonding Agents."—In order to obtain a better understanding of the solubilizing mechanism, a comparison was made of the relative effectiveness of a wide variety of polar organic compounds so that a correlation could be made between structure and the "hydrogen-bonding activity." The method consisted in measuring the minimum concentration of the "hydrogen-bonding agent" required to inhibit

(6) R. K. Iler and P. S. Pinkney, *Ind. Eng. Chem.*, **39**, 1379 (1947).

(7) Cryoscopic measurements show 6 to 10 SiO_2 units per molecule.

the formation of the gelatin-silicic acid precipitate, all other factors remaining constant, particularly the characteristics of the silicic acid. It was not always possible to reproduce exactly the preparation of a silicic acid sol, and since it was found that the absolute concentration of hydrogen-bonding agent required to inhibit precipitation of the gelatin-silica complex varied several fold as the silica sol was aged for 24 hours, the following device was employed to give reproducible comparative values of hydrogen-bonding activity:

A particular hydrogen-bonding agent (HBA), dimethoxytetraethylene glycol (DMTEG), was used as a standard against which the relative effectiveness of the other organic compounds could be compared. Its relative effectiveness was arbitrarily assigned a value of 100. Then, the relative effectiveness of each HBA was defined as

$$\frac{\text{molar concentration of HBA required to inhibit precipitation}}{\text{molar concentration of DMTEG required to inhibit precipitation}} \times 100$$

The above ratio was found to be independent of the age of the silica sol within $\pm 5\%$.

However, many types of organic compounds do not have a solubilizing effect on the precipitate. Compounds which are insoluble in water have no effect; also highly hydroxylated compounds such as ethylene glycol or sugar are inactive. Other compounds tend to coagulate the silica even in the absence of gelatin.

Relation Between Structure and Activity.—The compounds which solubilize the silica-gelatin precipitate can be divided into two classes, (a) non-ionic water soluble compounds such as alcohols, ethers, ketones and amides, and (b) short-chain amines which are in the form of salts in the pH range employed (1.5–3.0). In general, it can be said that in any homologous series, the solubilizing activity increases with the size of hydrocarbon groups in the molecule to the point where the members become immiscible with water or cause independent precipitation of silicic acid, and thereby become ineffective. With a given number of carbon atoms in the molecules, the activity increases with decrease in the number of hydrogen atoms attached to the polar oxygen or nitrogen atoms. Thus, ethers are more effective than the isomeric alcohols and tertiary amines are more active than the isomeric primary and secondary amines.

The data in Table I suggest that in any given series the solubilizing action is in some way related to the ratio of the number of carbon atoms to polar atoms in the molecule. Thus, the solubilizing effect increases with the size of the hydrocarbon groups. In general, nitrogen (amides) is a more effective polar group than oxygen (ethers, ketones). The higher alcohols, glycols, ketones and amides are ineffective, probably because they are too insoluble in water. On the other hand, the higher amines, although soluble in water in the form of their salts, cannot be shown to have a solubilizing action on the gelatin-silica complex because they precipitate silica, probably in combination with some gelatin.

The introduction of hydroxyl groups into a given

molecule decreases the activity, since this results in a net decrease in the ratio of carbon atoms to electron rich atoms (nitrogen, oxygen). The effect may be similar to that observed when an extra solubilizing group is introduced into the hydrocarbon chain of a wetting agent, decreasing its effectiveness.

When two oxygen or nitrogen atoms are present in a molecule, the effect is additive, providing the ratio of non-polar to polar groups in the molecule is maintained. Thus, as shown in Table I, the activity of the 2-methyl-2,4-pentanediol is the same as that of one molecule of ethanol plus one of *t*-BuOH, to which it is structurally equivalent. Other examples are afforded by the *N*-substituted diamides.

Multiplicity of "Hydrogen-Bonding" Groups.—The association of a hydrogen bonding agent containing only one oxygen atom (*e.g.*, acetone) with the gelatin-polysilicic acid complex is probably relatively unstable, since the agent molecule is held to the complex by only one bond. However, when a number of electronegative atoms are located along the length of an organic molecule, as in a polyethylene glycol, with a certain number of carbon atoms separating the electronegative atoms to permit localized polarization, the "hydrogen-bonding" effect is much more pronounced. It is logical to expect that it would require a great deal more energy to break all the bonds simultaneously.

The increasing effectiveness of a hydrogen-bonding agent with increasing polyfunctionality in preventing precipitation of the gelatin-polysilicic acid complex is shown in Table II.

This increased activity with higher molecular weight is also evident in the behavior of water soluble polymers with polysilicic acid in the absence of gelatin. For example, the water-soluble polyamides or proteins such as gelatin, higher polyethylene oxides, and methyl cellulose, combine with polysilicic acid forming either liquid or solid precipitates, depending on the degree of polymerization of the silicic acid and the concentration of salt in the solution.

Relation Between "Hydrogen-Bonding Activity" and "Surface Activity."—Polar molecules tend to become concentrated at the vapor-liquid interface of their aqueous solutions, the hydrocarbon groups being oriented toward the vapor phase.⁸ The same forces apparently tend to concentrate the polar molecules at the interface between salt solution and the polysilicic acid-gelatin complex or, in the absence of gelatin, between salt solution and the polysilicic acid micelles. The forces at the interface may involve the formation of hydrogen bonds. Thus, W. D. Harkins and G. E. Boyd⁹ indicate that the polar group is strongly oriented toward polar solids such as silica; in such a case, a bond involving hydrogen may be postulated.

It is observed in Table III, that the "potential surface energy" (*A*) is proportional to the square root of the "hydrogen-bonding activity" as measured by our empirical method. It will be noted

(8) Irving Langmuir, *J. Am. Chem. Soc.*, **39**, 1848 (1917).

(9) W. D. Harkins and G. E. Boyd, *ibid.*, **64**, 1203 (1942).

TABLE I

Com- parison	Compound	Relative molar effectiveness
(Standard)	Dimethoxytetraethylene glycol	100
Alcohols	Methanol	3
	Ethanol	6
	Isopropyl alcohol	11
	<i>t</i> -Butyl alcohol	16
Glycols	Ethylene glycol	0
	Propylene glycol	7
	3-Methyl-1,2-butanediol	18
	Hexamethylene glycol	27
Ketones	Acetone	17
	Methyl ethyl ketone	25
Amides	Formamide	0
	N-Dimethylformamide	25
	N-Diethylformamide	40
	Acetamide	11
	N-Dimethylacetamide	41
	N-Diethylacetamide	54
	N-Isobutylacetamide	22
	Urea	7
	N-Tetramethylurea	44
Amines (as salts)	Primary	
	Methylamine	0
	Cyclohexylamine	25
	2-Ethylhexylamine	32
	<i>m</i> -Toluidine	58
	Secondary	
	Dimethylamine	0
	Diethylamine	19
	Piperidine	38
	Dibutylamine	65
	Diamylamine	70
	Tertiary	
	Trimethylamine	14
	Pyridine	42
	Quinoline	66
	Cyclohexyldiethylamine	117
Effect of hydroxyl group	(C ₂ H ₅ O-C ₂ H ₅ O-C ₂ H ₅)	Activity = 32
	(C ₄ H ₉ O-C ₂ H ₅ O-C ₂ H ₅ OH)	30
	(CH ₃ -CO-O-CH ₃)	10
	(HO-CH ₂ -CO-OCH ₃)	8
	((C ₂ H ₅) ₂ N-CO-CO-N(C ₂ H ₅) ₂)	68
	((HOC ₂ H ₅) ₂ N-CO-CO-N(C ₂ H ₅ OH) ₂)	27
Compari- son of polar groups	CH ₃ COOH	6
	CH ₃ -CH ₂ OH	6
	CH ₃ CN	6
	(CH ₃ -CO) ₂ (diacetyl)	13
		(6.5 per CH ₃ -CO radical)
	C ₂ H ₅ -COOH	13
	C ₂ H ₅ -CH ₂ OH	11
Additive effects	(2Me-2,4-pentane diol)	23
	(CH ₃ -CHOH-CH ₂ -C(OH)(CH ₃) ₂)	
	(Ethanol + <i>t</i> -butyl alcohol)	22
	(CH ₃ -CH ₂ OH + CH ₃ -C(OH)(CH ₃) ₂)	
	(NNN'-tetramethylsuccinamide)	
	((CH ₃) ₂ N-CO-CH ₂ -CH ₂ -CO-N(CH ₃) ₂)	80
	(2 moles of N-dimethylacetamide)	
	((CH ₃) ₂ N-CO-CH ₃ + CH ₃ -CO-N(CH ₃) ₂)	82
	(NNN'-tetramethyloxamide)	
	((CH ₃) ₂ N-CO-CO-N(CH ₃) ₂)	59
	(2 moles of dimethylformamide)	
	((CH ₃) ₂ N-CO-H + H-O-C-N(CH ₃) ₂)	50

TABLE II

EFFECTIVENESS OF ETHER GROUPS IN POLYETHYLENE

GLYCOLS		
No. of ether groups per mole	Molar effectiveness	Effectiveness per ether group
1	15	15
2	31	15.5
3	49	16.3
5	103	20.6
8	229	28.7

TABLE III

Compound	(A) Potential surface energy, cal. per mole	(B) H.B. activity	Calcu- lated (A/√B)
CH ₃ COOH	1710	6	700
C ₂ H ₅ COOH	2290	13	635
CH ₃ OH	1240	3	715
C ₂ H ₅ OH	1820	6	745
C ₃ H ₇ OH	2430	11	730
C ₄ H ₉ OH	2825 (3080)	16	706
CH ₃ -COOCH ₃	2340	10	740
CH ₃ -CO-CH ₃	2170	17	525
CH ₃ OH-CH ₃ OH	563	About 1 or less	...
CH ₃ -CONH ₂	740	11	223

that $A/\sqrt{B}$ is essentially constant except in the cases of acetone and acetamide, in which lower values are obtained. This would indicate that these two materials are more effective in their interaction with silicic acid than would be predicted on the basis of the surface tension of their aqueous solutions. It is thus probable that in measuring hydrogen-bonding activity we are actually measuring a quantity which is a direct function of the surface activity. Irving Langmuir⁸ cites data by Gurvich to show that the surface energy is also related to the heat of absorption of organic fluids on clay and fullers earth, and also that it is related to the ability of these fluids to disperse fullers earth (a siliceous material).

This leads to the conclusion that what we have termed the "hydrogen-bonding effect" may amount to measuring the relative preferential adsorption of organic compounds from aqueous salt solution on the surface of the molecular units of polysilicic acid or the gelatin-polysilicic acid complex.

Fundamental Nature of the Complex Between Polar Organic Molecules and Polysilicic Acid.—The structure of a complex involving polysilicic acid and the "hydrogen-bonding agent" may be visualized as consisting of molecules of the organic reagent adsorbed on the surface of the highly branched, roughly spherical polysilicic acid molecule. The hydrocarbon groups of the reagent are probably oriented away from the polar polysilicic acid surface. If gelatin is not present, saturation of the solution with salt will further increase the concentration of the "hydrogen-bonding agent" at the surface of the polysilicic acid molecules, until the surface is completely covered, forming essentially a droplet of the organic reagent containing the silica. If the units of polysilicic acid are small, a separate liquid phase consisting of "hydrogen-bonding agent" and silica may be formed. If the molecular weight of silicic acid is high, an emulsion or a precipitate is formed.

Experimental

The following solutions of gelatin, hydrogen-bonding agent, and silica sol were prepared in such a way as to contain about equivalent concentrations of electrolyte (Na₂SO₄) and to have a pH of about 2.5. Thus, upon mixing these in various proportions, a relatively constant ionic strength and pH were maintained.

Standard Solutions. Sodium Silicate.—Grasselli JM grade sodium silicate containing an SiO₂/Na₂O weight ratio of 3.25 (29.6% SiO₂, 9.1% Na₂O) was dissolved in distilled water to give a solution which was 2.11 molar with respect to SiO₂.

Sulfuric Acid.—A 20% solution of sulfuric acid (C.P.) was standardized against the above sodium silicate solution as follows: 100 ml. of the acid solution was diluted with about 200 ml. of water and titrated with the sodium silicate solution with violent agitation until the pH of the mixture reached 2.5. The exact volume of sodium silicate solution was noted for the purpose of calculating the relative quantities to be used subsequently in preparing the sol.

Gelatin Solution.—Twenty grams of high grade Knox XXX gelatin was swollen in 380 g. of distilled water at 25°. To this was added 1400 ml. of distilled water at 70° and the mixture stirred until solution was complete. After the gelatin had dissolved there was added 68 g. of anhydrous sodium sulfate and 16.2 ml. of 20% sulfuric acid solution. The mixture was then adjusted to a pH of 2.5 by the addition of a few ml. of 20% sodium hydroxide solution.

Hydrogen-Bonding Agent Solution.—Twenty grams of the hydrogen-bonding agent, together with sodium sulfate and sulfuric acid, were made up into a total volume of 100 ml. at a pH of 2.5. For convenience in making up the solution, a stock solution of sodium sulfate was prepared, containing 200 g. of sodium sulfate and sufficient sulfuric acid to bring the final pH to 2.5, dissolved to a total volume of 1 liter. The solution of hydrogen-bonding agent was then made up as follows: 20 g. of hydrogen-bonding agent, 0.8 ml. of 20% sulfuric acid, 20 ml. of the stock sodium sulfate solution, made up to a total volume of 100 cc. The amount of acid used was adjusted so that the pH of the final solution was 2.5. The gelatin solution should be stored at about 30°. It is unstable and should not be used after it is two days old.

Preparation of Silicic Acid Sol.—A typical sol was prepared as follows: 118.3 ml. of 20% sulfuric acid was diluted with 282 ml. of distilled water. This was placed in a beaker and agitated violently by means of an air-driven stirrer; 400 ml. of the standard silicate solution was then added from a pipet (or other small orifice) to the vortex of the stirred acid. The sol was then kept at a relatively constant temperature between 25 and 30°. The pH should be between 2.3 and 2.5.

Method of Conducting Titration.—Five ml. of the silica sol was pipetted into a 1 × 6" test-tube. From 0.2 to 10 ml. of the standard hydrogen-bonding agent solution was added, and the mixture then titrated with standard gelatin until a definite heavy turbidity was reached, the sample being shaken after each addition of gelatin. The end-point was observed by holding a tube against a 1/4" diameter aperture in a shield behind which was located a 100-watt lamp. The end-point was taken arbitrarily as the point at which the turbidity was sufficient to blur the edges of the aperture. Since the turbidity developed rapidly at the end-point, any convenient method of noting the increase in turbidity seemed satisfactory. In later work a photoelectric method was used.

In conducting the titration the mixture should be well shaken for 5 to 10 seconds after each addition of reagent. The temperature should be 27 ± 2°; this can conveniently be adjusted by shaking the tube in warm or cold water as required.

Most of the comparisons of the hydrogen-bonding agents were conducted on silicic acid sols which had been permitted to age between 1 and 3 hours after preparation at a temperature of 25–30°. Since during this time the silicic acid polymerized to an appreciable extent and the precipitation characteristics had changed, comparisons of the different

hydrogen-bonding agents with the standard were carried out within a period of a few minutes. In order to avoid this inconvenience, a somewhat different procedure was used in the latter part of the work. The silicic acid sol was made up with sufficient acid to give a pH of 2.5, aged for 1 hour at 25°, and then sufficient 20% sulfuric acid added to lower the pH to between 1.8 and 2.0, and the sol stored at 0°. Samples for titration were then warmed to 27° and used without further pH adjustment, since it was found that in the final mixture the pH was usually between 2.2 and 2.5, a variation insufficient to affect the results.

With each hydrogen-bonding agent a series of titrations was made, for example using 1, 1.5, 2, 2.5 and 3 cc. of the solution of hydrogen-bonding agent and the corresponding volumes of gelatin required to cause the appearance of turbidity were noted. On a triangular graph paper, the percentage by volume of these solutions (a) silicic acid sols, (b) hydrogen-bonding agent solutions and (c) gelatin solutions were plotted, giving a curve running more or less parallel to the gelatin-silica sol axis. Since the curve is slightly concave toward the silica-gelatin axis, the maximum value of the concentration of the hydrogen-bonding agent was noted. Comparison of these maximum concentrations for a candidate hydrogen-bonding agent and the standard hydrogen-bonding agent (dimethoxy tetraethylene glycol) was then noted. The ratio of the effectiveness of the candidate with respect to the effectiveness of the standard was taken to be inversely proportional to the maximum concentration required in each case to prevent precipitation.

While the absolute concentrations required to prevent precipitation varied several-fold as the silica sol was aged for 24 hours, the ratio of the two values checked within ±5%.

Other procedures for comparing the relative solubilizing effect of different hydrogen-bonding agents under fixed conditions of pH, electrolyte concentration, and degree of polymerization of the silicic acid have been used successfully. Since the freshly formed gelatin-silica precipitate is readily redissolved, the order of addition of the reagent is not important. For example, a relatively satisfactory procedure is to mix equal volumes of the gelatin solution and silicic acid sol and immediately titrate with the solution of hydrogen-bonding agent until the precipitate is dissolved. However, it has been noted that if the gelatin-silica precipitate stands for more than a minute or two, it becomes more difficult to dissolve. Consequently the method described above is preferred, since the end-point is reached from the side of increasing rather than decreasing turbidity. Typical data on the maximum concentration of dimethoxy tetraethylene glycol in the final titration mixture, as read from the triangular plot of a titration curve, is given in Table IV, which shows the increase in the required concentration as the sol is aged at 25° and at pH 2.5.

TABLE IV

Concn. of dimethoxytetraethylene glycol, g. per 100 ml.	Age of sol, hours
8	0.5
11	1
15	2
22	5
33	18
35	29

POLYMERIZATION OF SILICIC ACID: RETARDING EFFECT OF CHROMATE ION

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The chromate ion is unique among the common inorganic anions, in that it retards the gelling of aqueous silicic acid in the pH range about 1 to 2. It is postulated that the concentration of polymerizable silicic acid may be reduced through formation of an unstable silico-chromic acid which exists in equilibrium with the free acids. However, the complex does not seem to be sufficiently stable to prevent polymerization, since the silicic acid eventually gels.

It has been found that chromic acid is unique among inorganic acids in retarding the polymerization of silicic acid. Since chromic acid is effective in retarding gel formation over the range where either hydroxyl ions or fluoride ions¹ function as catalysts, but instead may reduce the concentration of polysilicic acid by forming a loose complex, possibly analogous to a heteropoly acid. While no further investigation is planned, the identification of the postulated silicochromic acid would be of interest.

Experimental

Reagent Solutions. **Sodium Dichromate.**—One hundred grams of Mallinckrodt Analytical Grade was dissolved in 100 ml. of water, and the pH adjusted by adding 2.0 ml. of 4 molar CrO_3 solution and 1.50 ml. of 6 *N* NaOH solution. The final volume was 132 ml., and the pH was 1.9.

Chromic Acid.—Four moles per liter of reagent grade CrO_3 .

Sodium Silicate.—6453 g. of Grasselli JM Grade sodium silicate solution, containing 29.7% by weight of SiO_2 and 9.2% Na_2O , was diluted to 17.7 liters, giving a solution 1.8 molar in SiO_2 and 1.08 normal in sodium ion.

Sulfuric Acid.—Grasselli C.P. H_2SO_4 was diluted to a strength of 4.65 *N*.

Procedures. (a) **Preparing Sols from Acids and Sodium Silicate.**—In all cases, silicic acid sols were prepared by placing the solution of acid and required additional water in a beaker fitted with a high speed stirrer operating upwards

of 3000 r.p.m., with propeller blades set to force the liquid toward the bottom in a steep vortex. The silicate solution was run from a dropping funnel through a quarter-inch glass tube, with the end constricted to form an orifice about 1.5 mm. in diameter, situated so that the stream was directed into the vortex. The time of addition ranged from one to five minutes, and within this variation, appeared to have no effect on the nature of the sol.

(b) **Noting Gel Time.**—The sols were permitted to stand at room temperature ($25 \pm 3^\circ$) until they began to appear viscous, after which they were observed carefully by tilting the beakers slightly. Gelling was assumed complete when the sol was sufficiently solid to show no signs of flowing when tilted. Gelling was rapid once it started, usually becoming complete within a period of less than 5% of the total time required to gel.

Results

Two series of experiments were required to explore the variation in gel time with variation of $\text{CrO}_3:\text{SiO}_2$ ratio at relatively constant pH in the range 1.3 to 1.7.

Series A.—These sols, 1.0 molar in SiO_2 , were made from sodium silicate and mixtures of H_2SO_4 and H_2CrO_4 . However, in the case of sols in the desired pH range, there is an upper limit of the ratio of $\text{CrO}_3:\text{SiO}_2$ obtainable by this method.

Series B.—In this case, sodium dichromate solution was added to a sol made from chromic acid and sodium silicate, in order to obtain a higher ratio of $\text{CrO}_3:\text{SiO}_2$ than in Series A. It was also established that it made no difference whether chromate was present at the moment of formation of silicic acid, or immediately afterward. A sol was made from 82.5 ml. of 4.0 molar chromic acid, 44.0 ml. of water and 276.5 ml. of sodium silicate solution. Some of the water was thus omitted, so that the SiO_2 concentration was greater than 1.0 molar. Varying proportions of dichromate solution and water were then added to achieve the desired $\text{CrO}_3:\text{SiO}_2$ ratio and concentration.

The data from Series A and B are shown in Fig. 2.

Comparison of Chromic with Other Acids.—Series of sols with chromic and other acids were prepared having a silica concentration of 1.0 molar SiO_2 and ranging in pH from about 0 to 2.5. The unique behavior of chromic acid is shown in Fig. 1.

Discussion

Assuming that CrO_3 in some way combines with a portion of the silicic acid, and knowing from earlier unreported experiments that in this type of sol in the pH range 1.3–1.7, the gel time varies inversely with the square of the concentration of silicic acid, it is possible to calculate how much silicic

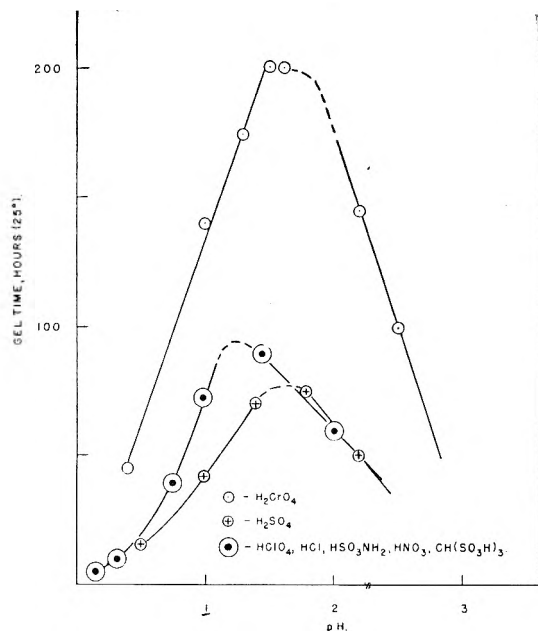


Fig. 1.—Gelling of silicic acid sols made with various strong acids.

(1) R. K. Iler, *This Journal*, **56**, 673 (1952).

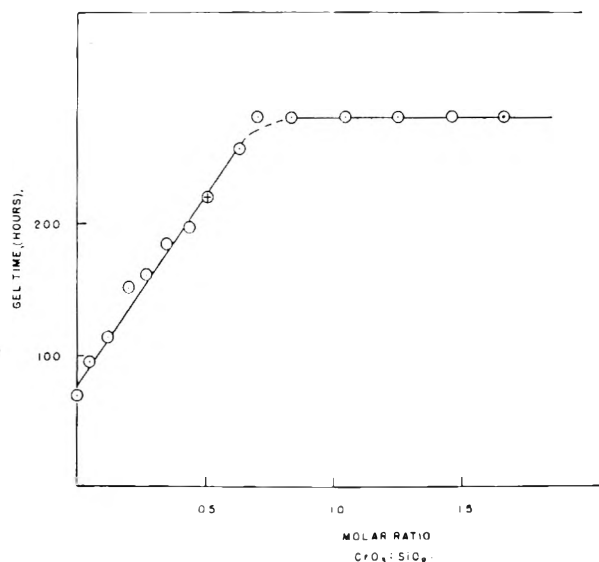


Fig. 2.—Effect of $\text{CrO}_3:\text{SiO}_2$ ratio on 1.0 molar SiO_2 sols at pH 1.4 to 1.6.

acid might be combined with the chromic acid: Thus

$$F^2t = K$$

where F = molar concentration of free silicic acid calculated from the gel time; t = gel time in hours. When no chromic acid is present

$$K = (1.0)^2(69) = 69$$

Let S = total molar concentration of SiO_2 present and C = molar concentration of chromic acid present, then the ratio of combined silicic acid to total chromic acid is $(S - F)/C$. Data from Fig. 2 were employed to plot the curve of Fig. 3.

The results of this calculation suggest that when CrO_3 is present at low concentration, as many as two moles of SiO_2 combine with one mole of CrO_3 . However, at higher concentrations, chromic acid itself at pH 1.3–1.7 undoubtedly polymerizes to polychromic acid. This may explain the ineffectiveness of excess chromic acid in preventing the gelling of silicic acid, since at higher concentrations

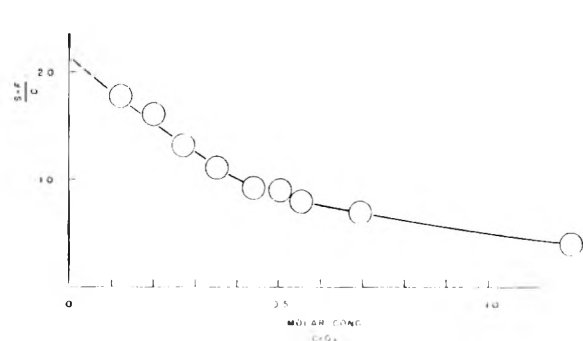


Fig. 3.—Ratio of "combined SiO_2 ": CrO_3 versus concentration of CrO_3 .

only a limited, relatively constant concentration of monomeric CrO_4^{-2} may be present in solution to combine with the silica.

In order to ensure that chromic acid is not in some way combining with trace amounts of fluoride, which is known to catalyze gelling, tests were repeated at pH 1.0 and 1.4 with a $\text{CrO}_2:\text{SiO}_2$ ratio of about 0.6, using very pure sodium silicate, containing less than 1 p.p.m. fluorine, as compared with several times this amount found in the sols made from commercial silicate. The sols were not appreciably more stable. It is concluded that combination with fluoride is probably not a factor.

In order to learn whether molybdic acid affects the rate of gelling, sufficient sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) was added to sodium silicate to give a molar ratio of $\text{SiO}_2:\text{MoO}_3$ of 20:1. This was then used with sufficient sulfuric acid to produce a mixed sol 1.0 molar with respect to SiO_2 , at a series of pH values.

pH	Gel time, hours
1.15	16.5
1.35	20.0
1.68	26.0
1.83	34.0
2.20	26.0
Control 1.65	32.0 (contained no molybdate)

It is thus evident that, unlike chromic acid, molybdic acid accelerates gelling.

POLYMERIZATION OF SILICIC ACID: CATALYTIC EFFECT OF FLUORIDE

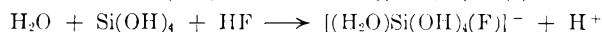
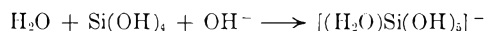
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The observed maximum stability of silicic acid in aqueous solution at about pH 1.5 has been found to be due to the fact that polymerization and gelling is catalyzed above this pH by the hydroxyl ion and below this pH by trace impurities of fluoride. The reaction rate at low pH is proportional to the concentration of hydrogen as well as fluoride ions. The catalytic action of fluoride is inhibited by traces of aluminum, beryllium, thorium or iron, which probably lower the concentration of free fluoride ion through complex ion formation. Acidic sols made from very pure sodium silicate are less stable than those made from commercial silicate which contains traces of aluminum and other stabilizing metals.

It has long been known that in weakly acidic solution there is a pH range of from about 1 to 3, where silicic acid polymerizes to form silica gel least rapidly. Above this pH range, the gel time varies inversely with the hydrogen ion concentration, according to Hurd, Raymond and Miller.¹ Thus, from pH 3 to 5 the rate is a function of hydroxyl ion concentration. However, below about pH 3, Hurd and Barclay² present data which indicate that the rate of polymerization is proportional to the concentration of the hydrogen ion rather than the hydroxyl ion. Further evidence that two different reaction mechanisms are involved, is the fact that the energy of activation of the polymerization is of the order of 16.0–17.0 kcal./mole in the higher pH region,^{3,4} while at very low pH, where the reaction appears to be catalyzed by hydrogen ion, the energy of activation is in the range of 9.0 to 11.0 kcal./mole.²

A further investigation of the gelling of silicic acid at low pH has now revealed that the polymerization is not catalyzed by hydrogen ion alone, but is simultaneously dependent upon trace amounts of fluoride ion present as an impurity. It has been further found that the effect of fluoride may be offset by trace amounts of aluminum ion, also present as an impurity. Since the rate of polymerization in the presence of a constant concentration of fluoride (and aluminum) is proportional to the concentration of hydrogen ion, it is concluded that the effective catalyst is hydrogen fluoride. The polymerization of silicic acid is therefore catalyzed by HF and OH⁻. The hypothesis is advanced that the polymerization mechanism involves the temporary expansion of the coordination number of silicon from four to six, yielding unstable intermediate complexes, for example



In the absence of these catalysts, monosilicic acid should be quite stable. The reported difference in the energy of activation of the polymerization reaction at higher and lower pH is undoubtedly due to the fact that two different catalysts are involved.

The stabilizing effect of Al⁺³ is probably due to the removal of fluoride ion through the formation of a stable ion such as [AlF₆]⁻³. Other metal ions

which have a similar effect are beryllium, thorium and iron.

Experimental

Preparation of Silicic Acid Sols.—Solutions were prepared as follows: 6453 g. of Grasselli JM Grade sodium silicate solution containing 29.7% SiO₂ and 9.2% Na₂O (as alkali) was diluted to a volume of 17.7 liters, giving a solution 1.8 molar in SiO₂ and 1.08 normal in alkali. Grasselli C.P. sulfuric acid was diluted to a strength of 4.65 normal.

In a typical preparation of a silicic acid sol 1 molar with respect to SiO₂, 86 ml. of the sulfuric acid solution and 138 ml. of water were placed in a deep narrow beaker, fitted with a high speed stirrer with blades rotated so as to force the liquid downward into a vortex. Then 276.5 ml. of the solution of sodium silicate was introduced from a dropping funnel into the center of the vortex through a glass tube having the tip constricted to an orifice about 1.5 mm. in diameter. The time of addition was regulated to be within the range of one to five minutes. The pH of the sol was then determined immediately, and was about 1.5. However, by varying the proportion of water and acid, any pH from 0.5 to 3.0 was easily reproduced. Where solutions of sodium fluoride and aluminum sulfate were to be added, a corresponding amount of water was omitted in making up the sol, so that the final silica concentration remained 1.0 molar.

The gel time was observed by tilting the beaker and noting when the sol failed to flow. All gel-times were noted in the temperature range 25 ± 2°.

Preparation of Pure Sodium Silicate.—Since silicic acid sols made from commercial sodium silicate were found to contain a few parts per million of fluorine, a sample of pure silicate was obtained by hydrolyzing ethyl silicate, and dissolving the intermediate organosol in alkali. Thus, 528 ml. of ethyl orthosilicate and 50 g. of solid reagent grade sodium hydroxide were stirred in 2 liters of distilled water at 60–80° and CO₂-free air was bubbled through the mixture. After 24 hours, the solution became clear, and it was then evaporated to a volume of 1400 ml. during which time all the alcohol had been removed. The solution was adjusted to 1.855 molar with respect to SiO₂, and 1.02 normal in alkali as titrated to an end-point at pH 3.6.

Analysis for Fluoride.—The fluoride content was expressed as millimoles of NaF per liter. Fluorine was determined by a modification of the Willard–Winter method, similar to that described by Hammond and MacIntire.⁵

Effect of Adding Fluoride to Sols Made from Pure Silicate.—As shown in Fig. 1, the addition of trace amounts of fluoride to the silicic acid sol made from pure sodium silicate greatly accelerated gelling. A typical sol was prepared by adding 27.0 ml. of the sodium silicate solution to a mixture of 6.95 ml. of acid solution and 16.0 ml. of distilled water in the manner described above. In order to prepare a similar sol containing additional fluorine, the required amount of standard solution of sodium fluoride was added, after omitting an equal volume of water in making up the sol.

In this series, analysis of the "pure" sol indicated the presence of about 2 parts per million of fluorine, or a concentration of 0.1 millimolar. Total fluorine concentration was therefore estimated and shown on the graphs.

Effect of Adding Fluoride to Sols at pH 2.0.—Analysis showed that the 1.0 molar silicic acid sol made from commercial silicate contained fluoride as an impurity, corresponding

(1) C. B. Hurd, C. L. Raymond and P. S. Miller, *THIS JOURNAL*, **38**, 663 (1934).

(2) C. B. Hurd and R. W. Barclay, *ibid.*, **44**, 847 (1940).

(3) C. B. Hurd and H. A. Letteron, *ibid.*, **36**, 604 (1932).

(4) C. B. Hurd and P. Schuyler Miller, *ibid.*, **36**, 2194 (1932).

(5) J. W. Hammond and W. H. MacIntire, *J. Assoc. Official Agr. Chem.*, **23**, 398 (1940).

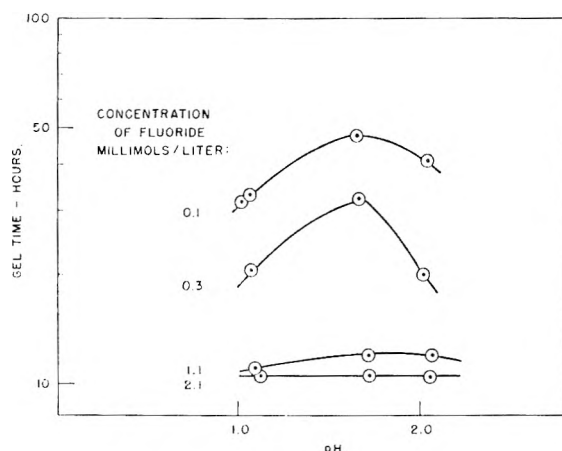


Fig. 1.—Effect of fluoride on silicic acid sols made from pure sodium silicate.

to a 0.67 millimolar concentration of fluoride ion. A series of sols at pH 2.0, was prepared, with added fluoride; the logarithm of the gel time, shown by line A, Fig. 2, decreased linearly with increasing fluoride concentration. However, as shown in Fig. 3, further data at pH 1.7 and pH 2.3 over a wider range of fluoride concentration showed that the relationship was more complex.

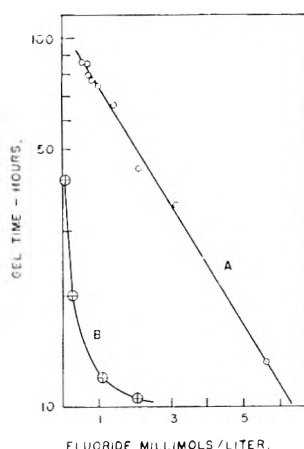


Fig. 2.—Effect of fluoride on: A, sol from commercial sodium silicate; B, sol from pure sodium silicate.

The effect of adding fluoride to a sol made from very pure silicate is shown in curve B in Fig. 2. Since fluoride was a potent catalyst for gelling, yet the less pure sol was more stable, it was concluded that the latter contained some impurity which inhibited the effect of fluoride. A search was therefore made for materials that would offset the effect of added fluoride. Two liters of 1.0 molar silicic acid sol were made up to pH 1.92, using the commercial sodium silicate, and at once divided into 100-ml. portions. The inhibitor candidate was added with good stirring, followed by 0.50 ml. of 1.0 normal sodium fluoride solution to give a fluoride concentration in the sol of 5.6 millimoles per liter. The gel time at 25° was then noted, as in Table I.

From the results, it was evident that aluminum, thorium and beryllium had an outstanding effect; the effect of iron was less marked. Since aluminum occurs as an impurity in most silicates, it seemed logical to investigate its effects in some detail.

It is interesting to note that the order of effectiveness of aluminum, beryllium and iron varies inversely with the known dissociation constants of the corresponding fluoride complexes as given by Kleiner.⁸

$(\text{Me}^{+n})(\text{F}^-)/(\text{MF}^{n-1}) \times 10^6$	Al	Be	Fe
Gel time/control	9.0	5.2	2.8

(6) K. E. Kleiner, *Zhur. Obshchei. Khim. (J. Gen. Chem.)*, **21**, 18 (1951); *C. A.*, **46**, 5557 (1951).

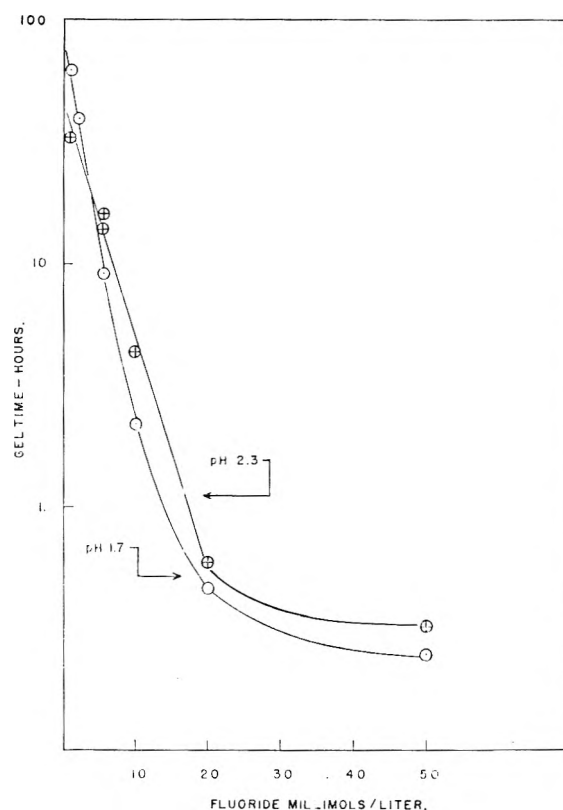


Fig. 3.—Effect of fluoride on sols from pure sodium silicate at constant pH.

Effect of Adding Aluminum Sulfate.—To samples of a sol containing a total of 6 millimoles per liter of fluoride, at pH 1.85 to 1.95, different amounts of aluminum sulfate solution were added and the gel time noted. The results are shown graphically in Fig. 4.

TABLE I

Added agent	Amt., g.	Resulting pH	Gel time, hours
H ₃ BO ₃	0.5	1.90	9.0
Alum	3	1.87	72.0
Satd. NaH ₂ PO ₄ soln.	5	1.98	8.3
CrCl ₃ ·6H ₂ O	1	1.80	7.3
CuSO ₄ ·5H ₂ O	1	1.93	8.3
Fe ₂ (SO ₄) ₃	2	1.79	22.0
ZrOCl ₂ ·8H ₂ O	1	1.60	9.8
Th(NO ₃) ₄ ·12H ₂ O	1	1.80	45.0
Ce ₂ (C ₂ O ₄) ₃ ·9H ₂ O	1	1.92	6.5
MoO ₃	1	1.90	7.3
Tl(SO ₄) ₃ ·7H ₂ O	1	1.97	10.6
W ₂ O ₃	1	1.94	10.6
Yttrium nitrate	1	1.98	12.8
La, Pr, Nd sulfamates	1	1.90	12.8
Ti ₂ (C ₂ O ₄)·H ₂ O	1	1.60	2.5
Bismuth nitrate	1	1.80	11.0
UO ₂ (CH ₃ COO) ₂ ·2H ₂ O	1	2.42	19.0
BeSO ₄ ·4H ₂ O	1	1.90	41.0
None (control)		1.82	8.3

It is of interest to note that a concentration of Al₂O₃ of as low as 0.5 millimole per liter begins to inhibit the effect of fluoride which was present at a concentration of about 6 millimoles per liter. This corresponds to a ratio of Al:F = 1:6, which might suggest the formation of the ion (AlF₆)⁻³.

Combined Effects of Fluoride, Aluminum and Hydrogen Ions.—Sols made from commercial silicate were found to contain Al₂O₃ equivalent to 0.3 millimole of Al₂O₃ per mole of SiO₂, and fluoride equivalent to 0.7 milliequivalent per mole

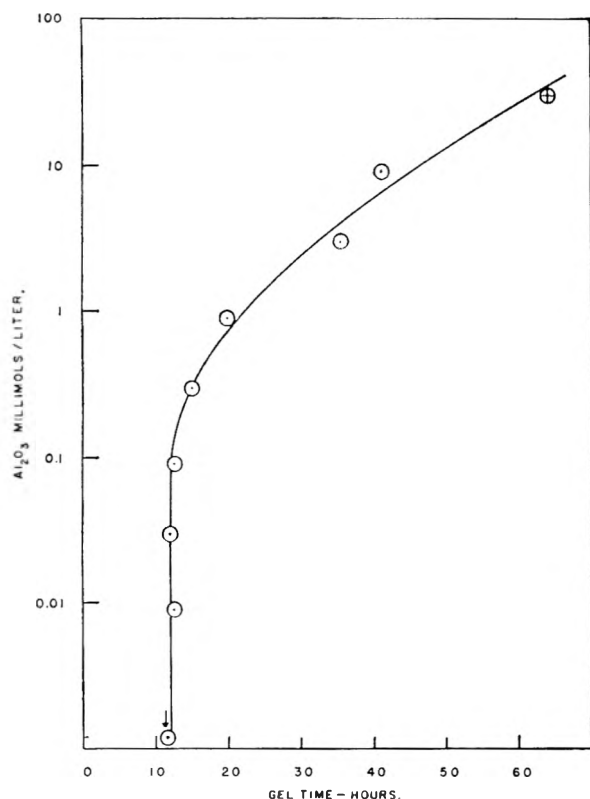


Fig. 4.—Effect of aluminum ion on sol containing 6 millimoles per liter of fluoride at about pH 1.9.

of SiO_2 . In Fig. 5 is shown the effect of adding fluoride (as sodium fluoride) at various pH values. The upper curve corresponding to 0.7 millimolar fluoride is the control for the series. It will be noted that above pH 2.0, where only small

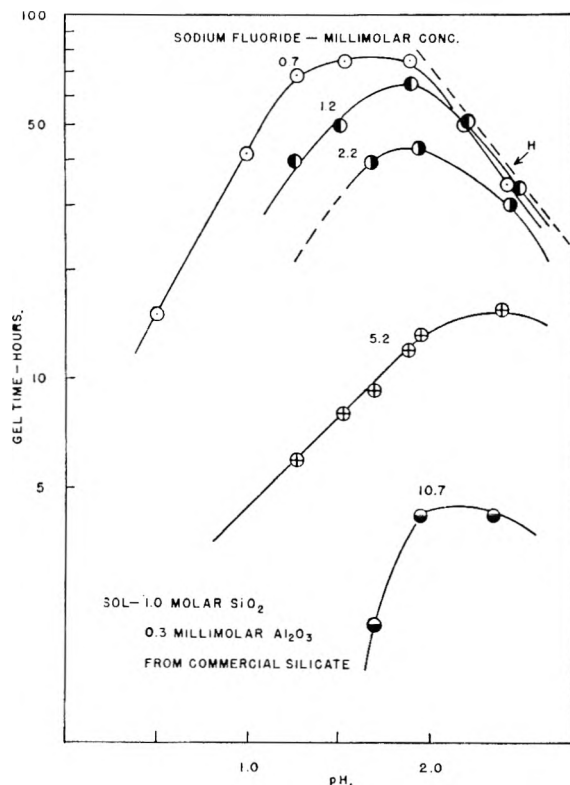


Fig. 5.—Effect of pH and fluoride ion concentration on sols containing 0.3 millimole per liter of Al_2O_3 .

amounts of fluoride are present, the curves appear to become asymptotic to the line H. This line corresponds roughly to the rate of polymerization when the reaction is catalyzed by hydroxyl ion alone.

In Fig. 6, the effect of adding aluminum ion is indicated. With only a small amount of fluoride present, as in B, the addition of more aluminum has an effect only at around pH 1.5. Below this pH, the fluoaluminate complex is probably

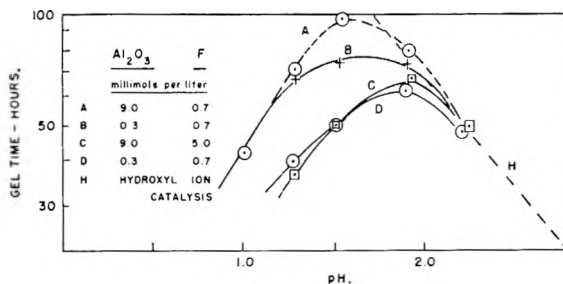


Fig. 6.—Effect of pH and concentration of Al_2O_3 on sols containing fluoride.

decomposed by H^+ to give HF, while above this pH, hydroxyl ion catalysis becomes predominant. At still higher concentration of fluoride, as in C and D, the amount of added aluminum ion was without effect. Accordingly, the effect of

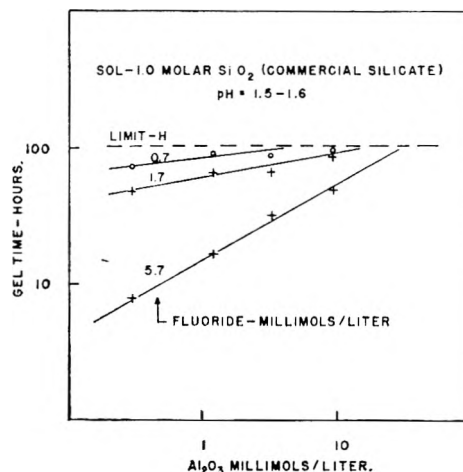


Fig. 7.—Effect of Al_2O_3 on sols containing fluoride at pH 1.5 to 1.6.

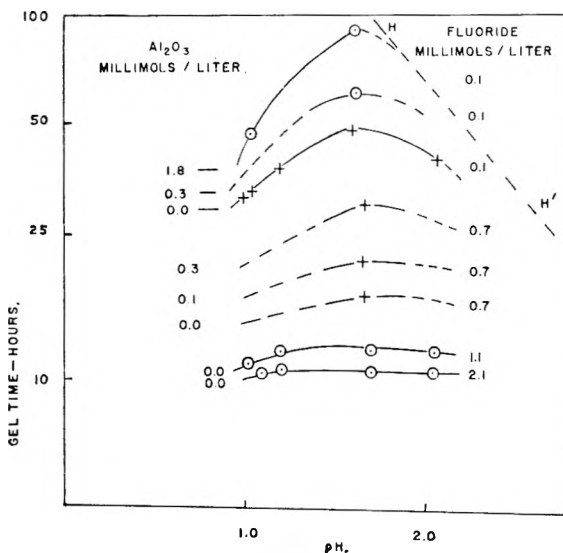


Fig. 8.—Effect of trace amounts of fluoride and aluminum on 1.0 molar SiO_2 sols made from pure sodium silicate.

aluminum ion was examined at lower fluoride concentrations, as shown in Fig. 7. This was carried out at constant pH 1.5 to 1.6, where the effects are most readily noted. It will be noted that the limit H represents the gel-time as catalyzed by hydroxyl ion alone. Thus, for a given concentration of fluoride ion, there is required a certain concentration of aluminum ion to inactivate the fluoride. Extrapolation of the curve for 5.7 millimolar fluoride, to the limit H, gives an Al_2O_3 concentration of 30 millimolar. This would correspond to about 5 moles of Al_2O_3 per fluoride equivalent, or an atomic ratio of $Al:F = 10:1$, at this pH, in order to inhibit completely the catalytic effect of the fluoride ion.

In the case of sols made from pure sodium silicate, the effect of trace amounts of fluoride and aluminum ions is still more marked. In Fig. 8, it is shown that at pH 1.5, 1.8 millimoles of Al_2O_3 inhibit the catalytic effect of 0.1 millimole of fluoride.

In the absence of aluminum ions, traces of fluoride greatly accelerate gelling. Comparison of the sols from the two types of silicates cannot be made, however, because additional unknown trace impurities appear to play a role. For example, a sol was made up from the purified silicate to which aluminum and fluoride was added to concentrations of 0.3 and 0.7 millimolar, corresponding to the aluminum and fluoride contents of the sol made from commercial silicate. However, the sol from commercial silicate gelled in around 75 hours at pH 1.5, while the sol from the "pure" silicate, with Al and F added, gelled in 30 hours. Additional unknown stabilizers are probably present in the commercial silicate.

Acknowledgment.—The author is grateful to Ralph E. Lawrence for analyses carried out in connection with this investigation.

MATHEMATICS OF ADSORPTION IN BEDS. V. EFFECT OF INTRAPARTICLE DIFFUSION IN FLOW SYSTEMS IN FIXED BEDS

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Equations have been derived for heat and mass transfer operations in fixed beds of solids through the interstices of which a fluid flows. The effect of intraparticle diffusion or conduction is considered as well as the resistance to transfer at the particle surface. This paper contains essentially a generalization of the results of Anzelius,¹ Schumann,² Nusselt,³ Wicke⁴ and Hougen and Marshall.⁵ The use of the derived equations may be limited because of the restrictive assumption of a linear isotherm for adsorption. The case of heat transfer should be more readily amenable to experimental verification. Although the functions involved in the solution are only exponential and Bessel the form of the solution may seem prohibitively complicated. However, the presence of the exponential factors should produce such rapid convergence that not more than a few terms should be needed in a calculation.

Introduction

The problem of the transfer of heat or mass from a fluid to a granular bed through which it is flowing has been the subject of a voluminous literature both from the experimental and mathematical viewpoints. Early work in the field was concentrated on heat exchange because of the importance of heat regenerators, blast furnaces, and similar operations. In recent years the problem received further impetus by the widespread industrial use of selective adsorption schemes for difficult separations and of fixed and moving bed catalytic reactors, and further by the interest of chemists in the theory of chromatography. In general it has been assumed that the rate-determining step in these processes is the rate of mass or heat transfer from the fluid to the solid surface of the packed bed. In a few other cases, as in chromatography, it has been assumed that the flow of fluid through the bed is so slow there is either, virtually, an equilibrium established between the fluid and the solid at each point of the bed or the rate determining step is the kinetic process of adsorption itself. These researches all have the common defect of neglecting the effect of intraparticle diffusion or conduction. This assumption is probably valid for very small particles but the experimental evidence is inconclusive. Two recent

studies by Foster and Daniels⁶ and Eagleton⁷ have shown that in the cases of adsorption of nitrogen dioxide on silica gel and of water on activated alumina the diffusion of adsorbate inside the particle may be the rate-determining step.

With these facts in mind the authors sought to derive equations which would describe the phenomenon of heat or mass transfer from a fixed bed of solid to a flowing fluid stream. The discussion will be confined to adsorption although it will be shown what modifications need be made for heat transfer. It is assumed that the packed bed of solids consists of porous spheres of uniform diameter. The solid has adsorbent properties and therefore adsorbs solute from the stream of fluid flowing through the interstices. The solute must be transferred from the bulk of the fluid in the void volume among the particles by turbulence to the bounding film of fluid about a sphere. The solute diffuses through the film and also through the void volume of the particle and is then adsorbed on the internal surface of the adsorbent. Hence it is obvious that there are many rate processes occurring and that these occur in series. Which one, or ones, determine the overall rate depends probably on the system being investigated, and it would be more than coincidence if intraparticle diffusion never played a role.

If one knows the initial condition of the system, along with flow rates, particle size, method of packing, adsorbent properties of the solid, etc., it would be desirable to have formulas which would predict

(1) A. Anzelius, *Z. angew. Math. Mech.*, **6**, 291 (1926).

(2) T. E. W. Schumann, *J. Franklin Inst.*, **208**, 405 (1929).

(3) W. Nusselt, *Z. Ver. deut. Ing.*, **55**, 2021 (1911); *Tech. Mech. Thermo.*, **1**, 417 (1930).

(4) E. Wicke, *Kolloid Z.*, [2] **93**, 129 (1940).

(5) O. A. Hougen and W. R. Marshall, *Chem. Eng. Progress*, **43**, 197 (1947).

(6) E. G. Foster and F. Daniels, *Ind. Eng. Chem.*, **43**, 986 (1951).

(7) L. C. Eagleton, private communication.

the concentration of the effluent for any depth of bed at any time. If, in addition, one desires to know the adsorbate concentration in a sphere at a given bed depth at a given time, the radius variable inside the sphere must be specified since each sphere is in a transient state, with the result that concentration gradients exist in the sphere. Thus, it is clear that once all physical conditions are specified, this is a mathematical problem of three independent variables, two in space and one in time. Physical problems of three independent variables are complicated and it is to be expected that the solution of such a system is forbidding in appearance and perhaps removed from the slide rule and desk calculator domain. Modern high speed computing machines are forcing scientists to revise their definition of the word complicated with respect to numerical calculations

Table of Notation

a	$= (\gamma + k_1)/\gamma D$
c	$=$ concentration of intraparticle solution
$\bar{c}$	$=$ concentration of interparticle solution
c_i	$=$ initial concentration of intraparticle solution
c_0	$=$ inlet concentration of interparticle solution
D	$=$ diffusivity of solute in intraparticle solution
D_α	$=$ diffusivity of solute in interparticle solution
G	$=$ mass velocity of fluid
$h_x, h_y, h_{xy}, H_x, H_y, H_{xy}$	$=$ Laplace transforms of c and $\bar{c}$
k	$=$ thermal conductivity of solid
k_t	$=$ mass transfer coefficient at particle surface
k_1, k_2	$=$ constants in adsorption isotherm
n	$=$ concentration of adsorbed material on solid
N	$=$ number of spheres per unit volume of bed
p	$=$ transform parameter for x
q	$=$ transform parameter for y
q_n	$= -(w_n^2/R_a^2)$
r	$=$ radius variable in sphere
R	$=$ external radius of the sphere
t	$=$ time
T	$=$ temperature inside sphere
T_i	$=$ initial temperature of spheres
V	$=$ velocity of fluid through interstices
w	$= R \sqrt{-aq}$
w_n	$=$ root of a transcendental equation
x	$= z/V$
y	$= t - z/V$
z	$=$ bed depth
α	$=$ interparticle void fraction
β	$= (6D\gamma(1 - \alpha)/aR^2)$
γ	$=$ intraparticle void fraction
ρ	$=$ density of solution
θ	$=$ temperature of interparticle solution
θ_0	$=$ inlet temperature of interparticle solution
μ	$= (D/k_t R)$

Other symbols are defined as they occur.

Derivation of Equations

Suppose an adsorbent bed of spheres of radius R initially contains a solution whose concentration is c_i in the particle void volume and c_i in the bed void volume. Adsorbate concentration on the solid is n_i moles per unit volume of particle. Let the intraparticle void fraction be γ and the interparticle void fraction be α . At time zero a solution whose concentration is $\bar{c}_0$ is admitted at one end of the bed, say at $z = 0$. The concentration $\bar{c}$ of the interparticle solution as a function of z , the bed depth, and t , the time, is desired. Let G be the mass velocity of the solution, ρ the solution density, D the intraparticle diffusivity, and r the radius variable inside a particle. It is a simple exercise⁸ then to de-

rive the equation for adsorption and diffusion inside the particle

$$\gamma D \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) = \gamma \frac{\partial c}{\partial t} + \frac{\partial n}{\partial t} \quad (1)$$

This follows directly from the examination of a spherical shell inside a sphere. The condition at the particle surface is described by the well known relation

$$-D \left(\frac{\partial c}{\partial r} \right)_{r=R} = k_t (c - \bar{c}), \text{ when } r = R \quad (2)$$

where k_t is a measure of the film resistance to mass transfer at the particle surface.

If one examines an element of length of the bed Δz , a further relation between the concentration of the interparticle fluid and intraparticle fluid may be derived. The rate at which solute enters the element at z by hydrodynamic flow is

$$\left(\frac{G}{\rho} \bar{c} \right)_z$$

and the rate at which it leaves is the same expression evaluated at $z + \Delta z$. Superimposed on the hydrodynamic flow is the rate at which solute enters at z by diffusion. This is

$$\left(-\alpha D_\alpha \frac{\partial \bar{c}}{\partial z} \right)_z$$

The rate at which it leaves the element by diffusion is the same expression evaluated at $z + \Delta z$. D_α is the diffusivity in the interparticle solution. If, for the moment, one assumes that desorption is taking place, the rate at which solute leaves a single sphere is

$$-4\pi R^2 D \gamma \left(\frac{\partial c}{\partial r} \right)_{r=R}$$

and the rate at which solute leaves all the particles in the element is

$$-4\pi R^2 D \gamma N \left(\frac{\partial c}{\partial r} \right)_{r=R} \Delta z$$

where N is the number of spheres per unit volume of bed. All these relations are written for a unit cross sectional area of bed. Thus, equating rate of inflow minus outflow to the rate of accumulation, there results

$$\left(\frac{G}{\rho} \bar{c} \right)_z - \left(\frac{G}{\rho} \bar{c} \right)_{z+\Delta z} - D_\alpha \alpha \left(\frac{\partial \bar{c}}{\partial z} \right)_z + D_\alpha \alpha \left(\frac{\partial \bar{c}}{\partial z} \right)_{z+\Delta z} - 4\pi R^2 D \gamma N \left(\frac{\partial c}{\partial r} \right)_{r=R} \Delta z = \alpha \left(\frac{\partial \bar{c}}{\partial t} \right)_z \Delta z$$

where $z < \bar{z} < z + \Delta z$. As $\Delta z \rightarrow 0$, this expression reduces to

$$\frac{\partial}{\partial z} \left(\frac{G}{\rho} \bar{c} \right) + 4\pi R^2 D \gamma N \left(\frac{\partial c}{\partial r} \right)_{r=R} + \alpha \frac{\partial \bar{c}}{\partial t} = \alpha D_\alpha \frac{\partial^2 \bar{c}}{\partial z^2} \quad (3)$$

It has been assumed in this relation that the fluid velocity profile is flat and that no concentration gradients exist in the interparticle solution normal to the direction of net fluid flow. The usual physical parameters are supposed constant.

These relations are the differential equations which hold pointwise in the bed. To these must be added the relations describing the initial condition of the bed as well as the condition of the entering fluid. Because Equation 3 is essentially the diffusion equation in one dimension it is clear that the

(8) P. R. Kasten and Neal R. Amundson, *Ind. Eng. Chem.*, **42**, 1341 (1950).

proper initial condition to state is the condition of the bed at $t = 0$,

$$\left. \begin{aligned} c &= c_i \\ \bar{c} &= c_i \text{ at } t = 0 \\ n &= n_i \end{aligned} \right\} \quad (4)$$

These relations imply that the bed is full of fluid and that the fluid contains a uniform concentration of solute which is in equilibrium with the adsorbed adsorbate. It is stressed that these are the proper initial conditions since Equation 3 is the diffusion equation.

The condition of the incoming fluid is given by

$$\bar{c} = \bar{c}_0, \text{ when } z = 0 \quad (5)$$

This merely states that the fluid entering at $z = 0$ has a constant composition with time. The manner of stating Equations 5 and 6 will permit the use of the resultant equations for either adsorption or desorption.

It is still necessary to say something of the adsorption process itself. Equation 1 is the relation between the rate of diffusion and the rate of adsorption and it is necessary to make some assumption about the adsorption mechanism. In general, the rate of adsorption is given by an equation of the form

$$\partial n / \partial t = f(n, c)$$

where $f(n, c)$ is some function depending upon the concentrations of solute in the solution and on the adsorbent. If the rate of adsorption is very high, equilibrium is almost immediately established at each point and

$$n = g(c)$$

which would be the adsorption isotherm. For the purposes of this paper it will be assumed that

$$n = k_1 c + k_2 \quad (6)$$

The isotherm of nitrogen dioxide on silica gel is almost linear while the isotherm of water vapor on activated alumina has a linear portion.

Equations 1 through 6 make up a complete mathematical description of the system for an infinitely long bed. A further simplification will be made by neglecting the effect of the longitudinal diffusion, *i.e.*, diffusion in the direction of net hydrodynamic flow, in the interparticle solution. This has a deeper mathematical significance than is immediately apparent since it changes the basic character of the problem. Equation 3 is no longer a diffusion equation when $D_\alpha = 0$. The equation is changed from one of second order to one of first order, and hence it is necessary to re-examine the auxiliary conditions to determine if the problem is properly stated.

There appears to be no difficulty with the condition at $z = 0$. However, it is obvious that the condition at $t = 0$ needs some modification since there are times after $t = 0$ when the condition of the bed at z is unchanged, or, more generally, is independent of the concentration of the inlet fluid. In fact, under the uniform conditions assumed here for the initial state of the bed, the adsorbate concentrations at z will not be altered until fluid has traveled from the bed inlet to the point in question, or until $t = z/V$. With longitudinal diffusion neglected, it makes no difference whether the adsorption process

is initiated with the bed full of interparticle solution or with the bed empty but with particles containing intraparticle solution. If longitudinal diffusion is taken into consideration, the two problems, bed full or bed empty of solution, are fundamentally different. The general behavior described above is a characteristic one in partial differential equations in which the type of equation changes with the variation of a parameter.

The problem which will be solved in this paper is

$$\gamma D \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) = (\gamma + k_1) \frac{\partial c}{\partial t} \quad (7)$$

$$-D \left(\frac{\partial c}{\partial r} \right)_{r=R} = k_t (c - \bar{c}), \text{ when } r = R \quad (2)$$

$$\left. \begin{aligned} c &= c_i \\ \bar{c} &= c_i \end{aligned} \right\}, \text{ when } t \leq z/V \quad (8)$$

$$\bar{c} = \bar{c}_0, \text{ when } z = 0 \quad (9)$$

$$V \frac{\partial \bar{c}}{\partial z} + \frac{3D\gamma(1-\alpha)}{\alpha R} \left(\frac{\partial c}{\partial r} \right)_{r=R} + \frac{\partial \bar{c}}{\partial t} = 0 \quad (10)$$

where the changes

$$G = \rho \alpha V$$

$$4/3\pi R^3 N = 1 - \alpha$$

have been made. It has also been assumed that G/ρ is constant which implies that dilute solutions are being considered and that the temperature is unchanged as the solution passes through the bed. From the discussion above it should not be necessary to state the condition $\bar{c} = c_i$, $t = z/V$, and the following analysis makes no use of this fact.

To solve the problem mathematically, consisting of the system of Equations 2, 7, 8, 9 and 10, it is convenient to make the changes of independent variables

$$r = r$$

$$x = z/V$$

$$y = t - (z/V)$$

There results, then

$$\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} = a \frac{\partial c}{\partial y} \quad (11)$$

$$-D(\partial c / \partial r)_{r=R} = k_t(c - \bar{c}), \text{ when } r = R \quad (12)$$

$$c = c_i, \text{ when } y = 0 \quad (13)$$

$$\bar{c} = \bar{c}_0, \text{ when } x = 0 \quad (14)$$

$$\frac{\partial \bar{c}}{\partial x} + \frac{3D\gamma(1-\alpha)}{\alpha R} \left(\frac{\partial c}{\partial r} \right)_{r=R} = 0 \quad (15)$$

where $a = (\gamma + k_1)/\gamma D$.

Because the bed may be considered to be infinitely long and because the system is defined for all times, the method of solution which lends itself most readily is the double Laplace transformation, or iterated transform, taken with respect to x and y . The transforms are defined as

$$L_x [c(r, x, y)] = \int_0^\infty e^{-px} c(r, x, y) dx = h_x(r, p, y) = h_x$$

$$L_y [c(r, x, y)] = \int_0^\infty e^{-qy} c(r, x, y) dy = h_y(r, x, q) = h_y$$

$$L_{xy} [c(r, x, y)] = \int_0^\infty \int_0^\infty e^{-px - qy} c(r, x, y) dx dy = h_{xy}(r, p, q) = h_{xy}$$

$$L_x [c(x, y)] = H_x(p, y) = H_x$$

$$L_y [c(x, y)] = H_y(x, q) = H_y$$

$$L_{xy} [c(x, y)] = H_{xy}(p, q) = H_{xy}$$

Under the proper assumptions

$$L_x(h_y) = L_y(h_x) = h_{xy}$$

and

$$L_{xy}\left(\frac{\partial c}{\partial y}\right) = q h_{xy} - \frac{c_i}{p}$$

Also, if the function whose transform is desired is a product of a function of x by a function of y , the double transform is the product of the single transforms.

The transform of Equation 11 is

$$\frac{d^2 h_{xy}}{dr^2} + \frac{2}{r} \frac{dh_{xy}}{dr} - aqh_{xy} = -\frac{ac_i}{p}$$

The general solution of this equation which remains finite as r approaches zero is

$$h_{xy} = \frac{A}{r} \sin \frac{rw}{R} + \frac{c_i}{pq} \quad (16)$$

where $w = R\sqrt{-aq}$ and A is a constant whose value must be determined. A term in the cosine has been omitted because of the finiteness required as r approaches zero.

The transforms of Equations 12 and 15 are

$$-D \left(\frac{dh_{xy}}{dr} \right)_{r=R} = k_i(h_{xy} - H_{xy})$$

and

$$pH_{xy} - \frac{\bar{c}_0}{q} + \frac{3D\gamma(1-\alpha)}{\alpha R} \left(\frac{dh_{xy}}{dr} \right)_{r=R} = 0$$

respectively. H_{xy} may be eliminated between these two equations to give

$$- \left(D + \frac{3D\gamma(1-\alpha)k_i}{\alpha R p} \right) \left(\frac{dh_{xy}}{dr} \right)_{r=R} = k_i h_{xy} - \frac{k_i \bar{c}_0}{pq}$$

When Equation 16 is substituted into this relation the value of A may be determined with the result that h_{xy} may be written

$$h_{xy} = \frac{c_i}{pq} + \frac{R(c_i - \bar{c}_0)}{rq[(\mu-1)\sin w - \mu w \cos w]} \frac{\sin(rw/R)}{p + Z}$$

where

$$Z = \frac{3D\gamma(1-\alpha)}{\alpha R^2} \frac{\sin w - w \cos w}{(\mu-1)\sin w - \mu w \cos w}$$

Note that in these expressions p occurs in such a way that the inverse transform taken with respect to p may be directly taken. Hence

$$h_y = \frac{R(c_i - \bar{c}_0)}{rq[(\mu-1)\sin w - \mu w \cos w]} \sin \frac{rw}{R} e^{-zx} + \frac{c_i}{q} \quad (17)$$

where

$$\mu = D/k_i R$$

If one had H_y instead of h_y , $\bar{c}$ could be obtained since this is the interesting function. If one takes the single transform of Equation 12

$$\frac{dH_y}{dx} + \frac{3D\gamma(1-\alpha)}{\alpha R} \left(\frac{dh_y}{dr} \right)_{r=R} = 0$$

a differential equation in H_y is obtained since $(dh_y/dr)_{r=R}$ may be computed from Equation 17.

This calculation gives

$$\frac{dH_y}{dx} = \frac{c_i - \bar{c}_0}{q} Z e^{-zx}$$

Integration of this equation followed by use of the relation $H_y = (\bar{c}_0/q)$ when $x = 0$ results in

$$H_y = \frac{\bar{c}_0 - c_i}{q} e^{-zx} + \frac{c_i}{q} \quad (18)$$

Equation 18 is the transform of the desired solution. Although, superficially, it appears to be simple enough some effort must be expended to obtain the inverse. To this end the function Z will be expanded into its partial fraction expansion⁹ by the conventional method

$$\frac{\sin w - w \cos w}{(\mu-1)\sin w - \mu w \cos w} = 2q \sum_{n=1}^{\infty} (\mu^2 w_n^2 + 1 - \mu)^{-1} \left(q + \frac{w_n^2}{R^2 a} \right)^{-1}$$

where w_n is a root of the equation

$$(\mu-1)\sin w - \mu w \cos w = 0 \quad (19)$$

and the summation is made over all the roots of Equation 19. It is known that all roots of Equation 19 are real for non-negative μ ,¹⁰ which is always the physical situation. Hence

$$Z = \beta q \sum_{n=1}^{\infty} \frac{k_n}{q - q_n}$$

where

$$\beta = (6D\gamma(1-\alpha)/\alpha R^2)$$

$$k_n = (\mu^2 w_n^2 + 1 - \mu)^{-1}$$

$$q_n = -(w_n^2/R^2 a)$$

$$H_y = \frac{\bar{c}_0 - c_i}{q} \exp \left(-\beta x \sum_{n=1}^{\infty} \frac{k_n q_n}{q - q_n} \right) + \frac{c_i}{q}$$

or

$$H_y = \frac{\bar{c}_0 - c_i}{q} \pi \sum_{n=1}^{\infty} \left[\exp \frac{-\beta k_n x q}{q - q_n} \right] + \frac{c_i}{q}$$

Let

$$F_n = \exp \frac{-\beta k_n x q}{q - q_n} - 1$$

so that

$$H_y = \frac{\bar{c}_0 - c_i}{q} \pi \sum_{n=1}^{\infty} (1 + F_n) + \frac{c_i}{q} \quad (20)$$

At this point it would be desirable to expand the infinite product in the form

$$\begin{aligned} \frac{1}{q} \pi \sum_{n=1}^{\infty} (1 + F_n) &= \frac{1}{q} + \frac{1}{q} \sum_i F_i + \\ &\frac{1}{q} \sum_{i,j} F_i F_j + \frac{1}{q} \sum_{i,j,k} F_i F_j F_k + \\ &\frac{1}{q} \sum_{i,j,k,m} F_i F_j F_k F_m + \dots \quad (21) \end{aligned}$$

where each summation is taken over all possible combinations of subscripts but with $i \neq j \neq k \neq m \neq \dots$ and no repetitions. It can be rigorously proved¹¹ that the above expansion is valid, that the series itself converges uniformly and absolutely in a suitable interval, that each of the series, single, double, triple, etc., making up each term of the overall series converges uniformly and absolutely, that the inverse Laplace transform may be taken term by term in the whole series and in each term of the whole series, and that integration term by term in a

(9) E. C. Titchmarsh, "The Theory of Functions," Oxford University Press, London, 1939.

(10) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, London, 1948.

(11) S. E. Warschawski, private communication.

similar manner can be effected. These are strong and demands to be made on such an expression but

the detailed steps may be justified. The proof of these facts will be omitted here but it gives confidence to know that these apparently arbitrary operations have a rigorous mathematical foundation.

Consider the function F_n and suppose, momentarily, that a function $g_n(y)$ exists such that

$$F_n = L_y (dg_n/dy) = L_y (f_n) = qG_n - g_n(0)$$

where

$$L_y (g_n) = G_n$$

provided $g_n(0) = 1$. Let

$$\begin{aligned} G_n &= \frac{1}{q} \exp \left(\frac{-\beta k_n x q}{q - q_n} \right) \\ &= \frac{1}{q} e^{-\beta k_n x} \exp \left[\frac{\beta k_n x w_n^2}{R^2 a (q - q_n)} \right] \end{aligned}$$

and consider

$$\begin{aligned} H_n &= \frac{1}{q} \exp \left[\frac{\beta k_n x w_n^2}{R^2 a (q - q_n)} \right] \\ &= \frac{\exp \left[\frac{\beta k_n x w_n^2}{R^2 a (q - q_n)} \right]}{q - q_n} - \frac{q_n \exp \left[\frac{\beta k_n x w_n^2}{R^2 a (q - q_n)} \right]}{q - q_n} \end{aligned}$$

From a table of transforms one may easily show that

$$L_y^{-1} (H_n) = e^{-(w_n^2 y / R^2 a)} I_0 \left(2 \sqrt{\frac{\beta k_n x y w_n^2}{R^2 a}} \right) + \frac{w_n^2}{R^2 a} \int_0^y e^{-(w_n^2 s / R^2 a)} I_0 \left(2 \sqrt{\frac{\beta k_n x s w_n^2}{R^2 a}} \right) ds$$

where $I_0(z)$ is the modified Bessel function of the first order and the first kind. Differentiation gives

$$f_n = \frac{dg_n}{dy} = e^{-(w_n^2 y / R^2 a)} I_1 \left(2 \sqrt{\frac{\beta k_n x y w_n^2}{R^2 a}} \right) \times \sqrt{\frac{\beta k_n x w_n^2}{R^2 a y}} e^{-\beta k_n x}$$

It is to be noted that $g_n(0) = 1$. Hence the inverse transform of F_n is f_n .

In order to take the inverse transform of Equation 21 it is seen that each term after the second consists of a product of transforms and hence their inverses will appear in the form of convolutions of the functions appearing in Equation 22. Therefore

$$L^{-1}(F_i F_j) = \int_0^y f(s_1) f_i(y - s) ds \quad (22)$$

and

$$L^{-1}(F_i F_j / q) = \int_0^y du \int_0^u f_j(s) f_i(u - s) ds$$

The order of integration may be changed to give

$$L^{-1} \left(\frac{F_i F_j}{q} \right) = \int_0^y f_i(s) ds \int_s^y f_j(u - s) du$$

In the inner integral let $u - s = s_1$ and in the outer integral let $y - s = s_2$

$$M_{ij} = L^{-1}(F_i F_j / q) = \int_0^y f_j(y - s_2) ds_2 \int_0^{s_2} f_i(s_1) ds_1$$

From this it follows at once using the convolution principle

$$M_{ijk}^* = L^{-1} \left(\frac{F_i F_j F_k}{q} \right) = \int_0^y f_k(y - s_3) ds_3 \int_0^{s_3} f_j(s_3 - s_2) ds_2 \int_0^{s_2} f_i(s_1) ds_1$$

The manner of proceeding from this point on is obvious. Let

$$L^{-1} \left[\frac{F_i F_j \cdots F_n}{q} \right] = M_{ij \cdots n}$$

then the complete solution of the problem may be written in the form

$$\frac{\bar{c} - \bar{c}_0}{\bar{c}_0 - c_i} = \sum_i M_i + \sum_{i,j} M_{ij} + \sum_{i,j,k} M_{ijk} + \cdots \quad (23)$$

where the summations omit repetitions in subscripts and $i \neq j \neq k \neq m \neq \cdots$. This is the complete solution of the problem. It is relatively complicated and its general use will be limited until integrals of the type appearing in Equation 23 have been tabulated. The solution is given in the form of the variables x and y and it seems convenient to leave it that way. Experimental data may be converted to these variables quite easily.

Special Cases

A special case of Equation 23 should be mentioned. If the rate of mass transfer to the particle surface is rapid as might be the case for a loosely packed bed with high velocity of fluid through the interstices, then, essentially, $k_i \rightarrow \infty$, and $\mu \rightarrow 0$. In this case Equation 18 reduces to

$$H_y = \frac{\bar{c}_0 - c_i}{q} e^{-Yx} + \frac{c_i}{q}$$

where

$$\begin{aligned} \bar{Y} &= (3D\gamma(1 - \alpha)/\alpha R^2)(w \cot w - 1) \\ &= \frac{6D\gamma(1 - \alpha)}{\alpha R^2} \sum_{n=1}^{\infty} \frac{q}{q + \frac{n^2 \pi^2}{R^2 a}} \end{aligned}$$

The method of procedure is the same from here on and the functions f_n are

$$f_n = e^{-(n^2 \pi^2 y / R^2 a)} I_1 \left(2 \sqrt{\frac{\beta x y n^2 \pi^2}{R^2 a}} \right) \sqrt{\frac{\beta x n^2 \pi^2}{R^2 a y}} e^{-\beta x} \quad (24)$$

The complete solution for this case is the same as Equation 23 with the functions f_n defined by Equation 24.

The case of the transfer of heat may be analyzed in a similar manner. Details will be eliminated in the derivation of the equations but it may be shown quite easily that the system of equations to be solved is

$$k \left(\frac{\partial T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) = c_s \rho \frac{\partial T}{\partial t} \quad (25)$$

$$-k(\partial T / \partial r)_{r=R} = h_r(T - \theta), \text{ when } r = R \quad (26)$$

$$\left. \begin{aligned} T &= T_i \\ \theta &= T_i \end{aligned} \right\}, \text{ when } t \leq \frac{z}{V} \quad (27)$$

$$\theta = \theta_0, \text{ when } z = 0 \quad (28)$$

$$G c_s \frac{\partial \theta}{\partial z} + \frac{3k(1 - \alpha)}{R} \left(\frac{\partial T}{\partial r} \right)_{r=R} + c_s \rho \alpha \frac{\partial \theta}{\partial t} = 0 \quad (29)$$

In this case it is being assumed that a fixed bed of spheres which has an initial temperature T_i is contacted with a fluid whose temperature at entrance is $\bar{\theta}_0$. Conduction in the fluid in the direction of net hydrodynamic flow has been neglected but this term may be included in Equation 29 with the consequent change in Equation 27. If there is a possibility of heat generation in the sphere Equation 25 is replaced by

$$k \left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) + Q = c_p \frac{\partial T}{\partial t}$$

where Q is the rate of heat generation per unit volume of sphere. The function Q may depend upon many variables. If it is assumed that $Q = c_1 + c_2 T$, for example, the system of equations may be solved but with complications in details rather than in method.

If one were interested in the problem of washing a solution from porous spheres as is commonly the case in catalyst preparation, the set of equations given in 2, 7, 8, 9 and 10 with $k_1 = 0$ will solve this problem.

STUDIES OF THE FISCHER-TROPSCH SYNTHESIS. XIII. STRUCTURAL CHANGES OF A REDUCED IRON CATALYST ON REOXIDATION AND ON FORMATION OF INTERSTITIAL PHASES¹

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Upon complete reduction at 450° or 550°, a fused iron synthetic ammonia catalyst develops an extensive pore structure corresponding to about 45% porosity. On reoxidation, the volumes of the individual particles remain constant, while the surface areas and pore volumes decrease. Reoxidation proceeds at an initially rapid rate, which becomes very slow after a few hours. The reoxidized catalyst is reduced much more easily than the raw catalyst. Formation of the interstitial nitrides and carbides causes the catalyst particles to expand and the pore volume and average pore diameters to increase. The per cent. porosity, however, remains about constant.

Although catalysts may sinter or otherwise change their physical structure in many catalytic processes,³⁻⁵ their chemical composition is appreciably altered in only a few cases. When chemical changes do occur, they usually have a marked effect on the process. The Fischer-Tropsch synthesis over initially reduced iron is one instance of a catalyst undergoing chemical change in the course of operation, namely, reoxidation and carburization. Various authors⁶⁻¹⁰ have attributed deactivation and short catalyst life to some of these reactions, and attempts have been made to find promoters and iron phases^{6,11-13} that will catalyze the synthesis while resisting chemical changes. The present study deals with the physical changes accompanying the nitriding, carburizing and reoxidation proc-

esses on a fused iron synthetic ammonia type catalyst.

The structural changes accompanying the initial reduction of this catalyst and its chemical changes during the synthesis have been described previously.^{14,15} Kölbel and Engelhardt⁸ have measured the rate of reoxidation of induced iron catalysts with water vapor. The carbides and nitrides of iron have been extensively studied.^{6,16-23} Podgurski, Kummer, DeWitt and Emmett²⁴ showed that little or no change in surface area occurred upon carburizing, while the carbon monoxide chemisorption decreased 10- to 30-fold as the reaction progressed. Our exploratory experiments confirmed this work. The densities of the iron carbides and nitrides are known to be lower than the density of iron,²⁵ but nowhere have the changes in catalyst structure been described concurrent with the formation of these phases or the oxide phase.

Experimental

All experiments were carried out in glass tubes equipped with special four-way stopcocks.²⁶ To facilitate charging

(1) Studies of the Fischer-Tropsch Synthesis. XII. *J. Am. Chem. Soc.*, **74**, 637 (1952).

(2) Mellon Institute, Pittsburgh, Pa.

(3) Anderson, Hall, Krieg and Seligman, *J. Am. Chem. Soc.*, **71**, 183 (1949).

(4) Brunauer and Emmett, *ibid.*, **59**, 310, 1553, 2682 (1937); **62**, 1732 (1940).

(5) McCartney, Seligman, Hall and Anderson, *THIS JOURNAL*, **54**, 505 (1950).

(6) Anderson, Shultz, Seligman, Hall and Storch, *J. Am. Chem. Soc.*, **72**, 3502 (1950).

(7) Crowell, Benson, Field and Storch, *Ind. Eng. Chem.*, **42**, 2376 (1950).

(8) Kölbel and Engelhardt, *Erdöl und Kohle*, **3**, 529 (1950).

(9) Kölbel, TOM Reel 115-X, Frames 1181-1196.

(10) Storch, Golumbic and Anderson, "The Fischer-Tropsch and Related Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1951 (a) pp. 111, 112; (b) pp. 29, 30.

(11) Shultz, Seligman, Shaw and Anderson, *Ind. Eng. Chem.*, **44**, 397 (1952).

(12) Shultz, Seligman, Lecky and Anderson, *J. Am. Chem. Soc.*, **74**, 637 (1952).

(13) Unpublished results of the Bureau of Mines indicate that Hägg carbide and cementite resist oxidation in the Fischer-Tropsch synthesis up to 7.8 atmospheres and ϵ -nitrides and ϵ -carbonitrides do so up to 21 atmospheres.

(14) Anderson, Hofer, Cohn and Seligman, *J. Am. Chem. Soc.*, **73**, 944 (1951).

(15) Hall, Tarn and Anderson, *ibid.*, **72**, 5436 (1950).

(16) Brunauer, Jefferson, Emmett and Hendricks, *ibid.*, **53**, 1778 (1931).

(17) Cohn and Hofer, *ibid.*, **72**, 4662 (1950).

(18) Eisenhut and Kaupp, *Z. Elektrochem.*, **36**, 392 (1930).

(19) Hägg, *Nova Acta Reg. Soc. Ups.*, [4] **7**, 6 (1929).

(20) Hofer, Cohn and Peebles, *J. Am. Chem. Soc.*, **71**, 189 (1949).

(21) Hofer and Cohn, *J. Chem. Phys.*, **18**, 766 (1950).

(22) Jack, *Proc. Roy. Soc. (London)*, **A195**, 34, 56 (1948).

(23) Lehrer, *Z. Elektrochem.*, **36**, 383, 460 (1930).

(24) Podgurski, Kummer, DeWitt and Emmett, *J. Am. Chem. Soc.*, **72**, 5332 (1950).

(25) Hodgman, "Handbook of Physics and Chemistry," 30th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio.

(26) Anderson, *Ind. Eng. Chem., Anal. Ed.*, **18**, 156 (1946).

and removing the samples and to maintain the constant volume of the sample tube, the charging inlet was extended to the level of the stopcock and closed with a ground glass joint. After the tube was filled, a close-fitting glass rod was inserted into this inlet to minimize the dead space. These sample vessels were heated in a horizontal position in a small resistance furnace with automatic temperature control to $\pm 3^\circ$. The changes of the samples were determined by weighing the entire tubes in an analytical balance, and the loss or gain of oxygen, carbon or nitrogen was calculated.

Dry electrolytic H_2 , freed from traces of O_2 and H_2O vapor by passing over Cu heated to 350° and then over anhydrous $Mg(ClO_4)_2$, was used in the reductions. The 6- to 8-mesh magnesia-potassium oxide promoted iron catalyst (D-3001) had about 45% porosity²⁷ and an average pore diameter of about 800 Å. when completely reduced at 550° .¹⁵ The oxidations²⁸ were carried out with prepurified (99.98% pure by mass spectrometer) nitrogen, saturated with freshly boiled distilled water by successive passage through Pyrex sintered disc saturators at 40° and at room temperature (27 to 33°), respectively. The preparation of the nitrides has been described previously⁶; anhydrous NH_3 was used after further drying over fused potassium hydroxide. In both cases, the space velocity²⁹ of the gas was 1,000.

The carbide was formed at a fairly constant rate with pure carbon monoxide, at a space velocity of 100, by increasing the temperature from 150 to 350° so that the exit gas always contained about 20% carbon dioxide. The exit gas was passed through a thermal conductivity gas analysis apparatus, which controlled the rate of temperature increase of the electric furnace. Nearly pure Hägg carbide was formed in this way.³²

The methods for making the absorption and density measurements were described earlier.^{3,5,15,33-35} All gases used for these measurements were analyzed with the mass spectrometer and found to be more than 99.8% pure. No wetting of the catalyst by mercury was observed. Surface areas were calculated from the V_m values obtained from the simple B.E.T. equation,³⁶ using 16.2Å^2 as the cross-sectional area of the absorbed nitrogen molecule.

Results

Figure 1 shows the variation of the oxygen content of the catalyst during reduction (open symbols) and oxidation

(solid symbols). The amount of oxygen is expressed as per cent. of the total oxygen, associated with iron, that has been removed. After initial reduction with pure dry H_2 at 550° (curve O-A), the rate of oxidation of the catalyst at 250° with water vapor (A'-B) was rapid at first and then decreased to a low value. Re-reduction of the partly re-oxidized catalyst at only 300° (B'-C) was almost as rapid as was the initial reduction at 550° . The sample was again oxidized (C'-D), this time at 325° , with similar results. At the end of about 100 hours, the temperature was increased to 450° in an attempt to increase the rate of oxidation. An increase was observed, but this may have been caused by a surface oxidation to hematite rather than by bulk oxidation to magnetite, as indicated by the reddish color of the catalyst. On re-reduction at 300° (D'-E), the rate of reduction was again much greater than that of the raw catalyst under the same conditions, as demonstrated by reduction of this catalyst for about 50 hours at 300° (O-F). After a raw sample had been reduced nearly 50% at 300° and 450° (O-F-G), it was again treated with hydrogen for about 40 hours more at 300° (G-H). These data show clearly that the reoxidized catalyst was much easier to reduce than the raw or the partly reduced catalyst.

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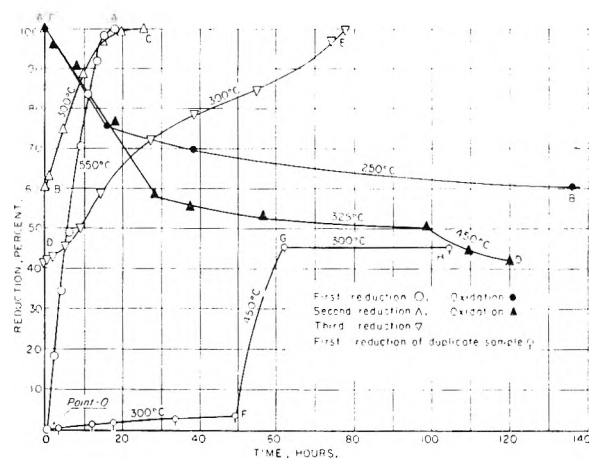


Fig. 1.—Oxidation and reduction of fused iron catalyst D-3001.

Adsorption measurements made at the end of the various steps shown in Fig. 1 are given in Table I. In all cases the surface area decreased on reoxidation and increased to about its initial value when re-reduced. The chemisorption of carbon monoxide was sharply decreased by reoxidation; the ratios of V_{CO}/V_m ³⁷ indicate that the relative amount of free iron on the surface of the reoxidized catalyst was less than half of the amount of the reduced catalyst. As the total surface area was decreased proportionally by reoxidation, the amount of iron (on the surface) available for oxidation was very small when the rate of reoxidation became low. The same behavior was observed for the sample initially reduced at 450 and 500° (last two rows of Table I), except that the surface areas were about twice as large as those measured on the sample initially reduced at a higher temperature.¹⁵

The structural data for various solid phases prepared from this catalyst are summarized in Table II. Per gram of unreduced catalyst the reduced and reoxidized samples displaced the same volume of mercury as the raw sample, but the carbided and nitrified catalysts displaced 12 to 19% more (column 5). On reduction, the catalyst developed nearly all its pore volume (column 6), which decreased on reoxidation but increased enough on nitriding and carbiding to keep the per cent. porosity approximately constant (column 8). The average pore diameters, calculated from the equation of Emmett and DeWitt,³⁸ increased from that of the reduced catalyst, with both reoxidation and the forma-

(37) V_{CO} and V_m are the volumes of chemisorbed carbon monoxide and the nitrogen monolayer capacity in cc. (STP), respectively. The carbon monoxide chemisorbs only on the part of the surface that is iron.⁴ The ratio of V_{CO}/V_m , therefore, gives a measure of the fraction of the surface that is iron.

(38) Emmett and DeWitt, *J. Am. Chem. Soc.*, **65**, 1253 (1943).

$$K_1 = P_{CO_2}/P_{CO} \quad (1)$$

varies from 2.5 to 1.5 between 225 and 325° , so that the partial pressure of carbon dioxide must be several times that of carbon monoxide for oxidation to take place. On the other hand, water vapor, either as a primary or as a final product of the synthesis, is much more favorable for oxidation. The equilibrium constant for the reduction of magnetite to α -Fe

$$K_2 = P_{H_2O}/P_{H_2} \quad (2)$$

varies from 0.019 to 0.058 in the same temperature range. Thus, only a few per cent. water vapor in the gas can oxidize the catalyst. Further, Almquist and Black³¹ showed that appreciable amounts of oxygen were retained by an iron catalyst treated at 444° with $3H_2:1N_2$ gas containing only 0.016% of water vapor. Under these conditions the massive iron was not oxidized, but the amount of oxygen taken up was equivalent to the oxidation of one iron atom in 400. Köbel⁹ found that an induced precipitated catalyst was completely reoxidized with $2N_2:1H_2O$ at 200 to 240° in 8 to 16 hours.

(29) Space velocity is defined as volumes of gas (STP) per volume of catalyst space per hour.

(30) Emmett and Shultz, *J. Am. Chem. Soc.*, **52**, 4268 (1930); **55**, 1376 (1933).

(31) Almquist and Black, *ibid.*, **56**, 35 (1934).

(32) Process patent applied for.

(33) Anderson, McCartney, Hall and Hofer, *Ind. Eng. Chem.*, **39**, 1618 (1947).

(34) Anderson, Hall, Hewlett and Seligman, *J. Am. Chem. Soc.*, **69**, 3114 (1947).

(35) Anderson, Hall and Hofer, *ibid.*, **70**, 2465 (1948).

(36) Brunauer, Emmett and Teller, *ibid.*, **60**, 309 (1938).

TABLE I
 ADSORPTION MEASUREMENTS ON REDUCED AND REOXIDIZED CATALYST D-3001

Gas	Treatment Temp., °C.	Time, hr.	Point on Fig. 1	Extent of reduction, %	Surface area mg./g. of unreduced catalyst	V_m^a cc./g. (STP)	V_{CO}^b cc./g. (STP)	V_{CO}/V_m	Area ^c f	Area ^c $f^{1/2}$
.....	..	..	O	0.0	0.0	0.0	0.0	..	..	..
H ₂ ^d	550	18	A	99.7	4.7	1.07	(.4) ^e	(0.4) ^e	4.7	4.7
N ₂ + H ₂ O	250	136	B	60.4	2.6	.59	.1	.2	4.3	3.3
H ₂	300	27	C	100.0	4.5	1.04	.5	.5	4.5	4.5
N ₂ + H ₂ O	{ 325 450	{ 98 21.5	D	42.1	1.7	.39	.04	.1	4.1	2.6
H ₂ ^d	550	19	..	99.9	..	..	..	..	..	..
N ₂ + H ₂ O	250	70	.. ^f	68.4	2.9	.66	..	..	4.2	3.5
H ₂ ^d	550	18.5	.. ^f	99.8	..	..	..	..	..	..
N ₂ + H ₂ O	250	66	.. ^f	68.2	2.8	.64	..	..	4.1	3.4
H ₂ ^d	{ 450 500	{ 56 5	..	98.0	8.2	1.88	..	..	8.4	8.3
N ₂ + H ₂ O	250	65	..	49.8	3.9	.89	..	..	7.8	5.5

^a Calculated by use of the simple BET equation.³⁶ (Per gram of raw catalyst). ^b Difference between the N₂ and CO isotherms at -195°, per gram of raw catalyst. ^c f = extent of reduction. ^d Original reduction of raw catalyst. ^e V_{CO}/V_m from previous work;¹⁵ V_{CO} was calculated using V_m for this sample. ^f Density measurements were made on this sample.

 TABLE II
 STRUCTURAL DATA AS A FUNCTION OF SOLID PHASE IN CATALYST D-3001^a

Treatment of catalyst	Phases present, X-ray analysis	d_{Fe}^d g./cc.	$d_{H_2}^d$ g./cc.	V_{H_2} cc./g. unreduced catalyst	Pore volume, cc./g. unreduced catalyst	Pore volume, cc./g. unreduced catalyst	Porosity, %	Surface area m. ² /g. unreduced catalyst	Average pore diameter Å.
None (raw)	Fe ₃ O ₄	4.96	4.91	0.203	0.002	0.00	1	0.0	..
Reduced at 550°	α-Fe	6.95	3.71	.201	.093	.093	46	4.7	785
Reoxidized ^c (f = 0.684)	α-Fe, Fe ₃ O ₄	5.94	4.13	.200	.061	.064	30	2.9	820
Reoxidized ^c (f = 0.682)		5.93	4.13	.200	.061	.063	30	2.8	860
Carbided ^f	Hägg-FeC, α-Fe (?)	6.28	3.63	.225	.096	...	43	^g	(820) ^g
Nitrided ^h	ε-Fe ₂ N	6.37	3.48	.237	.107	...	45	4.8	898

^a Except for the raw catalyst, all samples were reduced for 19 hours at 550°, and at a space velocity of 1000 volumes H₂/volume catalyst/hour. ^b Pore volume is the difference of the volumes of helium and mercury displaced per gram of unreduced catalyst. ^c Porosity = 100 × pore volume/mercury volume. ^d d = 4 pore volume/surface area.³⁸ ^e See footnote f , Table I. ^f Atom ratio, C/Fe = 0.494. ^g Surface area not determined; several other samples showed no change in surface area with carbiding for this catalyst; see also.²⁴ The surface area was assumed unchanged, and the pore diameter was calculated on this basis. ^h Atom ratio, N/Fe = 0.482.

tion of interstitial phases. The density measurements on the reoxidized catalysts agree almost exactly with those for the same catalyst at the same extent of reduction during its initial reduction.¹⁵

The density of Fe₂N, calculated from the data of Eisenhut and Kaupp,¹⁸ is 7.02 as compared to 6.82 from our data; thus by assuming that the volumes of the phases present were additive, the density of our nitrided catalyst calculated from their data should be 6.50 compared to the observed 6.37. Similarly, according to Jack²² the density of Fe₃C is 7.20 (which leads to a catalyst density of 6.62 compared to the measured 6.28) compared to 6.77 calculated from our data.

Discussion

Reactions of oxygen or water vapor with metals generally start with the formation of a new phase at the surface with the oxide-metal interface moving into the metal either by diffusion of oxygen into the metal or metal diffusing through the oxide layer. The work of Evans³⁹ indicates that, after the magnetite forms an interface on the iron surface, the oxide grows by migration of iron through the oxide layer. Such a mechanism explains the initially rapid reoxidation decreasing to a very slow rate, which, in the limit, becomes dependent on the rate of diffusion of iron into the oxide.

Because of the greatly increased oxide surface available to the hydrogen, the reduction of this oxide layer would be more rapid than the initial reduction. On this basis, also, it is possible to form oxide in the pores without expanding the framework of the pore system and increasing the volume of mercury displaced by the catalyst. All the results can thus be explained qualitatively. To account quantitatively for the observed changes in surface area (Table I), however, it is necessary to consider the geometrical changes in the pores themselves. Two limiting cases present themselves: (1) The pore volume decreases by reduction of the total length of pores of constant average diameter. (2) The pores maintain their length, but their diameters decrease as the reaction proceeds.

In the first case since the length is the only variable

$$A_x/A_R = L_x/L_R \quad (3)$$

where A and L are the area and total length of pores, respectively, and the subscripts x and R refer to the partly reduced or oxidized catalyst and the completely reduced catalyst, respectively. The pore volumes V_x and V_R can be expressed in terms of

(39) Evans, *Nature*, **164**, 909 (1949).

the initial and final volumes, V_0 and V_F , of the catalyst, and of the extent of reduction, f ¹⁵

$$V_x = (V_0 - V_F)f = V_R f \quad (4)$$

Equation 4 requires only that the volume of mercury displaced by a gram of unreduced material does not change on reduction. As this condition is fulfilled for the reoxidized catalyst also, equation 4 may be used to relate the surface area to the extent of reduction. Thus, from equations 3 and 4

$$\frac{A_x}{A_R} = \frac{L_x}{L_R} = \frac{V_x}{V_R} = f \quad (5)$$

if this were the mechanism of reoxidation, $A_x/f = A_R$. As shown in column 10 of Table I, the ratio is about 10% low for the reoxidized catalyst. This is an upper limit, because the effects of thermal sintering are superimposed on the results.

The same sort of treatment was applied to the second limiting case, yielding

$$\frac{A_x}{A_R} = \frac{d_x}{d_R} = \left(\frac{V_x}{V_R}\right)^{1/2} = f^{1/2} \quad (6)$$

By equation 6, $A_x/f^{1/2} = A_R$. This ratio is about 25 to 30% too low (column 11 of Table I).

Thus, while neither mechanism is in good agreement with experiment, the second postulate is worse than the first. It is rather surprising that both postulates give low results, as the most logical explanation, *i.e.*, a combination of the two effects, is precluded because it would necessarily give intermediate (low) results. There are at least three plausible explanations for the fact that the observed surface areas are smaller than those predicted by the two simplified mechanisms: (1) The smaller pores are preferentially and more or less completely filled with oxide. (2) Some of the pores have developed bottlenecks, that is, become partly plugged with oxide, so that they are permeable to helium at 30°, but impermeable to nitrogen at -195°. (3) The pore walls, originally rough, become smoother as the reoxidation proceeds.

The available data are inadequate to differentiate between these possibilities. The first two ways seem improbable, because, in a real system, complete blocking of a fraction of the pores would be expected. This would be accompanied by an excessive decrease in the helium density, which is not observed. An inconclusive attempt was made to prove the presence of constrictions by studying the hysteresis of the nitrogen adsorption isotherms at -195°. ⁴⁰ The last possibility has several points

(40) The hysteresis loop of the nitrogen isotherm of the reoxidized catalysts seemed to be enlarged near P_0 , but P_0 had shifted to a value about 10 mm. greater than that of the gas-filled tube without catalyst. Mass spectrometric analysis of the nitrogen in the system showed that

in its favor, although there is little direct evidence to support it. In a previous paper¹⁵ it was shown that this catalyst developed average pore diameters ranging from 330 to 2400 Å. as the temperature of the reduction was increased from 450 to 650°. This effect was due almost entirely to change in surface area, rather than pore volume. Further, a catalyst reduced completely at 450°, when heat treated in helium for 16 hours at 550°, had the same pore diameter as that of the 550° reduction. McCartney and Anderson⁴¹ made electron micrographs of replicas stripped from a polished surface of this catalyst after reduction at 450° and 550°. While these showed pore openings that compared reasonably well with the pore diameters previously calculated from the surface area-pore volume data,⁵ no definite differences were observed in the dimensions of the replica structure from samples reduced at the two temperatures. By tacitly assuming the same roughness factor for the pore walls formed at all temperatures, the earlier results required that one pore system change as the reduction temperature increased and can be replaced by a new one with a smaller number (or total length) of pores of a larger diameter. A simple explanation of these data is that the pore walls originally are rough and thus yield low values for the pore diameter. As the temperature is increased, these walls smooth out, giving an apparent increase in the pore diameter. This example illustrates the danger involved in putting too much credence in the exact value of the pore diameters calculated from the Emmett-DeWitt equation; at the same time it offers a possible explanation of our data.

The changes in structure that occur concurrent with formation of the interstitial carbides and nitrides are much easier to interpret. As the metal lattice expands, the pore volume increases, whereas the surface area changes only slightly, if at all. Consequently, the average pore diameter increases, but the per cent. porosity remains constant. This is the behavior of an expanding matrix. If a solid containing a hole is expanded, the apparent volume, pore volume, and pore diameter increase, but the surface area increases only slightly, and the per cent. porosity remains essentially constant. The available data fit this simple picture.

Acknowledgment.—Thanks are due to Dr. R. A. Friedel for mass spectrometric analysis of the gases and to Mrs. W. C. Peebles for X-ray analysis of the catalysts.

the only impurity was 0.005% argon. These observations were reproducible but cannot, at present, be explained.

(41) McCartney and Anderson, *J. Appl. Phys.*, **22**, 1441 (1951).

SELF-ABSORPTION PHENOMENA IN THE MEASUREMENT OF THE RADIOACTIVITY OF NICKEL-63

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The self-absorption characteristics of nickel-63 are quite regular, behaving as would be predicted from self-absorption data on other low-energy β -emitters. Two methods of sample preparation seem to yield good results, that of electroplating, and that of precipitation of nickel dimethylglyoxime. An average mass absorption coefficient of 1.48 cm.²/mg. has been observed.

Introduction

Nickel-63, a 69 ± 2 kev. β -emitter with a half-life of 85 ± 20 years² could become a tracer nuclide of some utility. In order to make proper measurements of its radioactivity, some knowledge of the self-absorption characteristics of this low-energy β -emitting nuclide would be desirable. The purpose of this investigation was to develop methods for the preparation of nickel-63 samples and to ascertain their self-absorption characteristics.

Apparatus and Materials.—All measurements of radioactivity were made in a Tracerlab SC-16 Windowless Flow Counter which was connected to a Tracerlab P-4 Preamplifier and a Tracerlab SC-2A Scalar with an attached time clock. Flow gas consisting of 99.05% commercial grade helium plus 0.95% isobutane, obtained from the Matheson Company, was employed with the flow counter.

Electroplating was carried out in a Tracerlab E-16 Electroplating Cell using a copper planchet as the cathode plating surface and a rotating platinum coil as the anode. A six-volt potential was employed.

The nickel-63 used in these experiments was obtained from the Oak Ridge National Laboratory as nickel chloride solution in dilute hydrochloric acid containing a small amount of cobalt-60.

All chemicals were of C. p. quality.

Preparation of Active Nickel-63 Solution.—To the approximately 0.6 ml. of original nickel-63 solution, which contained 0.11 millimole of nickel, sufficient reagent grade nickel chloride was added to give approximately 0.50 millimole of nickel. Also, 0.75 millimole of cobalt as cobalt(II) chloride was introduced to serve as a carrier for the cobalt-60 which was present. This solution was diluted to 100 ml., 15 ml. of a 1% solution of dimethylglyoxime in ethyl alcohol

added, ammonium hydroxide introduced until the odor above the solution was distinct, and then digested on a steam-bath for 15 minutes. The nickel dimethylglyoxime precipitate was filtered off, dissolved in aqua regia and evaporated until nitrogen oxides were evolved. At this point, a few ml. of concentrated sulfuric acid was added and the resulting solution was evaporated almost to dryness. The remainder was diluted with distilled water, made slightly alkaline with ammonium hydroxide, and the entire precipitation and digestion procedure was repeated. This gave a solution free from cobalt-60 as was evidenced by a gamma count.

To the cobalt-free solution was added 2.00 moles of nickel as nickel sulfate and the whole was diluted to a liter volume. This gave a proper specific activity for the experiments which were to follow.

Sample Preparation.—Samples of metallic nickel containing nickel-63 were prepared by electroplating from the stock solution of ammoniacal nickel sulfate. Samples of varying surface density were obtained by plating for different lengths of time. The amount of nickel deposited was determined by weighing the copper planchet on a microbalance both before and after electrodeposition.

Samples of nickel dimethylglyoxime of different surface densities were made by adding a slight excess of a one per cent. solution of dimethylglyoxime in ethyl alcohol to a given amount of the nickel stock solution. The resulting precipitate was transferred into a lucite centrifuge tube equipped with a stainless steel cup serving as a bottom. The mixture was centrifuged, the supernatant liquid drawn off, 5 ml. of ethyl alcohol added, and the centrifugation repeated. The sample was then removed and allowed to air dry. The amount of nickel dimethylglyoxime present was determined from the weights of the cup and of the cup plus the precipitate. From these values and the area of the cup bottom, surface densities were calculated.

TABLE I

SELF-ABSORPTION DATA FOR NICKEL-63 SAMPLES

Plated samples			Dimethylglyoxime samples		
$\bar{x}$, mg./cm. ²	$\bar{a}_m$, cm. ² /mg.	$\bar{\mu}$, cm. ² /mg.	$\bar{x}$, mg./cm. ²	$\bar{a}_m$, cm. ² /mg.	$\bar{\mu}$, cm. ² /mg.
0.01	120	1.20	0.27	148	1.88
.03	180	1.83	.51	114	1.71
.07	214	2.28	.55	112	1.77
.19	169	2.04	.86	84	1.50
.28	143	1.82	1.6	52	1.11
.31	136	1.77	1.7	49	1.02
.32	136	1.78	1.8	48	1.10
.40	130	1.82	2.0	46	1.25
.46	120	1.76	2.1	43	1.08
.55	109	1.66	2.8	34	1.04
.65	98	1.29	4.5	22	—
.70	94	1.52			
.88	83	1.47			
.99	76	1.40			
1.01	76	1.44			
1.10	71	1.36			
1.31	61	1.22			
1.49	55	1.15			

Average 1.56

Average 1.35

Over-all average $\mu = 1.48$

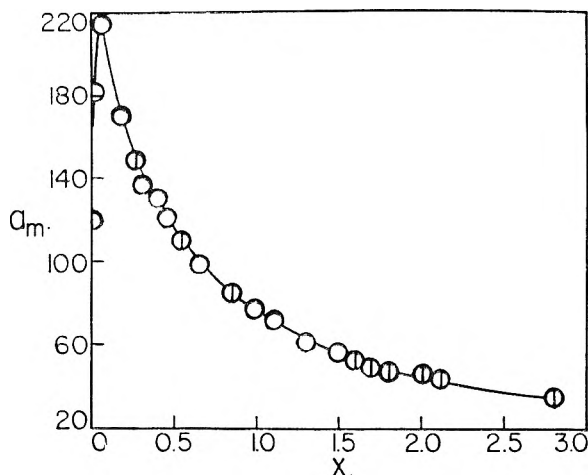


Fig. 1.—Per cent. specific activities of solid samples containing nickel-63: open circles, Ni metal; crossed circles, nickel dimethylglyoxime.

(1) Contribution No. 104.

(2) A. R. Brosi, C. J. Borkowski, E. E. Conn and J. C. Greiss, *Phys. Rev.*, **81**, 391 (1951).

Results

From the measured activities of the samples, the per cent. specific activities, a_m , were calculated using the formula

$$a_m = 100A_m/(xA_i)$$

where A_m is the measured activity of a given sample of surface density x (expressed in mg./cm.²), and A_i is the infinite thickness activity. This latter activity is that obtained from the flat portion of a curve of A_m versus x , this activity being attained at a surface density of approximately 4 mg./cm.².

The data obtained for both types of sample are presented in Table I. The mass absorption coefficient was calculated from the activities over the entire range of measurements giving an average value of 1.48 cm.²/mg. It can be seen from the

data that the individual mass absorption coefficients decrease as the surface density becomes larger, an effect that has been observed with other nuclides.³ Figure 1 is a plot of per cent. specific activities as a function of the surface density. As is observed, the per cent. specific activity shows a maximum in the region of 0.07 mg./cm.², this effect having been found in other self-absorption experiments.⁴

Acknowledgment.—This work was performed under the United States Atomic Energy Commission Research Contract No. AT-(40-1)-1058. The authors wish to express their gratitude for this financial assistance.

(3) G. K. Schweitzer and B. R. Stein, unpublished experiments.

(4) G. K. Schweitzer and J. W. Nehls, *THIS JOURNAL*, **53**, 541 (1952).

SOME RELATIONS BETWEEN INTRINSIC AND SPECIFIC VISCOSITY IN CELLULOSE SOLUTIONS AT A CONTROLLED VELOCITY GRADIENT

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Empirical equations relating the specific viscosity determined at a constant velocity gradient and at two convenient concentrations (0.25 and 0.50 g./dl.) with the intrinsic viscosity have been derived for solutions of cellulose in cuprammonium and cupri-ethylenediamine hydroxides. The relations are based on measurements on 14 celluloses of an intrinsic viscosity range of 20 or 30 to 0.2, the higher range variation depending on solvent used. For each of the concentration levels studied, the identical equation holds for measurements in both solvents. Use of the relations requires adjustment of viscosity data to a mean velocity gradient of 500 sec.⁻¹ whenever the cellulose has an intrinsic viscosity greater than 5 or 6, the difference depending on solvent used. The standard error of estimate of intrinsic viscosity by these equations is approximately 5%.

Introduction

The intrinsic viscosity, $[\eta]$, of a high polymer, defined as $\lim_{c \rightarrow 0} \left(\frac{\eta_{sp}}{c} \right)^2$ has come to be regarded as a fundamental characteristic of the material, directly related to the degree of polymerization (D.P.) and thereby to other significant properties. The practice of reporting intrinsic rather than absolute viscosity in communications is desirable, since interpretation of the absolute viscosity is often made difficult because of its variation with the widely different viscosimetric methods in use. The accepted methods of obtaining the intrinsic viscosity of such polymers as cellulose or its derivatives consist in the application of certain concentration extrapolation procedures which involve either manual plotting of viscosity data or the use of such data in empirical relations which contain the limiting value sought.^{3,4,5} Often these procedures are tedious or of doubtful accuracy, and some of the extrapolation equations which have been suggested for cellulose solutions have been developed for limited ranges of D.P. and do not always yield equivalent intrinsic viscosity values at other ranges. None of them

take account of the change in intrinsic viscosity that results from failure to control velocity gradient in the medium at higher D.P. ranges.⁶ The relations described in this paper are the result of an attempt to arrive at a simple and rapid means for obtaining reproducible intrinsic viscosity values of cellulosic materials with a minimum of effort.

Materials and Methods

The solvents used in the present work were limited to cuprammonium and cupri-ethylenediamine hydroxides which are still the most widely used solvents for cellulose viscosity measurements, although the employment of the quaternary ammonium bases⁸ or the preparation of the nitrate^{8,9} or acetate^{10,11} with the use of organic solvents has also been practiced.

The cuprammonium hydroxide was of American Chemical Society specifications (30 g./l. Cu, 165 g./l. NH₃, 10 g./l. sucrose),¹² having a fluidity of 78.6 ± 0.2 rhes; and the cupri-ethylenediamine hydroxide was of a conventional composition (0.5 M Cu, 1.0 M ethylenediamine),¹³ with a fluidity of 82.2 ± 0.2 rhes.

The cuprammonium viscosity measurements were made

(6) C. M. Conrad, V. W. Tripp and T. Mafes, *THIS JOURNAL*, **55**, 1474 (1951).

(7) M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 2716 (1942).

(8) Reference 5, p. 134.

(9) W. J. Alexander and R. L. Mitchell, *Anal. Chem.*, **21**, 137 (1949).

(10) F. Howlett, *J. Text. Inst.*, **35**, T123 (1944).

(11) F. Howlett, E. Minshall and A. R. Urquhart, *ibid.*, **35**, 133 (1944).

(12) American Chemical Society, Division of Cellulose Chemistry, *Ind. Eng. Chem., Anal. Ed.*, **1**, 49 (1929).

(13) F. L. Strauss and R. M. Levy, *Paper Trade J.*, **114**, No. 18, 33 (1942).

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) The definitions of the quantities whose relations are discussed in this paper follow the usual terminology, cf., for example, ref. 3, 6, 7.

(3) F. W. Billmeyer, Jr., *J. Polymer Sci.*, **4**, 83 (1949).

(4) W. E. Davis and J. H. Elliott, *J. Colloid Sci.*, **4**, 313 (1949).

(5) E. Ott, ed., "Cellulose and Cellulose Derivatives," Interscience Publishers, Inc., New York, N. Y., 1943, pp. 962-971.

TABLE I

SPECIFIC VISCOSITIES AT SELECTED CONCENTRATIONS, INTRINSIC VISCOSITIES, AND MARTIN'S K -VALUES OF CELLULOSE SAMPLES IN CUPRAMMONIUM AND CUPRI-ETHYLENEDIAMINE SOLVENTS ($G = 500 \text{ SEC.}^{-1}$)

Sample no.	Description	Cuprammonium				Cupri-ethylenediamine			
		$c = 0.25$ g./dl.	$c = 0.50$ g./dl.	$[\eta]$	K	$c = 0.25$ g./dl.	$c = 0.50$ g./dl.	$[\eta]$	K
1	Raw cotton	10.07	35.0	19.7	0.064	14.50	48.3	27.2	0.048
2	High D.P. chemical cotton	4.88	16.37	10.9	.094	7.50	26.1	14.4	.089
3	High viscosity cotton linters	2.90	8.98	7.65	.096	4.35	14.45	10.72	.080
4	Purified wood pulp	2.23	6.71	6.39	.097	3.31	10.80	8.69	.086
5	Chemical cotton	1.80	5.09	5.19	.109	2.50	8.05	6.83	.105
6	Cut cotton	1.33	3.52	4.08	.113	2.00	5.36	5.87	.092
7	Methanolized cotton	0.88	2.18	2.88	.124	1.25	3.17	3.83	.115
8	Viscose rayon	.55	1.25	1.93	.114	0.68	1.62	2.33	.122
9	Methanolized cotton	.40	0.88	1.44	.125	.55	1.29	1.96	.121
10	Hydrolyzed cotton	.22	.49	0.83	.135	.28	0.59	1.02	.138
11	Hydrolyzed rayon	.22	.47	.82	.112	.26	.54	0.95	.145
12	Hydrolyzed rayon	.15	.32	.57	.130	.19	.38	.70	.130
13	Methanolized cotton	.11	.21	.39	.124	...	...	...	...
14	Hydrolyzed rayon	.05	.10	.20	.163	.05	.12	.22	.181

according to the technique of Conrad.^{14,15} The cupri-ethylenediamine viscosity measurements were carried out following the method tentatively adopted by the American Society for Testing Materials,¹⁶ with only minor deviations for varying the concentration of the solute. Buret viscometers were used for all measurements. Concentration of the cellulose was varied, depending on the molecular weight of the specimens, in order to obtain dispersions of suitable viscosity. Four or five concentrations of each sample were employed. Duplicate or triplicate measurements were made at each concentration, and all viscosity data adjusted to a mean velocity gradient of 500 sec.⁻¹. All fourteen samples were measured in cuprammonium and 13 of these in cupri-ethylenediamine solvent. The general characteristics of the samples used are noted in Table I. Most of the samples approached cellulose contents of 100% as a result of various purifying treatments.

The intrinsic viscosity of cellulose was calculated from viscometric data by application of the Martin equation¹⁷

$$\log \eta_{sp}/c = \log [\eta] + K[\eta]c$$

which is similar in form to the widely used Huggins relation⁷

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c + \dots$$

This method requires only a few viscosity determinations per sample at suitably selected concentrations, and the extrapolation procedure is straightforward. The intrinsic viscosity obtained in this manner in other work has been correlated with some simple function of the absolute viscosity of solutions at convenient polymer concentration levels over limited D.P. ranges for the cuprammonium- and cupri-ethylenediamine-cellulose systems.^{13,18} However, the D.P. of the celluloses used in establishing these relations did not extend below 200,¹³ nor above 3,000.¹⁸ Also, none of these equations involved explicit consideration of the effect of rate of shear (velocity gradient) existing during the viscosity measurements. This effect, which becomes increasingly serious with increasing D.P., can introduce large differences in the results of measure-

ments, both of the absolute viscosity and of the intrinsic viscosity derived therefrom.^{6,14,15,19,20}

Attempts made in the present work to keep the relation between intrinsic viscosity and an absolute viscosity function at convenient concentration as simple as possible, consonant with precision, led to a choice of the specific viscosity as the most satisfactory function. Other functions, such as the relative viscosity η_r , or convenient empirical expressions, such as $(\eta_r + 1)$, etc., when plotted against intrinsic viscosity, produced curves more complex than the specific viscosity plot. The concentrations at which the specific viscosity was used for correlation were arbitrarily taken as 0.25 and 0.50 g./dl., as either of these yields solutions of easily measured viscosity over the range of D.P. studied.

In practice, the logarithm of the reduced viscosity, $\log (\eta_{sp}/c)$, was plotted against concentration, according to the Martin relation, the regression line being fitted through the points by the method of least squares. The antilogarithm of the intercept at zero concentration is the intrinsic viscosity.

Results

In Table I, along with the intrinsic viscosities of the different samples, the K values from the Martin regression equations are also listed for comparison. Figures 1 and 2 show the Martin plots of the data for cuprammonium and cupri-ethylenediamine, respectively. Each circle represents the mean of the measurements at that concentration adjusted to a velocity gradient of 500 sec.⁻¹. It will be observed that the linearity of the plots is in general very good and that there is a gradual decrease in the slope of the lines from Sample 1, which has the highest D.P., to Sample 14, which has the lowest. The regression lines for samples 1 and 2 were calculated omitting the data at the 0.5 g./dl. concentration level, as the data of these measurements definitely did not lie on the straight line through the lower

(14) C. M. Conrad, *Ind. Eng. Chem., Anal. Ed.*, **13**, 526 (1941).

(15) C. M. Conrad and V. W. Tripp, *Textile Res. J.*, **16**, 275 (1946).

(16) American Society for Testing Materials, Method D 539-48T, B.

(17) Reference 5, p. 966.

(18) O. A. Battista, *Ind. Eng. Chem., Anal. Ed.*, **16**, 351 (1944).

(19) The question of whether it is best to measure viscosities of polymer solutions which show anomalous behavior at constant arbitrary rates of shear or constant arbitrary shearing stresses is not yet settled.

(20) W. J. Lyons, *J. Chem. Phys.*, **13**, 43 (1945).

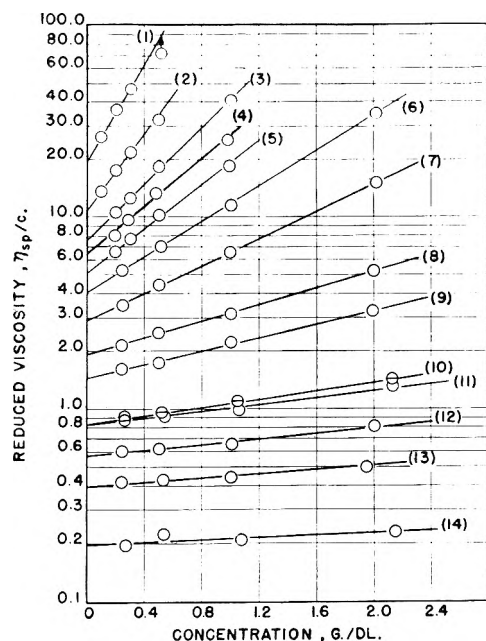


Fig. 1.—Martin plots for 14 celluloses measured in cuprammonium hydroxide.

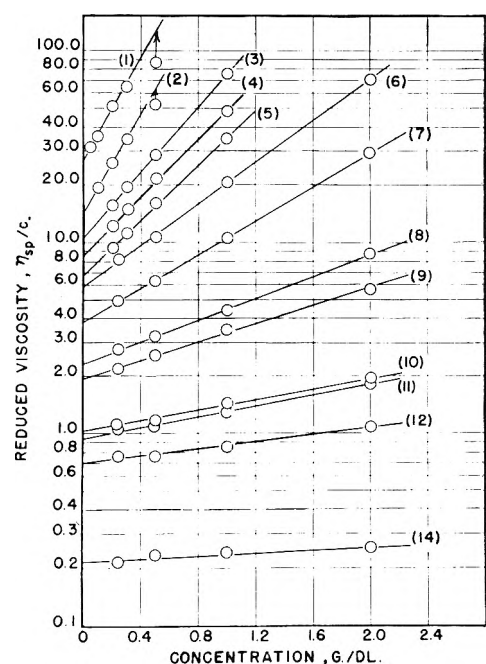


Fig. 2.—Martin plots for 13 celluloses measured in cupri-ethylenediamine hydroxide.

concentration points of these samples. The failure of the Martin equation at higher concentrations, particularly in the case of cellulose of high D.P., has been noted.^{4,6} The Martin K values show a decrease at the higher intrinsic viscosities.

The specific viscosity values used for the correlation are listed in Table I. Where measurements had not been made at the 0.25 g./dl. level, the specific viscosities were obtained by reading off the reduced viscosity at this concentration from the Martin plots and converting. In the case of samples 1 and 2, where the observed reduced viscosity at 0.50 g./dl. did not fall on the regression line plotted, the observed specific viscosity was never-

theless used, in order to provide a correlation of the observed data over the whole range of D.P. involved. An exponential relation between the specific viscosities observed and intrinsic viscosity was found to give the best fit. This plot is shown in Fig. 3.

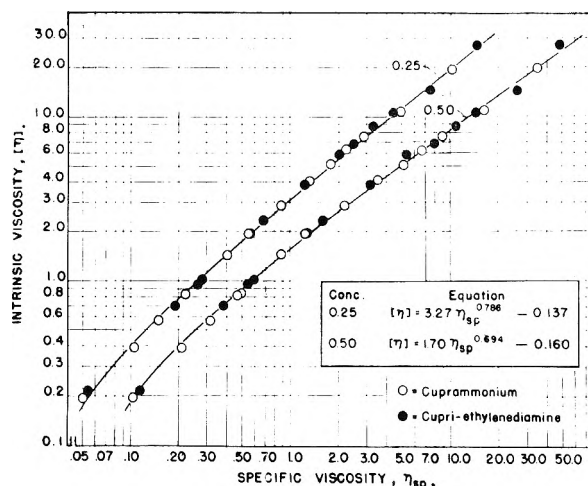


Fig. 3.—Relation between intrinsic and specific viscosities at 500 sec.⁻¹ at two selected concentrations for cuprammonium and cupri-ethylenediamine solutions of cellulose.

It is evident from the figure that the points representing cuprammonium (open circles) and cupri-ethylenediamine (dark circles) fall on the same curves. This obviously simplifies the application of the relations.

For the 0.25 g./dl. concentration level, the equation through the points for both solvents is

$$[\eta] = 3.27 \eta_{sp}^{0.786} - 0.137$$

or in logarithmic form

$$\log ([\eta] + 0.137) = 0.514 + 0.786 \log \eta_{sp}$$

The standard error of estimate of $[\eta]$ is 5.2% (27 observations).

For the 0.50 g./dl. level, the relation is

$$[\eta] = 1.70 \eta_{sp}^{0.694} - 0.160$$

In logarithmic form

$$\log ([\eta] + 0.160) = 0.230 + 0.694 \log \eta_{sp}$$

The standard error of estimate of $[\eta]$ for this expression is 5.4% (27 observations).

Discussion

In view of the rather large differences in intrinsic viscosity involved, it is interesting that the same equations hold for both cuprammonium and cupri-ethylenediamine solvents. This means that the specific viscosities in the two solvents maintain a corresponding ratio. While the equations presented herein offer a simple means of obtaining intrinsic viscosity values, either by mathematical substitution or by construction of a chart similar to Fig. 3, it must be borne in mind that their use is valid only for the two systems studied. Whether these same relations would be valid for solvents of wider differences in copper and amine content, or of different solvent nature, than the ones studied remains to be investigated.

A second consideration in the use of these equations is whether or not the viscosity data have been adjusted to a mean velocity gradient of 500 sec.⁻¹. As Conrad and others have shown,^{14,15} the apparent viscosity of 0.5 g./dl. solutions of cellulose in cuprammonium can vary as much as 100%, in the case of high D.P. cellulose, depending on the rate of shear existing during the measurement. This rate of shear effect becomes less significant at lower D.P., and in the case of celluloses having an intrinsic viscosity of less than 5-6, may be neglected for many purposes. Thus, the equations presented would be approximately valid for use with unadjusted data when the intrinsic viscosity was below 5-6, but their use with higher D.P. celluloses requires adjustment of the data to the gradient specified. While the velocity gradient effect is of lesser absolute magnitude at lower concentrations, it is of equal significance when the absolute viscosity is converted to reduced viscosity, so that it cannot be obviated by going to smaller concentrations.

The standard error of estimate of $[\eta]$ by these equations is about 5%. This error would amount to about 250 glucose units in the case of a cellulose

of D.P. 5,000, or about 3 glucose units in a cellulose of D.P. 50. Errors of this magnitude are usually permissible in cellulose investigations.

The ratio of the intrinsic viscosities measured in cupri-ethylenediamine to those measured in cuprammonium was shown in a previous investigation⁶ of a group of seven samples having intrinsic viscosities ranging from 20 or 30 to 2 to be approximately constant and equal to 1.365. For the thirteen celluloses measured in both solvents in this study, which included seven of those examined previously,⁶ this ratio was found to be 1.354, in excellent agreement with the earlier value. Thus, if the factor of 260 proposed for conversion of intrinsic viscosities to D.P. for cuprammonium measurements is accepted, over the entire range of D.P. from 50 to 5,000, 190 would seem to be appropriate for use with cupri-ethylenediamine data.

Acknowledgment.—Thanks are expressed to Miss Hilda M. Ziifle for the construction of the figures and the statistical calculations of the data, and to Mr. Bernard J. Barrett for some of the viscosity measurements.

PHYSICAL PROPERTIES OF FATTY ACIDS. II. SOME DILATOMETRIC AND THERMAL PROPERTIES OF PALMITIC ACID

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Pure palmitic acid has been examined by dilatometric and calorimetric methods. The properties investigated and the values found were expansion of the acid in the solid and liquid states, 0.000280 and 0.000968 ml./g./°C., respectively; melting dilation, 0.1806 ml./g.; specific volume over the range of temperature from solid to liquid; specific heat; heat of fusion, 51.2 cal./g. (13.12 kcal. per mole); and entropy. Equations were developed for expressing the specific heat (C_p) of palmitic acid at any temperature (°C.): (solid state) $C_p = 0.3831 + 0.0013t$; (liquid state) $C_p = 0.4624 + 0.00175t$.

The expansibilities and the volume changes which accompany melting of the saturated fatty acids have received scant attention. The data of Normann,² and Garner and Ryder³ on a limited number of fatty acids comprise the only sources of information on transition dilation. Garner, Madden and Rushbrooke⁴ have reported values for the heats of fusion and mean specific heats for some of the fatty acids.

The present investigation extends the previous work of the authors⁵ to cover the specific volume-temperature relationship, expansibility of the solid and liquid states, and the melting dilation of palmitic acid, and includes data for the specific heat, heat of fusion and entropy of this acid.

Purification of Palmitic Acid.—Commercial grade palmitic acid (85%) was sulfonated and thoroughly washed with water to remove unsaturated impurities. The sat-

urated portion was esterified with methanol, the methyl esters fractionally distilled, and the methyl palmitate fraction reconverted to palmitic acid. The free acid was crystallized from acetone 14 times which gave a product having a constant value for its solubility. After drying over phosphorus pentoxide, the palmitic acid melted (capillary tube) at 62.8-63.0°. Its freezing point, determined by a modification of the method of Glasgow, *et al.*,⁶ was 62.75° and its absolute density was 0.8414 g./ml. at 80.0°.

Palmitic acid has been shown by Francis, *et al.*,⁷ to exist in two principal polymorphic modifications one of which was obtained by crystallizing the acid on an X-ray mount from a solution of benzene; the other was obtained by a similar crystallization from a solution of glacial acetic acid. The forms were identified by X-ray diffraction patterns obtained immediately after formation of the crystals. The crystals which separated in the benzene solution were of the thermodynamically unstable B-form, those which formed in the solution of glacial acetic acid were of the stable C-form.

Thibaud and LaTour,⁸ however, experienced considerable difficulty in obtaining similar patterns by crystallizing thin layers of palmitic acid. These workers found it necessary to carry out the crystallization below room temperature in order to obtain the unstable B-form. At room temperature or above, they obtained the C-form of the acid and single crystals were always obtained in this form.

The present authors⁵ have shown that the temperature

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(2) W. Normann, *Chem. Umschau Fette, Öle, Wachse Harze*, **38**, 17 (1931).

(3) W. F. Garner and E. A. Ryder, *J. Chem. Soc.*, **127**, 720 (1925).

(4) W. F. Garner, F. C. Madden and J. E. Rushbrooke, *ibid.*, 2491 (1926).

(5) W. S. Singleton, T. L. Ward and F. G. Dollear, *J. Am. Oil Chemists' Soc.*, **27**, 143 (1950).

(6) A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *Natl. Bur. Standards, J. Research*, **35**, 355 (1945).

(7) F. Francis, F. J. E. Collins and S. H. Piper, *Proc. Roy. Soc. (London)*, **A158**, 691 (1937).

(8) J. Thibaud and F. D. LaTour, *J. chim. phys.*, **29**, 153 (1932).

at which crystallization from either polar or non-polar solvents occurs determines the polymorphic form of stearic acid which will separate from solution. The critical temperature is that at which the polymorphic transformation begins. The results of Thibaud and LaTour⁸ indicate that the same applies to palmitic acid, and that the transition of the B- to C-form begins in the vicinity of room temperature, thereby accounting for the inability of the latter workers to obtain single crystals of the B-form of this acid from solvents at room temperature.

In the present work, palmitic acid was crystallized from benzene and from glacial acetic acid at both 10 and 45°, to determine whether or not both the B- and the C-forms of the acid could be obtained from the same solvent by varying the temperature as in the case of stearic acid.⁵ X-Ray diffraction patterns (Fig. 1) of the acid were prepared immediately following crystallization from glacial acetic acid at different temperatures. The pattern of the acid crystallized at the higher temperature indicated only the C-form, whereas that of the acid crystallized at the lower temperature was a mixture of both B- and C-forms. Upon warming the latter, the B-form disappeared and only the form identical with that obtained by crystallizing the acid at 45° was observed.

Both the C-form and a mixture of the B- and C-forms of palmitic acid were obtained from benzene, depending on the temperature of crystallization.

Experimental

The dilatometric and calorimetric methods and the calculations employed have been described in previous publications.^{9,10} Palmitic acid, crystallized from glacial acetic acid, was placed in each of four calibrated dilatometers. The dilatometers were immersed in a controlled-temperature bath and cooled to an initial temperature of -26°. Dilatation measurements were made from -26.0° to approximately 10° above the melting point of the samples. The expansibility was also measured after filling the dilatometers with premelted palmitic acid followed by slow cooling to an initial temperature of -6.89°.

It was not possible to obtain expansion and transition data for the B-form of the acid by the dilatometric method employed. The technique used to fill and seal the dilatometers is such that the transition of the B- to the C-form may occur at room temperature.

For the thermal measurements the sample of palmitic acid was placed in the calorimeter in the melted form which on cooling produced the C-form.¹¹ The specific heat measurements were made over a temperature range of 183° to 360°K.

The B-form of the acid could not be produced by rapid cooling of the liquid phase.

Results and Discussion

Expansibility.—The expansion of palmitic acid in the solid state (-7 to +40°) was calculated to be 0.000280 ml./g./°C., and in the liquid state (62.9 to 72°), 0.000968 ml./g./°C. The melting dilation, calculated at 62.8°, was 0.1806 ml./g., or 46.4 ml./mole.

Specific Volume.—The specific volume of palmitic acid at different temperatures was calculated from the expansion data and from the density of the liquid acid at 80°.¹² The average values obtained for the specific volume of palmitic acid at each of several temperatures are shown in Table I. The density of the acid at any temperature over

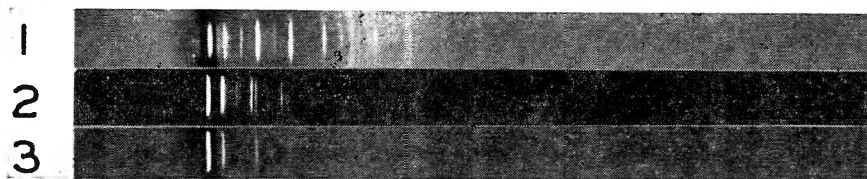


Fig. 1.—Diffraction patterns of palmitic acid crystallized from glacial acetic acid: (1) C-form; (2) mixture of B- and C-forms; (3) same as (2) after warming crystals.

the range of expansibility covered can readily be calculated as the reciprocal of the specific volume.

TABLE I
SPECIFIC VOLUMES OF PALMITIC ACID AT DIFFERENT TEMPERATURES

Temp., °C	Specific volume, ml./g.	Temp., °C	Specific volume, ml./g.
- 6.89	0.9917	39.50	1.0050
- 2.25	.9928	43.10	1.0067
+ 5.88	.9949	47.20	1.0093
12.00	.9965	53.25	1.0124
17.41	.9985	57.60	1.0138
21.55	.9998	61.60	1.0232
24.88	1.0006	62.90	1.1719
25.50	1.0009	68.10	1.1770
29.60	1.0016	72.00	1.1807
33.30	1.0029	80.00	1.1885

Specific Heat.—The specific heat of palmitic acid in both the solid and liquid states was determined and the data applied to developing equations for the specific heat in absolute calories per gram as a function of temperature in degrees centigrade, as

$$\begin{aligned} \text{Solid state } (-73 \text{ to } 40^\circ) \quad C_p &= 0.3831 + 0.0013t \\ \text{Liquid state } (63 \text{ to } 92^\circ) \quad C_p &= 0.4624 + 0.00175t \end{aligned}$$

The observed specific heats of palmitic acid are compared with the calculated values in Table II.

TABLE II
SPECIFIC HEAT OF PALMITIC ACID

Temperature, °K.	Calculated C_p , cal./g./°C.	Observed C_p , cal./g./°C.	Deviation, cal./g./°C.
200	0.2880	0.2890	-0.0010
250	.3530	.3520	+ .0010
280	.3920	.3960	- .0040
347	.5916	.5910	+ .0006
355	.6076	.6065	+ .0011
365	.6231	.6240	- .0009

Heat of Fusion.—From the specific heat and the fusion data, the latent heat of fusion of palmitic acid was calculated to be 51.2 cal./g. (13.12 kcal. per mole). The calorimetric melting point of the acid was 335.68°K. (62.58°).

The value, 51.2 cal./g., for the heat of fusion of palmitic acid is slightly higher than that (50.6 cal./g.) reported by Garner, *et al.*⁴ These results are consistent with those previously reported for stearic acid,⁵ the heats of fusion of both acids being higher than those observed by Garner, *et al.*

The latter workers observed that above a chain length of 10 carbon atoms the contribution of the terminal group to the heat of fusion becomes constant for any given homologous series and the increment of the chain component increases regularly with the addition of methylene groups. Plots of the

(9) A. E. Bailey and E. A. Kraemer, *Oil & Soap*, **21**, 251 (1944).

(10) A. E. Bailey, S. S. Todd, W. S. Singleton and G. D. Oliver, *ibid.*, **21**, 293 (1944).

(11) S. H. Piper, *Trans. Faraday Soc.*, **25**, 348 (1929).

(12) A. Dorinson, M. R. McCorkle and A. W. Ralston, *J. Am. Chem. Soc.*, **64**, 2739 (1942).

heats of fusion of the higher fatty acids and their triglycerides as functions of the number of carbon atoms should, therefore, yield parallel curves. Actually, the molar heats of fusion of palmitic and stearic acids observed in this and previous work² were found to be more closely parallel with the values for the triglycerides than are the values of Garner, *et al.*

Entropy.—The molar entropy of palmitic acid was calculated from the specific heat data, using the extrapolation method of Kelley, Parks and Huffman¹³ and revised data for standard substances. Expressed as molal entropy units, the entropy increment from 0 to 90°K. is 25.54 and the entropy increment from 90 to 298.6°K. is 79.30. The molal entropy at 298.60°K. then is 104.84.

The molar melting dilation and heat of fusion of palmitic acid are compared in Table III with those for the C₈, C₁₀, C₁₂ and C₁₈ saturated fatty acids. The values for stearic acid are from a previous publication of the authors⁵; the melting dilations of

(13) K. K. Kelley, G. S. Parks and H. M. Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

the C₈ to C₁₂ acids are those of Garner and Ryder³; and the heats of fusion of the latter acids are those reported by Garner, Madden and Rushbrooke.⁴ From a plot of the melting dilations and heats of fusion of these acids as functions of chain length the corresponding values for myristic acid were found to be 37 ml./mole and 11 kcal./mole, respectively.

TABLE III
MELTING DILATIONS AND HEATS OF FUSION OF SATURATED FATTY ACIDS

Acid	No. of C atoms	Melting dilation, ml./mole	Heat of fusion, kcal./mole
Caprylic	8	17.2	5.11
Capric	10	22.4	6.70
Lauric	12	28.6	8.75
Palmitic	16	46.4	13.12
Stearic	18	52.8	16.36

Acknowledgment.—The authors wish to express their appreciation to R. T. O'Connor and Mildred Murray for obtaining the X-ray diffraction patterns and photograph.

RATE OF ADSORPTION OF COBALT IONS ON HYDROUS FERRIC OXIDE

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The rate of adsorption of cobalt ions on hydrous ferric oxide has been studied using cobalt ion concentrations of 9×10^{-8} gram atom per liter (2.8×10^{-9} gram atom per 30 ml.) in the presence of excess adsorbent (0.5 to 2×10^{-5} gram atom of iron as hydrous oxide). The amounts of cobalt ion in solution were determined by means of radioactive tracer, Co 60. The rates of adsorption under the above conditions were found to be first order with respect to cobalt. They were, within experimental error, the same at 15 and 30°. The rates were faster when the quantities of adsorbent and pH were increased and were slower when the concentration of ammonium chloride in solution was increased. The rate was also studied using a cobalt concentration of 2×10^{-6} gram atom cobalt per liter (6.4×10^{-8} gram atom per 30 ml.) with 2×10^{-5} gram atom of iron as hydrous oxide adsorbent. Under these conditions the experimental rate was not first order but upon analysis gave two first order curves: one, having a half-life of one hour, which was attributed to adsorbent in the presence of excess cobalt ion and a second, having a half-life of 5.8 hours, which was attributed to cobalt concentration. The observed influence, on rate, of all the factors studied is consistent with the chemical equilibrium equation previously used to express the interrelation of cobalt concentration in solution, cobalt adsorbed, quantity of unreactant adsorbent, pH and chloride ion concentration in solution.

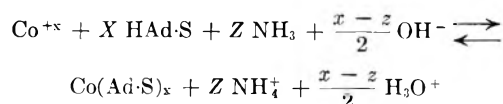
Introduction

It is well established that isotherms representing the adsorption of divalent ions, from very dilute solution, on hydrous ferric oxide have a region of unit slope. That is, the fraction adsorbed, or the distribution coefficient, remains constant while the divalent ion concentration is varied. This relation exists when there is an excess of adsorbent. For instance, in the case of cobalt, the constancy of the fraction adsorbed is observed when the quantity of cobalt is of the order of 10^{-8} gram atom or less in about 30 ml. of solution and the hydrous oxide adsorbent has 10^{-5} gram atom of iron or more.

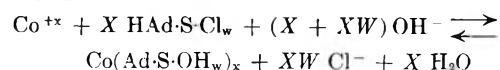
In recent papers,^{1,2} it was shown that the equilibrium adsorption of cobalt under these conditions

could be represented by chemical equations.³ The expressions for the corresponding equilibrium constants quantitatively relate the adsorption results observed upon varying the pH of the solution, the chloride ion concentration and the quantity of adsorbent.

(3) The equations, previously published, for systems containing ammonium chloride in solution are



In the above, HAd·S and Co(Ad·S) represent the adsorbent before and after reaction with cobalt ions. Concentrations of anions other than hydroxyl are assumed to be constant. When the ammonium chloride concentration was varied at constant pH the equilibrium results indicated a reaction



(1) M. H. Kurbatov, G. B. Wood and J. D. Kurbatov, *J. Chem. Phys.*, **19**, 258 (1951).

(2) M. H. Kurbatov, G. B. Wood and J. D. Kurbatov, *THIS JOURNAL*, **56**, 1170 (1951).

This paper reports a study of the rates of adsorption of cobalt on hydrous ferric oxide. According to the equations, the rate of adsorption should be increased by increased concentrations of cobalt and hydroxyl ions in solution and by increased quantities of adsorbent: the rate should be decreased by increased chloride concentration in solution. The rate results obtained are consistent with the equilibrium equations.

Experimental

Cobalt 60, produced by neutron activation of spectroscopically pure metallic cobalt at the Oak Ridge National Laboratories, was used as tracer throughout this work. Activated samples were dissolved, purified and converted to chloride as described previously.² The procedure used in the adsorption rate studies was that of coprecipitation. That is, hydrochloric acid solutions containing ferric chloride and cobalt chloride, including radioactive cobalt, were titrated with ammonia solution to a pH above that necessary for coagulation of the hydrous ferric oxide. The samples were allowed to stand for various periods of time which were measured from the completion of titration to removal of a known volume of solution. The activities of the portions of solution removed were measured and the amount of cobalt adsorbed was calculated from the total amount present and that which was left in a solution.

The experimental results are given in Tables I to VII. The conditions used and the half-lives of the reactions are summarized, for comparison, in Table VIII.

TABLE I

RATE OF ADSORPTION OF COBALT BY HYDROUS FERRIC OXIDE

Constant factors: Total Co, 2.80×10^{-9} gram atom; Fe, 2×10^{-5} gram atom; pH 8.0; volume, 31.4 ± 0.1 ml.; NH_4Cl , 0.034 *N*; temperature, 15°; equilibrium quantity of cobalt in solution, 2.0×10^{-10} gram atom.

Adsorption period, hr.	Cobalt adsorbed, %	Cobalt adsorbed, gram atoms $\times 10^9$	Cobalt in solution less equilibrium quantity in solution, gram atom $\times 10^9$
0.53	69.6	1.95	0.65
1.0	70.1	1.99	.61
2.0	77.6	2.17	.43
5.3	81.2	2.27	.33
7.5	83.7	2.34	.26
10.0	84.8	2.37	.23
14.0	89.2	2.50	.10
25.0	92.8	2.60	
35.1	93.0	2.60	
40.0	92.2	2.58	

TABLE II

RATE OF ADSORPTION OF COBALT BY HYDROUS FERRIC OXIDE

Constant factors: Total Co, 2.80×10^{-9} gram atom; Fe, 2×10^{-5} gram atom; pH 8.0; volume, 31.7 ± 0.34 ml.; NH_4Cl , 0.100 *N*; temperature 30°; equilibrium quantity of cobalt in solution, 1.8×10^{-10} gram atom.

Adsorption period, hr.	Cobalt adsorbed, %	Cobalt adsorbed, gram atoms $\times 10^9$	Cobalt in solution less equilibrium quantity in solution, gram atom $\times 10^9$
1.5	76.6	2.15	0.47
6.0	84.6	2.37	.25
7.1	85.2	2.39	.23
10.1	88.1	2.47	.15
13.2	90.3	2.53	.09
20.3	93.2	2.61	
35.1	93.5	2.62	
37.0	92.9	2.60	

TABLE III

RATE OF ADSORPTION OF COBALT BY HYDROUS FERRIC OXIDE

Constant factors: Total Co, 2.80×10^{-9} gram atom; Fe, 1×10^{-5} gram atom; pH 8.0; volume, 32.5 ± 0.8 ml.; NH_4Cl , 0.034 *N*; temperature 31.7°; equilibrium quantity of cobalt in solution, 3.0×10^{-10} gram atom.

Adsorption period, hr.	Cobalt adsorbed, %	Cobalt adsorbed, gram atoms $\times 10^9$	Cobalt in solution less equilibrium quantity in solution, gram atom $\times 10^9$
1.2	76.8	2.15	0.35
4.2	80.2	2.25	.25
6.3	82.3	2.31	.19
8.5	83.5	2.34	.16
11.0	85.6	2.40	.10
19.5	87.7	2.46	.04
30.0	89.4	2.51	
60.2	88.8	2.49	
72	88.8	2.49	
94	88.9	2.49	
236	88.8	2.49	

TABLE IV

RATE OF ADSORPTION OF COBALT BY HYDROUS FERRIC OXIDE

Constant factors: Total Co, 2.80×10^{-9} gram atom; Fe, 0.5×10^{-5} gram atom; pH 8.0; volume, 30.3 ± 0.1 ml.; NH_4Cl , 0.034 *N*; temperature, 36.3°; equilibrium quantity of cobalt in solution, 4.9×10^{-10} gram atom.

Adsorption period, hr.	Cobalt adsorbed, %	Cobalt adsorbed, gram atoms $\times 10^9$	Cobalt in solution less equilibrium quantity in solution, gram atoms $\times 10^9$
1.8	60.8	1.70	0.61
5.9	62.4	1.75	.56
10.1	68.4	1.92	.39
12	69.2	1.94	.37
14	72.8	2.04	.27
25	78.8	2.21	.10
31	79.8	2.23	.08
37	81.4	2.28	.03
50	83.2	2.33	
60	83.2	2.33	
73	82.2	2.30	
78	82.7	2.31	
135	81.9	2.29	

TABLE V

RATE OF ADSORPTION OF COBALT BY HYDROUS FERRIC OXIDE

Constant factors: Total Co, 2.80×10^{-9} gram atom; Fe, 2×10^{-5} gram atom; pH 8; volume, 30.23 ± 0.1 ml.; NH_4Cl , 0.100 *N*; temperature, 36.3°; equilibrium quantity of cobalt in solution, 2.2×10^{-10} gram atom.

Adsorption period, hr.	Cobalt adsorbed, %	Cobalt adsorbed, gram atoms $\times 10^9$	Cobalt in solution less equilibrium quantity in solution, gram atom $\times 10^9$
2	78.6	2.20	0.38
4	82.5	2.31	.27
6	84.4	2.36	.22
8	84.9	2.38	.20
11	86.6	2.43	.16
14	88.6	2.48	.10
17	89.3	2.50	.08
24	91.0	2.55	.03
40	92.0	2.58	
48	92.2	2.58	
60	92.2	2.58	

TABLE VI

RATE OF ADSORPTION OF COBALT BY HYDROUS FERRIC OXIDE

Constant factors: Total Co, 2.80×10^{-9} gram atom; Fe, 2×10^{-5} gram atom; pH 7; volume, 29.88 ± 0.05 ml.; NH_4Cl , 0.034 *N*; temperature, 36.3° ; equilibrium quantity of cobalt in solution, 1.73×10^{-9} gram atom.

Adsorption period, hr.	Cobalt adsorbed, %	Cobalt adsorbed, gram atoms $\times 10^9$	Cobalt in solution less equilibrium quantity in solution, gram atom $\times 10^9$
1	26.5	0.74	0.33
4	29.9	.84	.23
8	33.4	.94	.13
10	33.8	.95	.12
12	34.8	.97	.10
18	36.6	1.02	.05
24	37.4	1.05	.02
40	38.3	1.07	
48	38.3	1.07	
60	38.2	1.07	

In order to determine the rates of adsorption, the time in hours was plotted against the log of the difference between gram atoms of cobalt in solution at time, *t*, and gram atoms of cobalt in solution at equilibrium. The amount of cobalt in solution at equilibrium was subtracted since it represents the "zero" quantity or concentration in solution for this equilibrium reaction. The quantities of cobalt in solution are directly proportional to the concentrations since the rates were studied at constant volume.

The first six rates (Fig. 1 and 2) proved to be first order with respect to cobalt. In all of these the ratio of total cobalt to iron as hydrous oxide was not more than 2.8×10^{-9} gram atom of cobalt to 5×10^{-5} gram atom of iron in about thirty milliliters of solution. That is, the conditions were in each instance, those of a part of an isotherm in which Henry's law applies, or the quantity of cobalt adsorbed at equilibrium is proportional to the concentration of cobalt.

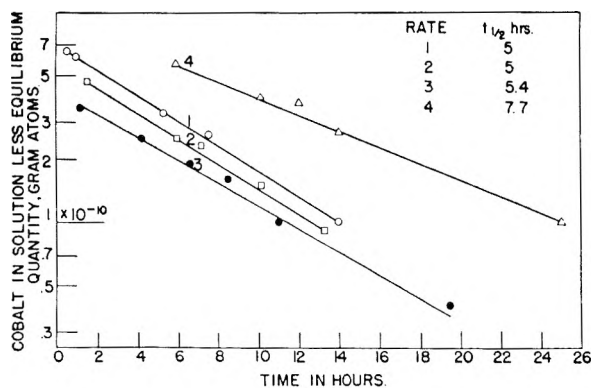


Fig. 1.

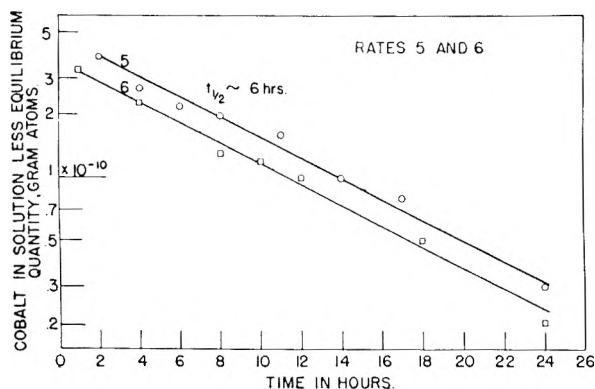


Fig. 2.

TABLE VII

RATE OF ADSORPTION OF COBALT BY HYDROUS FERRIC OXIDE

Constant factors: Total Co, 6.40×10^{-8} gram atom; Fe, 2×10^{-5} gram atom; pH 8.0; volume, 31.6 ± 2 ml.; NH_4Cl , 0.0345 *N*; temperature, 20° ; equilibrium quantity of cobalt in solution, 5.8×10^{-9} gram atom.

Adsorption period, hr.	Cobalt adsorbed, %	Cobalt adsorbed, gram atoms $\times 10^9$	Cobalt in solution less equilibrium quantity in solution, gram atom $\times 10^9$
0.3	65.0	4.16	1.66
0.6	69.8	4.47	1.35
1.25	73.9	4.76	1.06
2	76.4	4.89	0.93
4	81.9	5.24	.58
5	84.3	5.40	.42
8	86.2	5.52	.30
10	87.1	5.58	.24
14	88.1	5.64	.18
16	89.2	5.71	.11
20	90.6	5.80	
25	90.6	5.80	
30	92.0	5.88	
35	90.2	5.77	
40	92.0	5.88	
52	91.7	5.87	
60	90.6	5.80	
80	90.8	5.81	

TABLE VIII

SUMMARY OF RATE STUDIES

Table no. or rate no.	Total cobalt, gram atoms $\times 10^9$	Adsorbent quantity, gram atoms $\times 10^5$	pH	NH_4Cl normality	Temp., $^\circ\text{C}$.	$t_{1/2}$, hr.	Rate constant
1	2.8	2.0	8	0.034	15	5	0.14
2	2.8	2.0	8	.034	30	5	.14
3	2.8	1.0	8	.034	32	5.4	.13
4	2.8	0.5	8	.034	36	7.7	.09
5	2.8	2.0	8	.100	36	6	.11
6	2.8	2.0	7	.034	36	6	.11
7	64.0	2.0	8	.034	20	5.8	.12

Rates 1 and 2 obtained at 15 and 30° , respectively, show no difference in rate resulting from this temperature change. The half-life found in each rate study was five hours.

Rates 2, 3 and 4 show the results of decreasing the amount of adsorbent from 2 to 1 to 0.5×10^{-5} gram atom of iron as hydrous oxide. The half-lives obtained were 5, 5.4 and 7.7 hours. That is, less adsorbent resulted in a slower rate of adsorption.

Comparison of rates 2 and 6 (half-lives 5 and 6 hours) shows the effect of change in pH. Rate 2 was obtained at pH 8 and rate 6 at pH 7. The rate of adsorption at higher hydroxide ion concentration was greater.

Rate 5 was carried out in the presence of 0.100 *N* ammonium chloride while rate 2 had only 0.034 *N* salt with other conditions comparable. The half lives obtained were 6 and 5 hours. That is, the higher salt concentration resulted in a lower rate.

It is of some interest that rates 5 and 6 have the same half-lives, within experimental error, and that both of these are slower than rate 2 with which they are compared above. In other words, a threefold increase in salt concentration (from 0.034 to 0.1 *N*) was experimentally equivalent, in its effect on rate of adsorption, to a decrease in hydroxyl ion concentration from 10^{-6} to 10^{-7} . This emphasizes the known sensitivity of this adsorption system to rather large changes in hydroxyl ion (tenfold in this case) at low concentration levels and also points out the influence of smaller changes (three-fold in this case) of chloride concentration at much higher concentration levels (3×10^{-2} to 10^{-1}).

Rate 7 was obtained with 6×10^{-8} gram atom of cobalt and 2×10^{-5} gram atom of iron as hydrous oxide. This rate was not first order but gave a curve when plotted as the other rates were. The experimental curve is shown in Fig. 3 along with the curve obtained by subtraction. The latter curve indicates an initial first order rate having a constant of 0.69 and a half-life of one hour. The half-life of the subtracted curve is 5.8 hours.

The experimental conditions for rate 7 were those for a point on an isotherm above the region of cobalt ion to adsorbent ratios in which Henry's law holds. Under these conditions, the cobalt adsorbed at equilibrium is not directly proportional to its concentration in solution: the unreacted adsorbent is not in large excess but is significantly reduced by the cobalt adsorbed. It seems then that the initial rapid first order rate is due to the adsorbent, the cobalt ion being in excess. After 5.4×10^{-8} gram atom of cobalt was adsorbed, leaving 1×10^{-6} gram atom in solution, the rate became experimentally first order with respect to cobalt and its half-life was 5.8 hours. Reference to Table VIII shows that this half-life lies between those obtained for 1 and for 0.5×10^{-5} gram atom of iron as hydrous oxide when the total cobalt used was 2.8×10^{-9} gram atom.

It is a pleasure to acknowledge the continued interest of Professor Ed. Mack, Jr., in this work. This research was supported in part from funds granted

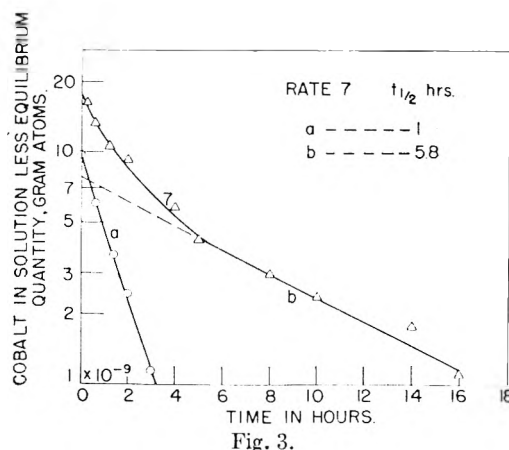


Fig. 3.

by The Ohio State University Research Foundation to the University for aid in fundamental research. We greatly appreciate a grant of the Ohio State University Development Fund for the purchase of instruments.

CRITICAL MICELLE CONCENTRATIONS BY A BUBBLE PRESSURE METHOD

By A. S. BROWN, R. U. ROBINSON, E. H. SIROIS, H. G. THIBAUT, W. MCNEILL AND A. TOFIAS

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Received July 20, 1951

The bubble pressure method of measuring surface tensions has been modified by using it kinetically. The air pressure needed to maintain a stream of bubbles in a surfactant solution is a complex function of concentration and bubble rate. Plots of bubble pressure against concentration have been obtained for the commercial cationic and anionic materials laurylpyridinium chloride, Santomerse #3 and Tergitol TMN-650. The major discontinuities were confirmed as critical micelle concentrations by conductance measurements for the L.P.C. and Santomerse. This technique shows considerable detail in the pressure-concentration plots, possible reasons for this being considered. The utility of the method for solutions containing electrolytes has been examined briefly for Santomerse in 1.84% sulfuric acid.

This Laboratory has recently been interested in the behavior of surfactant systems, particularly under non-equilibrium conditions which resemble practical applications of such agents. This study was initiated in the belief that the pressure required to eject a stream of air bubbles through a given orifice submerged in surfactant solutions would be such a function of both the concentration of the solution and the rate of bubble formation that the dependence of pressure upon concentration would change markedly at the critical micelle concentration at some critical bubble rate. During the first experimental work it was noted that a number of reproducible irregularities appeared in the plots of pressure against concentration and it was believed that these might correspond to the formation of different micelles. To test this interpretation it was decided to measure electrical conductances paralleling the bubble pressure studies since sharp discontinuities in the conductance plots clearly indicate the sudden formation of new species. The correlation between breaks in the two types of plots is encouraging.

Experimental

The bubble pressure apparatus is depicted in Fig. 1. The bubble-forming orifice comprised standard tubing, ther-

mometer tubing or 22 gage B & D hypodermic needles, the tip being immersed to a known depth of 3 to 10 mm. in the solution. The needle hub was attached horizontally to glass tubing by De Khotinsky (medium) cement, as shown separately on an enlarged scale in Fig. 1. Air pressure was measured on a simple manometer such as Cenco #73840 against atmospheric pressure, the open end being either free (for major adjustments) or restricted by a capillary to minimize pulses during readings. Air was supplied at a rate controlled either by a sensitive long-arm screw clamp on a supply from a Kipp generator operated with water or preferably, as shown in Fig. 1, by water displacement of the air in a 1- or 2-pint wide-mouth vacuum bottle. The latter technique permitted insertion of a manifold of restrictive capillary tubes above the vacuum bottle and in the water line from the constant head supply permitting a rapid shift from one water dropping rate to another with a minimum of delicate adjustment. The constant head water supply was a Matviak unit with the lower end of the water leg, the dropping tip, adjusted vertically to compensate for changes in the manometric pressure. Rate of water flow could be checked by counting drops. Glass tubing was connected with rubber tubing, and screw clamps, marked "X" in Fig. 1, served as valves.

Conductance measurements were made at 1000 cycles with student-grade boxed slide-wires operated near mid-point, adequate decade resistance boxes and Wagner grounds. Cells generally comprised Pyrex flasks with small dependent bulbs containing the Pt blacked electrodes connected to the bridge circuit with mercury filled side arms. Water-bath thermostats maintained a temperature of $25.00 \pm 0.02^\circ$.

(1) M. Matviak, *Chemist-Analyst*, **40**, 24 (1951).

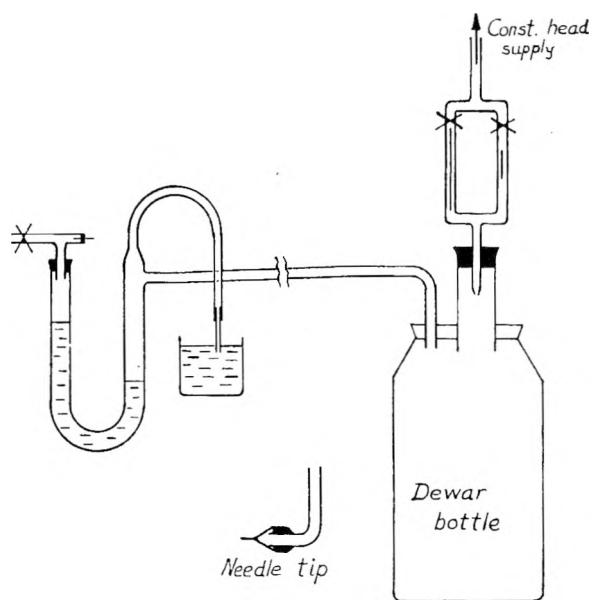


Fig. 1.—Apparatus for bubble pressure measurement.

Surfactants were commercial materials. Solutions were prepared from stock solutions whose concentrations were calculated on a dry basis after moisture estimates were obtained on other samples by prolonged drying at about 60° . Conductivity water was obtained by passing distilled water through a Barnstead "Bantam" demineralizer and had a conductivity about 8×10^{-7} mho cm^{-1} . In conductance work all glass containers were steamed after cleaning. There was no evidence of significant adsorption of surfactant on glass with the possible exception of the very lowest concentrations in the conductance measurements. It may be noted that the accuracy requirement on concentrations is only that demanded for assignment of critical concentrations.

Results

(A) **Laurylpyridinium Chloride.**—Laurylpyridinium chloride (L.P.C.) was selected as an important cationic surfactant. The results of bubble pressure measurements on solutions of L.P.C. are plotted in Fig. 2. These data were obtained with a capillary comprising a roughly 3.5-cm. length of thermometer tubing having a bore 0.027 cm. The plots of pressure against surfactant concentration (log scale) show an initial rapid decrease in pressure to a short plateau, a second drop to a longer plateau and finally a gradual approach to a low pressure. Discontinuities appear at con-

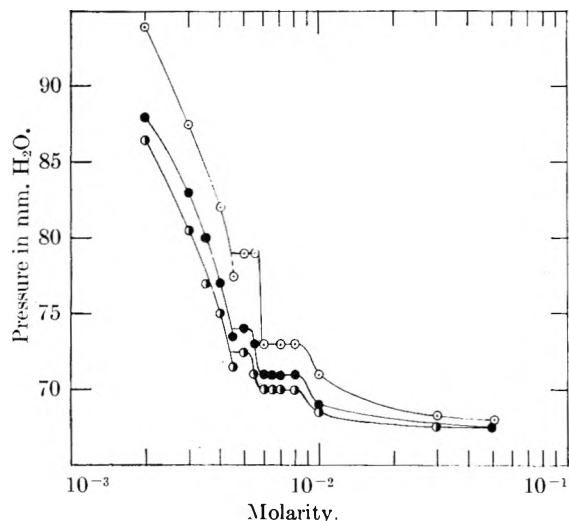


Fig. 2.—Bubble pressures for L.P.C. time for 10 bubbles: O, 5 sec.; ●, 10 sec.; ■, 16 sec.

centrations 4.4×10^{-3} , 5.7×10^{-3} and 8×10^{-3} molar. The second of these is particularly accentuated at higher bubble rates. At an infinitely slow bubble rate this technique becomes a traditional surface tension measurement. The trend of the plots at slower rates is consistent with the form of equilibrium surface tension curves. Attempts to use higher bubble rates were not satisfactory as results scattered widely, probably because of inadequate rate control chiefly, since at the time this work was done the rate had to be set manually for each measurement and there is an astonishingly sharp upper limit to counting rate. It is interesting to note the overshooting of the pressure drop at 4.5×10^{-3} M, the system acting as though a slight excess of a presumably simpler solute form must be present before effecting the change to a second structural form.

The conductivity data for L.P.C. are presented in Fig. 3. These results, which were obtained before the pressure data, were initially interpreted as indicating a single break at a concentration 0.0051 M, with rounding possibly due to an equilibrium between molecular and colloidal species. The detail shown by the bubble pressure plots now indicates that the conductivity results should be interpreted as a series of linear segments with breaks at $\sqrt{M}$ about 0.063 and 0.088, corresponding to molarities 0.0040 and 0.0077. This interpretation, allowing for the difficulty in fixing intersections of lines of only moderately differing slopes, confirms rather well the critical concentrations obtained by the bubble pressure technique. It will be noted that there is an indication of an intermediate break at about 5.2×10^{-3} molar but the data hardly warrant such an assignment. While it was not the purpose of these measurements to fix the conductance at infinite dilution such an extrapolation gave a limiting value between 89 and 90 mhos cm^2 mole $^{-1}$, the limiting slope being roughly 25% above theoretical.

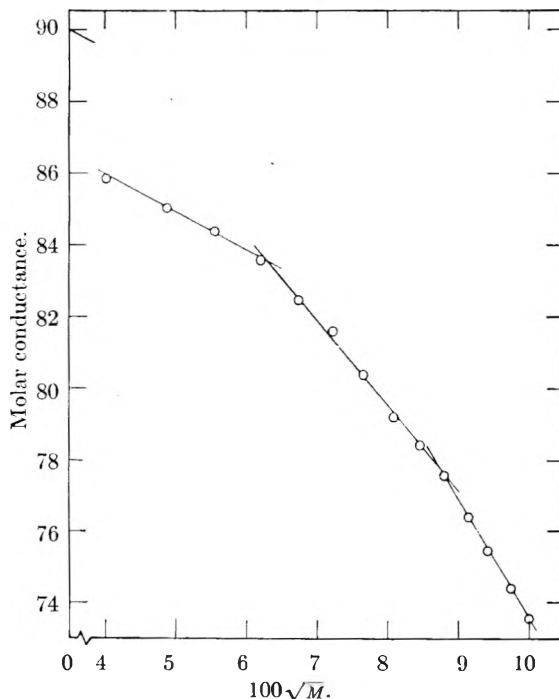


Fig. 3.—Conductance of L.P.C. at 25° .

(B) **Santomerse #3.**—Santomerse #3 was selected as an example of an alkyl aryl sulfonate available with a low degree of inorganic contamination. Its moisture content was 1.5%. For purposes of calculating molarities the molecular weight was taken to be 348.5.

A preliminary exploration of this material by the bubble pressure method, covering the concentration range 3.2×10^{-5} to 3.2×10^{-2} M, was obtained with a vertical capillary of 10.75 cm. length, having a bore 0.0316 cm. and an external diameter 0.567 cm. Bubble rates of 4 and 5 seconds for 10 bubbles were used. These results are plotted in Fig. 4 together with data obtained with a horizontal tip comprising a 0.3-cm. length of 22 gage stainless hypodermic needle at a rate of 15 seconds for 10 drops of air displacement water.

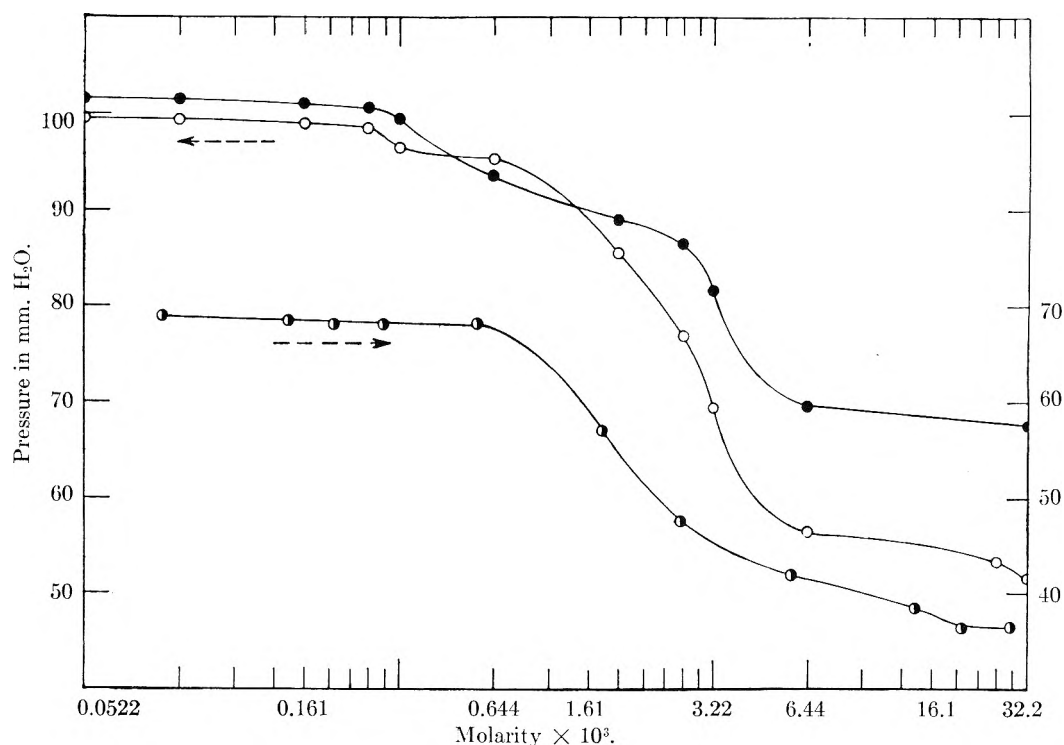


Fig. 4.—Santomerse bubble pressures at rates of 10 bubbles in: ●, 4 sec.; ○, 5 sec.; ◐, 15 sec.

It again appears that the higher rates of interface formation show greater complexity in such plots and that there are a number of concentration regions requiring more detailed examination. The needle tip also showed greater complexity in these plots at higher rates and in the lower concentration range but this tip is more difficult to operate under such conditions. Rates set with such widely differing tips are, of course, only roughly comparable.

The concentration range 2.6×10^{-4} to $8 \times 10^{-4} M$ was examined in more detail with the glass tip, the results being plotted in Fig. 5 for rates of 4 and 12 seconds per 10 bubbles. The pressures for distilled water were 109.2 and 98.2 mm. H_2O for these rates, respectively, the difference reflecting change in kinetic head and, particularly, changes in the mounting of the capillary which shows sensitivity to angular

deviation from vertical. While this sensitivity affects the pressure level and range somewhat it does not seem to affect the critical concentration estimation. These results show a downward break at about $4.2 \times 10^{-4} M$ and the formation of a plateau at about $6.4 \times 10^{-4} M$, this plateau being more prominent at higher rates (as confirmed at other high rates not plotted) than at the lowest rate used. The unexpected steeper slope of the low concentration branch of the plot at the higher bubble rate is confirmed by the drop in these

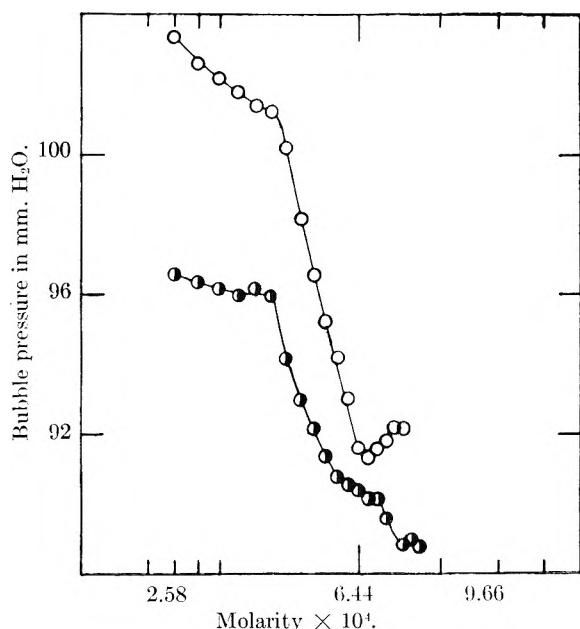


Fig. 5.—Santomerse detail at rates of 10 bubbles in: ○, 4 sec.; ◐, 12 sec.

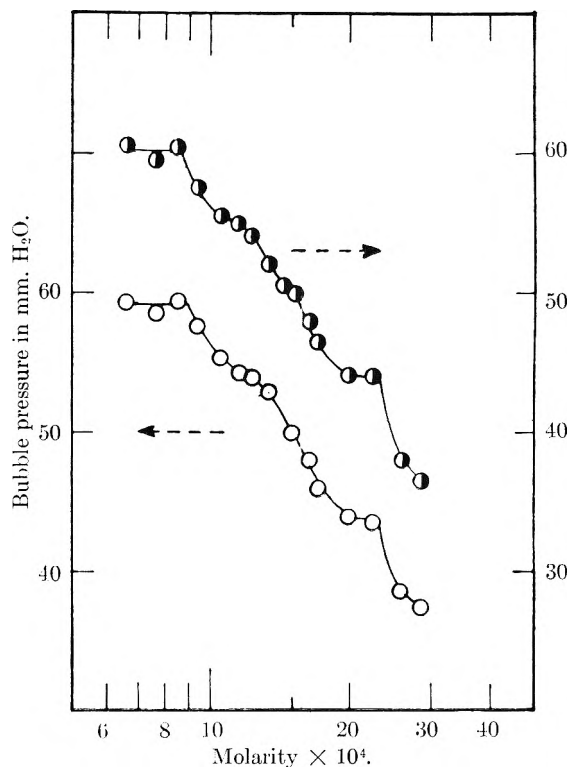


Fig. 6.—Santomerse detail at rates of 10 bubbles in: ○, 2.7 sec.; ◐, 4.7 sec.

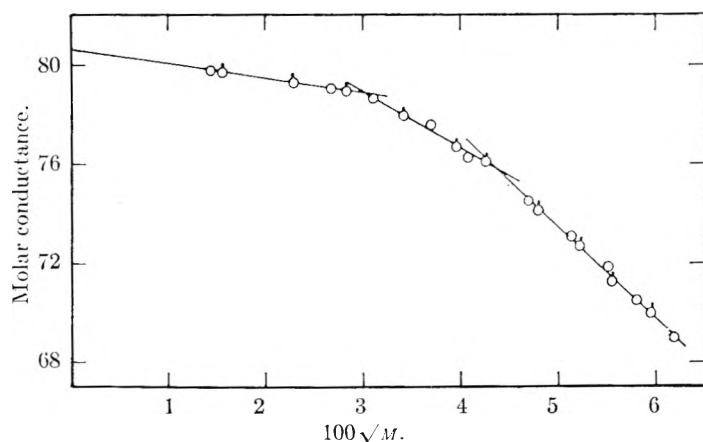


Fig. 7.—Santomerse conductance at 25°.

pressures from that observed in water. It may be significant that the high rate plot shows more prominent overshooting in the pressure drop at $6.4 \times 10^{-4} M$. In any event it appears that these very dilute solutions are somewhat more effective at higher rates of interface formation, a conclusion also obtainable from Fig. 4.

The concentration range 6.5×10^{-4} to $2.9 \times 10^{-3} M$ was studied in detail with the needle tip at the high rates 2.7 and 4.7 seconds per 10 drops of air displacement water. These results, plotted in Fig. 6, show erratic behavior at concentrations below about $7 \times 10^{-4} M$. At higher concentrations they are reasonably consistent and indicate a downward break at about $9 \times 10^{-4} M$, a short plateau from about 1.9 to $2.3 \times 10^{-3} M$ and a subsequent downward break. There is evidence for the existence of additional complexity in these plots.

Conductivity measurements on Santomerse #3 were made two years before the bubble pressure results were obtained but the conclusions were not available until afterwards. These data, plotted in Fig. 7, clearly indicate two breaks, one at about $9.1 \times 10^{-4} M$ and another at about $2.0 \times 10^{-3} M$, agreeing quite well with the more prominently critical concentrations estimated by the bubble pressure method. The conductivity data show no break below $9 \times 10^{-4} M$ but such measurements become increasingly more difficult at these dilutions while the need for precision increases because the slopes are low. At the lowest concentrations adsorption becomes troublesome; the experimental limiting slope being only $3/4$ of the theoretical value. It seems worthy of note that mildly erratic behavior in the conductivity measurements, over the concentration range studied, is observed at the same concentrations which exhibit minor uncertainties in bubble pressure plots. These concentrations may well be significant.

A fragmentary study of Santomerse #3 in solutions containing 1.84% H_2SO_4 was made to test the suitability of the bubble pressure technique for systems of high electrolyte content. These data, taken with a needle tip, are plotted in Fig. 8. These results were obtained before the detail in the region 5×10^{-4} to $10^{-3} M$ was appreciated and the dotted portion of the plot is merely speculative. The measurements are significant in showing the substantial effect of the acid in emphasizing a low-concentration drop in bubble pressure and in accentuating changes near $1.5 \times 10^{-3} M$ that are minor in simple aqueous solutions of this surfactant.

(C) Tergitol.—A sample of Tergitol marked TMN-650 by the manufacturer² was used in bubble pressure experiments with the 0.027 cm. bore capillary, to examine the behavior of a non-ionic surfactant. These data are plotted in Fig. 9. The results show an accentuation of the break at about 7.5×10^{-2} wt. % when rate was increased and possibly the existence of a critical rate of about 10 bubbles in 4 seconds. At high bubble rates and higher surfactant concentrations foaming became excessive and pressures were erratic. The region 0.2 to 0.3 wt. % appears to have interest but was not studied at this time. Again it will be noted that the pressure-concentration plot ap-

proaches equilibrium surface tension-concentration form at decreasing rate of interface formation.

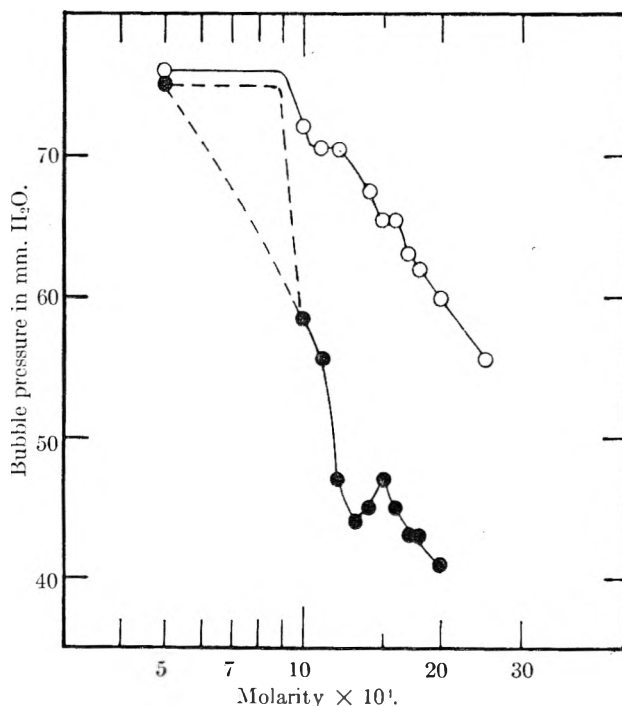
An attempt was made by D. L. Hoyt in this Laboratory to use the dye solubilization technique on this surfactant. While this method has been generally unreliable here it is interesting that there were indications of a discontinuity in solubilization at about 0.07% and that solubilization was increasing between 0.01 and 0.04%. This feature is confirmed by the bubble pressure results since the pressure in water was 110 mm., a value considerably higher than in 0.03% Tergitol solution.

(D) Summary of Results.—For purposes of facilitating comparison of the results obtained by the different experimental methods the concentrations at which anomalous behavior was observed, the "critical" concentrations, are collected in Table I. It will be noted that the several techniques gave results agreeing within about

TABLE I
SUMMARY OF CRITICAL CONCENTRATIONS

Material	Bubble pressure	Experimental method Conductance	Solubilization
L.P.C.	$4.4 \times 10^{-3} M$ 5.7 8	$4.0 \times 10^{-3} M$ (3.2) 7.7	?)
Santomerse #3	$4.2 \times 10^{-4} M$ 6.4 9 $2 \times 10^{-3} M$	$9.1 \times 10^{-4} M$ $2.0 \times 10^{-3} M$	
Tergitol-TMN	$7.5 \times 10^{-2} \%$		$\sim 7 \times 10^{-2} \%$

10%, this being considered reasonably satisfactory for the present objectives.

Fig. 8.—Santomerse in: O, H_2O ; ●, 1.84% H_2SO_4 at a rate of 10 bubbles in 8 sec.

Discussion

The main objective of the present investigation appears to have been attained in that a kinetic use

(2) Carbide and Carbon Chemical Corporation.

of the bubble pressure method of measuring surface tension shows the presence of critical surfactant concentrations which correspond fairly well with critical micelle concentrations determined by conventional methods. The importance of this lies in the suitability of the bubble pressure technique for systems containing electrolytes, which render conductometric and osmometric methods inoperative, and systems containing other light scattering particles which vitiate nephelometric approaches to this problem. It is believed that the method has particular merit for evaluating surfactants which are intended for use in processes characterized by the rapid formation of new interfaces.

The bubble pressure technique has shown more detail than had been anticipated. While this was originally ascribed to experimental uncertainty it has become increasingly evident that at least much of the detail is real. However, an unequivocal explanation of the breaks in the pressure-concentration plots is hardly available at this time for two reasons. The materials studied have been commercial products which may safely be assumed to have variants in surfactant structures and some inorganic contamination. The former might account for variations in the central concentration range of Fig. 6 while sulfate ions might cause the observed behavior in Fig. 8 at about 1.5×10^{-3} molar. This, of course, is pure speculation. Secondly, the introduction of kinetic factors gives prominence to the rate of orientation of surfactant at the air-liquid interface, with several orientations being possible. Furthermore, the question as to the equality of bulk concentration with that in the neighborhood of the orifice remains unanswered. The bubble stream provides substantial agitation and efforts to increase this significantly with added mechanical stirring resulted in erratic shearing of bubbles from the orifice tip.

A general approach to the interpretation of the bubble pressure-concentration plots may be attempted. At sufficiently low gross concentrations and at sufficiently high rates of interface formation both concentration and orientation of surfactant at the interface will be too small to lower bubble pressure from that in water. While these factors are not completely separable increase of gross concentration at constant bubble rate should affect primarily interface concentration and produce a lowering of bubble pressure. Downward breaks in the plots may be interpreted as marking the

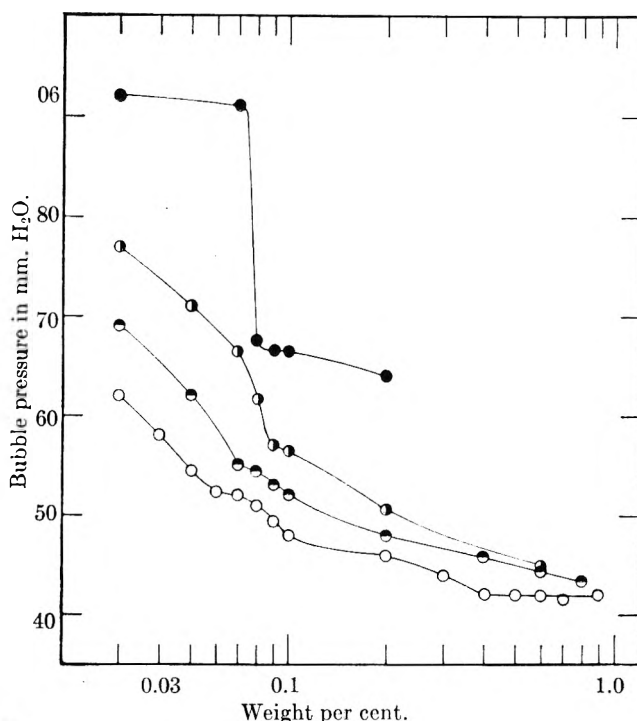


Fig. 9.—Tergitol at rates of 10 bubbles in: O, 15 sec.; ◐, 8.1 sec.; ◑, 5 sec.; ●, 4 sec.

attainment of some minimum interface concentration required for effectiveness. Diffusion of surfactant to the interface and its orientation may be expected to lower this minimum concentration as rate of interface formation decreases. At and above a critical micelle concentration the supply of surfactant to the interface should become less sensitive to gross concentration since one micelle provides many molecules. The effect of rate of interface formation then should reflect largely the rate of distribution of molecules from micellar to interface orientation. In the event that micelles are formed before the interface attains its minimally effective concentration the bubble pressure should drop very sharply at the critical micelle concentration.

The existence of several sequences of the pressure drop and plateau behavior argues compellingly for the recognition of several types of micelle structures. The major critical concentrations estimated by both bubble pressure and conductivity techniques for L.P.C. and Santomerse are in a roughly 2:1 ratio. This might indicate a doubling of the micelle, presumably more readily possible for lamellar than for spherical structures.

PRODUCTION OF NICKEL CARBIDE BY DECOMPOSITION OF *n*-HEXANE ON METALLIC NICKEL

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Received July 23, 1951

In recent years the formation and properties of low temperature metal carbides have been extensively studied.² We wish to report on some data on the production of nickel carbide (Ni_3C) by decomposition of *n*-hexane at nickel surfaces.

Experimental

Essentially the method of Bahr and Bahr³ and Hofer and Peebles⁴ was used to follow the progress of the carburization process, the subsequent hydrogenation of the solid product, and for X-ray analysis of the solid phase formed.

A stream of pure nitrogen was passed through *n*-hexane, kept at constant temperature ($\pm 0.5^\circ$) and then through a powdered active nickel (ex-nitrate) which was loaded in a Bahr-type reaction vessel. In a run three or four vessels were fitted in an heated aluminum block ($\pm 2^\circ$). One vessel was used to follow the reaction gravimetrically, a second in order to obtain data on the hydrogenation of the product, and a third for X-ray analysis. This was performed with $\text{CuK}\alpha$ radiation (Ni filter) and a camera of 57 mm. in diameter, calibrated with pure sodium chloride (Merck and Co., Inc.).

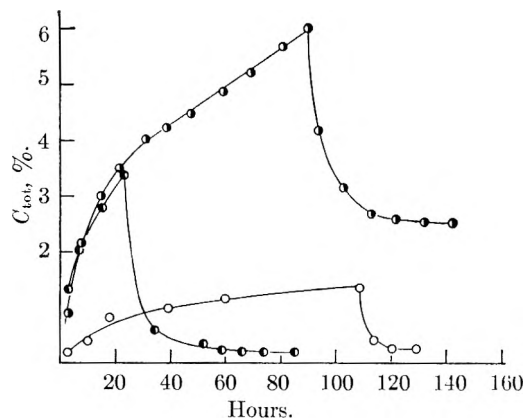


Fig. 1a.—Carburization-hydrogenation of nickel: O, $t = 250^\circ$; ●, $t = 293^\circ$.

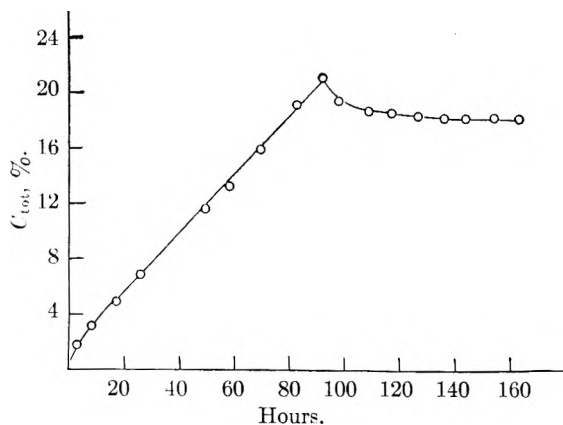


Fig. 1b.—Carburization-hydrogenation of nickel: $t = 327^\circ$.

Results

Some typical results are presented in Fig. 1 and all the data are summarized in Tables I and II.

TABLE I

CARBURIZATION AND HYDROGENATION OF NICKEL

Sample	Reaction with <i>n</i> -hexane			Hydrogenation			X-Ray analysis
	Temp., °C.	Hours	$C_{tot.}, \%$	Temp., °C.	Hours	$C_{carb.}, \%$	
A1	250	109	1.43	275	220	1.12	Ni
A2	250	109	1.37	275	20	1.12	Ni
A3	250	109	1.37	..	..	..	Ni, Ni_3C
B1	270	77	3.55 ^a	270	45	1.74	Ni
B2	270	77	3.09 ^a	..	..	..	Ni, Ni_3C
C1	293	90	7.19	..	..	..	Ni, Ni_3C
C2	293	90	5.99	293	52	3.50	Ni
C3	293	90	6.38	293	56	3.50	Ni
D1	327	92	21.04	299	88	3.16	Ni
D2	327	92	22.54	299	130	3.16	Ni
D3	327	92	17.55	..	..	..	Ni, Ni_3C

^a After treatment at 361° for 27 hours total carbon: B1 17.18%; B2 11.98%.

TABLE II

X-RAY ANALYSIS FOR SAMPLE C1

Intensity	Ni d/n obsd., Å.	Ni_3C d/n obsd., Å.	Ni_3C d/n calcd., ^a Å.	(<i>hkl</i>)
w		2.291	2.295	(100)
w		2.165	2.165	(002)
vs	2.030	2.030	2.027	(111) _{Ni} (101) _{Ni_3C}
s	1.760			(200)
m		1.572	1.575	(102)
m		1.325	1.325	(110)
s	1.247			(220)
m		1.221	1.221	(103)
m		1.132	1.130	(112)
w		1.109	1.109	(201)
s	1.064			(311)
w	1.021			(222)
m		0.984	0.979	(104)
w		.901	.898	(203)
w	0.885			(400)
w		.870	.867	(120)
m		.850	.852	(121)
w		.840	.838	(114)
m	.812			(331)
m	.790			(420)

^a For $a = 2.65$, $b = 4.33$.

Sample D2 was hydrogenated after treatment at 299° for 113 hours in an atmosphere of nitrogen. In one run a carburized sample was kept at room temperature for three months before hydrogenation. The content of carbide carbon of the sample remained unchanged.

The following conclusions can be drawn from these results: (1) in the range of temperature investigated *n*-hexane is decomposed at nickel surfaces; (2) the resulting solid phase is identified as nickel carbide, Ni_3C , and elemental carbon. As Bahr and Hofer have already shown the differ-

(1) Department of Chemistry, Princeton University, Princeton, N. J.

(2) Hofer, Cohn and Peebles, *This Journal*, **54**, 1161 (1950).

(3) Bahr and Bahr, *Ber.*, **61**, 2177 (1928).

(4) Hofer and Peebles, *J. Am. Chem. Soc.*, **69**, 893 (1947).

entiation of these two types of carbon products can be obtained upon treatment of the carburized phase with hydrogen; (3) under the present experimental conditions the decomposition of nickel carbide is not readily observed up to 300°. This is in order with previous findings of Bahr³ and more recently of Hofer.²

It can be noticed that the amount of carbidic carbon, which is removed upon hydrogenation, is almost equal to the amount deposited during the first rapid stage of the carburization process. Further proof of this observation was obtained by treatment with hydrogen of a sample carburized for 23 hours at 291° (these conditions correspond to the first rapid stage of the process, see Fig. 1). It was found that the total amount of carbon deposited was 3.3% and carbidic carbon 3.1%, which is 95% of the total carbon deposited.

The data of the first rapid stage of the carburization process can be fairly well fitted to a parabolic type of plot (Fig. 2), indicating that a diffusion process might be determining the rate of the overall process. From this plot an activation energy of 23.0 kcal./mole was derived. We conclude that,

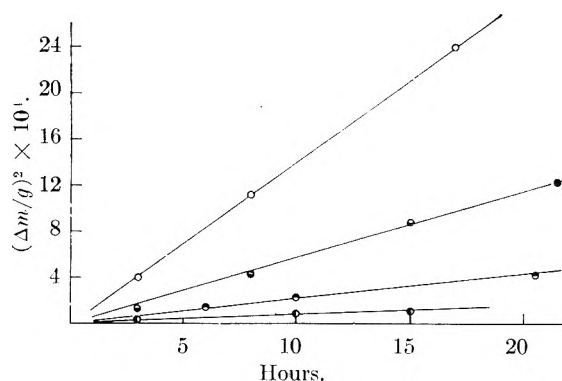


Fig. 2.—Weight increase per unit weight of nickel ($\Delta m/q$) during carburization with *n*-hexane; parabolic plot: ●, $t = 250^\circ$; ○, $t = 270^\circ$; ◐, $t = 293^\circ$; ◑, $t = 327^\circ$.

in the present case, carbide formation occurs through the following steps: (a) dissociative adsorption of *n*-hexane at nickel surfaces, and production of atomic carbon, (b) reaction to nickel carbide and material transport by diffusion through it.

Acknowledgment.—We thank Dr. L. J. E. Hofer for reading the manuscript before publication.

KINETICS OF CHAIN DEPOLYMERIZATION¹

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Received July 24, 1951

In the general theory of chain depolymerization reactions two parameters are important: the kinetic chain length $1/\epsilon$ and the transfer constant σ . In terms of these the molecular weight distribution, average molecular weights and rates of decomposition can be discussed. These rates decrease monotonously with conversion when the kinetic chain length is large in comparison with the D.P., regardless of the initiation mechanism. When it is small, there is a maximum rate, if the initiation is random or transfer is pronounced. If initiation is occurring only at the chain ends, the reaction becomes of zero order. Although the general theory for any value of the kinetic chain length has been developed, numerical solutions are so far available only for extreme cases. However, the initial rate has been given for all conditions. The theory is compared with experimental results on molecular weight change and rate of degradation for polystyrene and polymethylmethacrylate, respectively. In the former instance, an estimate of the kinetic chain length is made from the observed monomer yields. In the latter, ϵ and the rate constant for initiation are obtained from molecular weight and rate curves. The observed molecular weight decrease in methyl methacrylate is more pronounced for the larger molecular weights and higher degrees of conversion, than the theory neglecting chain transfer would predict. This has been tentatively ascribed to chain transfer becoming more important at later stages of the reaction. Thus, it would appear that the general state of affairs in thermal depolymerization of addition polymers is accounted for.² However, discrepancies remain which can at least qualitatively be explained in the framework of the general theory. Their quantitative interpretation requires a refinement of the reaction mechanism considered, in particular the initiation step, and further numerical evaluation of the rate equations. The theory was developed in order to interpret the thermal and photodecomposition of chain polymers. There are degradative processes which exhibit a striking similarity to the phenomena discussed here, although the detailed chemistry is, of course, entirely different. In the deterioration of textiles, some agents attack the fabric in such a way, as to leave the tensile strength of the residue unimpaired, while others produce a gradual decay in the tensile properties. Also, the breakdown of proteins by proteolytic enzymes seems to occur principally in two ways, one leaving intact material and small species, the other producing molecules of intermediate sizes.³ A kinetic description of these reactions could be similar to ours, which involves, in one extreme a slow process, followed by more rapid ones, and in the other a single, moderately rapid step.

In recent years interest in the quantitative aspects of thermal depolymerization processes has been catalyzed by experimental investigations in this country and abroad.² The results obtained on a variety of polymers indicate wide differences in respect to monomer yields, changes in molecular

weight and rates of decomposition. Sometime ago a general theory was developed by the authors in collaboration with Blatz,^{4a,b} which permitted one to reduce these divergent results to a common basis. It is based on the concept of the degradation process as an inverse chain polymerization, characterized by initiation, propagation, chain transfer and termination acts. Previous theories⁵ had been built on the premise of a step reaction, special cases of which are the analog of a poly-

(1) Paper presented in part at the Symposium on Degradation of Macromolecules, 119th Meeting of the American Chemical Society, Boston, Mass., April 1-5, 1951.

(2) For a more detailed analysis of experimental data see R. Simha, *Trans. N. Y. Acad. Sci.*, **14**, 151 (1952).

(3) See the lecture presented by K. U. Linderström-Lang at the 12th International Congress of Pure and Applied Chemistry, September 9-13, 1951, New York, N. Y.

(4) (a) R. Simha, L. A. Wall and P. J. Blatz, *J. Polymer Sci.*, **5**, 615 (1950); (b) R. Simha and L. A. Wall, *ibid.*, **6**, 39 (1951).

(5) R. Simha, *J. Appl. Phys.*, **12**, 569 (1941).

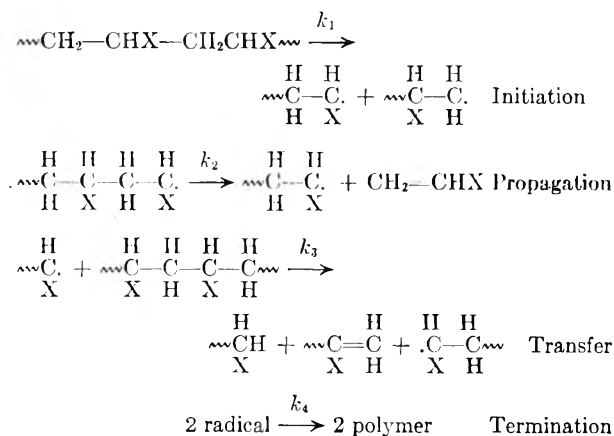
condensation reaction. It could be shown that the chain reaction reduces to a step process in case the kinetic chain length reduces to unity. Thus in particular, a mechanism by which the initial break can occur at random along the molecule, reduces to that obtaining for instance in the hydrolysis of cellulose. There the degradation consists (apart from terminal bonds) of a step-wise and random breaking of links.

The change of molecular weight with conversion predicted by the theory, is in general agreement with the results obtained for methyl methacrylate on the one hand and polyethylene on the other. These represent two extreme cases of slow and rapid variation of molecular weight on degradation.

In the following we wish to summarize again our general equations and to make a more detailed comparison of calculated and observed changes of molecular weight. Furthermore, only slight explicit attention has been given in previous publications to the over-all rate of conversion, its relation to the structure of the polymer and other characteristic behavior on degradation. We shall give explicit expressions and a comparison with experimental data. The same pronounced differences which appear in the molecular weight behavior, reappear in the rates of conversion.

I. General Rate Equations

We have previously postulated the following mechanism



Although in actual polymers radicals may be formed by the decomposition of thermolabile oxygen groups, catalyst fragments, or other impurities,⁶ it is assumed here that initiation occurs by a simple split of carbon bonds. Two extreme cases are treated, initiation at the ends and at random. The above set of reactions is analogous to those accepted for polymerization and consequently the propagation step is the reverse of the usual growth step. The abstraction of hydrogen atoms from the polymer chain by the radicals present is considered to occur readily in the depolymerization of many polymers. The assumption that in such a transfer act the chain attacked readily splits to form both a radical and unreactive species is justified by the relatively high temperatures of depolymerization.

(6) However, such cases can be included in the formal kinetics by a suitable interpretation of k_1 .

There is the possibility of a radical removing hydrogen atoms from its own chain, say from the third to seventh carbon along the radical end of the chain. However, while this type of process would give products other than monomer, in the mathematical treatment it will be absorbed in the propagation step. Experimental evidence for transfer has been presented by Oakes and Richards⁷ who found that in highly branched polyethylene, degradation produced fewer vinyl groups than in the samples with a small amount of branching. This would indicate that the tertiary hydrogens present at the branch points are preferentially removed by the radicals. The effect of a small amount of copolymerized acrylonitrile in methyl methacrylate polymers reported by Grassie and Melville⁸ can also be considered as evidence for transfer occurring through the α -hydrogen of the acrylonitrile.

The large differences in monomer yield, molecular weight change of residue, and rate of depolymerization for various polymers seem to correlate with the probability of transfer as deduced from the structure of the polymers. At least two factors are important for transfer, the reactivity of the radicals and the presence of susceptible hydrogen atoms along the polymer chain. From this point of view a polymer such as α -deuterostyrene should behave considerably differently from normal polystyrene on depolymerization due to the isotope effect. It should favor a higher monomer yield and slower drop in molecular weight of residual polymer.

With the possible exception of styrene where the radical intermediate is stabilized by the phenyl group, polymers containing α -hydrogens, such as polymethylacrylate and acrylonitrile⁹ give poor yields of monomer. Conversely polymethylmethacrylate and polytetrafluoroethylene give high yields of monomer. Presumably the transfer reaction is negligible due to the α -methyl group and the low activity of the radical intermediate in the former case. However, the decomposition temperature is also low. The tightly held fluorine atoms in the latter case make transfer improbable. In comparing styrene with α -deuterostyrene and α -methylstyrene, one finds the monomer yield increasing in this order. Substitution of the methyl group in the ring, on the other hand, does not greatly affect the yield.^{9,10} It should be noted that, unless modified, the scheme proposed here is not applicable to polymers such as polyvinyl chloride or polyvinyl acetate. There degradation proceeds mainly by the splitting off of pendant groups, and only secondarily by scission of the chain.

In order to facilitate the mathematical treatment, disproportionation has been assumed to be the only termination step.

Using a reduced time scale $\tau = k_1 t$, we require two kinetic parameters for the description of the

(7) W. G. Oakes and R. B. Richards, *J. Chem. Soc.*, 2929 (1949).

(8) N. Grassie and H. W. Melville, *Proc. Roy. Soc. (London)*, **A199**, 14, 24, 39 (1949).

(9) L. A. Wall, unpublished work.

(10) S. L. Madorsky, unpublished work.

process, the kinetic chain length $1/\epsilon - 1^{11}$ and the transfer constant σ . They are defined as

$$1/\epsilon = \frac{\text{probability of propagation} + \text{termination} + \text{transfer}}{\text{probability of termination} + \text{transfer}}$$

or

$$1/\epsilon = 1 + \frac{k_2}{k_4 R + (k_3 k_4 R^2 / 2k_1)} = 1 + \frac{k_2}{k_4 R (1 + \sigma/2)} \text{ random initiation} \quad (1)$$

$$1/\epsilon = 1 + \frac{k_2}{k_4 R + k_3 \sum i Q_i - (3k_3 k_4 R^2 / 2k_1)} \text{ initiation at the ends}$$

$$\sigma = \frac{\text{probability of transfer}}{\text{probability of initiation}}$$

or

$$\sigma = k_3 R / k_1$$

The usual steady state assumption in respect to the radical concentration R has been made. It involves the condition

$$k_1 / k_4 R < < 1$$

The second formula for $1/\epsilon$ is only approximately valid. The sum represents the total number of monomer units in the residue. In the later stages of the reaction, R , ϵ and σ can no longer be regarded as constants and the resulting differential equations are non-linear. No attempt has been made at this stage to evaluate approximate solutions under these conditions.

An approximate measure for the kinetic chain length is the ratio p between monomeric and non-monomeric volatiles when conversion has been completed, since each termination or transfer act changes the monomer unit. The estimates become inaccurate when the kinetic chain length is large, that is, when the molar ratio in question is very large. Furthermore under such conditions or for small initial molecular weights, the "impurities" produced by the polymerization are not negligible. Since intramolecular transfer³ is not explicitly considered, the present estimate gives a lower limit for the kinetic chain length. Each transfer or termination act produces two changed monomer units. Some of these disappear again in the course of events. Disregarding this, one finds for polyethylene, polystyrene and polyisobutylene, respectively, $1/\epsilon = 1.01, 4.1, 4.1$. In polymethyl methacrylate, it must equal at least 200.¹²

The rate equations³ for all depolymerizing species Q_i assume the following form, with $N - 1$ denoting the initial number of carbon atoms in the chain skeleton and $\tau = k_1 t$.

(a) Initiation at random

$$\begin{aligned} dQ_n/d\tau = & -(1 + \sigma)(n - 3)Q_n + 2(K_0 - \sigma/4)Q_{n+2} \\ & + 2 \sum_{i=1}^{(N-n-3)/2} K_i Q_{n+2i+2}; \quad 4 \leq n \leq N - 3, n \text{ even} \end{aligned} \quad (2a)$$

(11) The designation of $1/\epsilon - 1$ as a "kinetic" chain length does not correspond to the usage customary in free radical reactions, since a kinetic chain is stopped only by termination and not by transfer. $1/\epsilon - 1$ represents the number average number of monomers produced by the propagation, since the probability of producing i monomers equals $\epsilon(1 - \epsilon)^i$. Thus $1/\epsilon - 1$ may be regarded as a kinetic chain length referring to a given molecule. It is the analog of the number average degree of polymerization in polymerization reactions.

$$dQ_{N-1}/d\tau = -(1 + \sigma)(N - 4)Q_{N-1} \text{ with}^{13}$$

$$K_i = (2 + \sigma)[1 - (1 - \frac{3}{4}\epsilon)(1 - \epsilon)^i] + \sigma$$

(b) Initiation exclusively at ends

$$\begin{aligned} dQ_n/d\tau = & -[2 + (n - 3)\sigma]Q_n + 2(K_0 - \sigma/4)Q_{n+2} \\ & + 2 \sum_{i=1}^{(N-n-3)/2} K_i Q_{n+2i+2}; \quad 4 \leq n \leq N - 3 \quad (2b) \end{aligned}$$

$$dQ_{N-1}/d\tau = -[2 + (N - 4)\sigma]Q_{N-1}$$

with¹³

$$K_i = \sigma[1 - (1 - \frac{3}{4}\epsilon)(1 - \epsilon)^i] + \sigma + \epsilon(1 - \epsilon)^i$$

The physical meaning of these equations is as follows. A particular stable chain Q_n is destroyed by initiation or transfer. It can be produced from all larger chains Q_{n+2i+2} . However, they do not contribute equally but according to a statistical weight factor K_i , since "zips" of various lengths i are necessary to arrive at the desired end-product. Examining for instance equation (2b) for $\sigma = 0$, we notice that K_i reduces to $\epsilon(1 - \epsilon)^i$, the probability of "zipping" down the line i monomer units, after initiation at the chain end has taken place. It is the appearance of this sum, due to the presence of intermediate products, which makes the kinetics more complicated than in vinyl polymerization, except in the extremes of infinitely large or small kinetic chain length. This has not always been recognized by other authors in attempting to formulate kinetic relations analogous to the simple equations in polymerization.

Equations (2a) and (2b) represent an apparent step reaction characterized by a whole spectrum of rate constants K_i . These depend on the location of the bond to be broken. In case (a) interior bonds are more readily attached. In case (b) there is a competition between two terms. The one has the same structure as in case (a) and is produced by the transfer step which acts as random initiator of radicals. The other term, due to the initiation step, makes bonds at the extremities of the chain more vulnerable. In both cases the transfer constant σ appears also as an additive term independent of i , which tends to randomize the process, as is to be expected. The existence of this spectrum is, of course, a statistical effect. It has to do with the number of ways in which a particular spot along the chain molecule can be reached by the ways and means indicated in the postulated mechanism. No assumption as to the existence of actual weak links in the structure has been introduced.

The statistical effect disappears in the two limits when the kinetic chain length is very large, $N\epsilon \ll 1$, and very small, $N\epsilon \gg 1$, respectively. In the former instance, stable chains are produced practically by transfer alone and completely decomposed by propagation. In the other extreme, the degradation reduces essentially to the random type prevalent in the hydrolysis of polysaccharides,

(12) These numbers differ from those given in reference 3 due to the omission of a factor of two. The correct equation should read $p = 1/2(1/\epsilon - 1)$.

(13) This definition differs from the one given in reference 3 by the factor $1/k_1$.

in case (a). In case (b) there is a competition between the exclusive splitting of terminal bonds in the initiation step and the random breakdown produced by transfer.

The solution of the linear differential equations (2a) and (2b) offers no particular analytical difficulties. For practical purposes, however, they have so far been solved only for the two extremes discussed above.³ For large kinetic chain lengths, the solution can be expanded in a power series of the product ϵN , provided σ is negligible. For $\epsilon = 1$, the solution for case (a) has been obtained by several authors. Case (b) has also been treated previously.⁵ Thus, at present, quantitative comparison is feasible only for methyl methacrylate and polyethylene. It is hoped that the necessary numerical solutions applicable to other polymers will be obtained by the Applied Mathematics Laboratory of the National Bureau of Standards. Nevertheless it is possible to analyze the behavior of polymers with relatively small kinetic chain length or of samples of large molecular weight.

Furthermore, there is the possibility of obtaining significant information by determining the initial rates of conversion, as discussed later on. The solution of our rate equations reduces, regardless of the initiation mechanism, to

$$\lim_{\tau \rightarrow 0} Q_n = 2Q_{N-1}(0)K_{(N-n-3)/2\tau}, n \neq N-1 \quad (2')$$

II. Molecular Weight Decrease

For the case $\sigma = 0$, the expressions for the molecular weight and the conversion as function of τ have been given previously for small ϵN .¹⁴ For $\epsilon \rightarrow 1$, and random initiation, the corresponding equations have been discussed by taking into consideration the evaporation of short chain molecules, before they are degraded to monomer.⁴ This effect mitigates somewhat the sharp initial decrease in molecular weight, characteristic for random depolymerization. It has been pointed out by Grassie and Melville¹⁵ that the exclusive splitting off of terminal monomer units leads to a linear decrease of the molecular weight with increasing conversion C . Previous calculations of Simha⁵ confirm this fact. One can show from the relations given,¹⁶ that the ratio between the number average molecular weight $M_n(\tau)$ of the degrading mixture excluding monomer and the initial molecular weight $M(0)$ is

$$\frac{M_n(z)}{M(0)} = \frac{\sum_{i=1}^{N-1} iQ_i}{N-1} = \frac{1-C}{\sum_{i=1}^{N-1} Q_i} = \frac{1 - e^{-z} \sum_{r=\frac{N-3}{2}}^{\infty} \frac{z^r}{r!} + e^{-2z(N-5)/2} \sum_{r=\frac{N-3}{2}}^{\infty} \left(\frac{z}{2}\right)^r \frac{1}{r!}}{1-C} \quad (3)$$

(14) See equations (13) and (14) of reference [3], for random initiation and equation (13') for terminal initiation. There the symbol τ was used for $2k_1t$.

(15) N. Grassie and H. W. Melville, *Discussions Faraday Soc.*, 378 (1947).

(16) Equation (2a, 2') of reference 5 and equation (8') of reference 3.

Here $z = 2\tau$. C represents the conversion

$$C = 1 - \frac{\sum_{i=1}^{N-1} iQ_i}{(N-1)Q_{N-1}(0)} \quad (4)$$

As long as $z < N/2$, which corresponds to practically complete conversion, the denominator reduces to

$$1 - \frac{1}{2} e^{-z} \times Z^{(N-3)/2} / [(N-3/2)!]$$

which is practically unity. The experiments of Grassie and Melville¹⁵ indicate that in methyl methacrylate initiation occurs at the molecule ends, at least during the first stages of the reaction. The following equation then has to be considered when $N \rightarrow \infty$ and $(\epsilon N/2) \ll 1^3$.

$$\frac{M_n(z)}{M(0)} = \frac{1 + \frac{\epsilon N}{4} z - \frac{(\epsilon N)^2}{24} \left(z - \frac{z^2}{2}\right) + \frac{(\epsilon N)^3}{192} \left(z - z^2 + \frac{z^3}{6}\right) + \dots}{1 + \frac{\epsilon N}{2} z - \frac{(\epsilon N)^2}{8} \left(z - \frac{z^2}{2}\right) + \frac{(\epsilon N)^3}{48} \left(z - z^2 + \frac{z^3}{6}\right) + \dots} \quad (5)$$

Even for large kinetic chain length, this expansion breaks down, as τ tends toward its limiting value $\tau = \infty$. Actually, according to equation (5), at complete conversion the molecular weight is reduced only by a factor $1/4$. In other words, for high conversions, corresponding to values of $(\epsilon N/2)z$ of the order of unity, this equation must be replaced by the one resulting from the exact expression (8') of reference.³ For high conversions it reduces formally to the one valid for small kinetic chain length, *i.e.*, equation (3). So far we have no numerical evaluation to bridge the gap between (3) and (5). The further discussion and application of these expressions requires equations for the conversion C as function of τ .

III. Conversion and Reaction Rates

Equation (2a) for random initiation gives the following result for the conversion, when N is large and ϵ small¹⁷

$$1 - C = e^{(N/4)\tau} \left\{ 1 + \frac{2\epsilon}{N} \left[e^{(N-1)\tau} S_2 - \frac{N^2}{4} \right] \right\}$$

where

$$S_2(1 - e^{-2\tau})^2 = (1 - e^{-2\tau})[2e^{-4\tau} - (N-1)e^{-(N-1)\tau}] + 2[e^{-4\tau} - e^{-(N+1)\tau}]$$

For the rate of conversion we obtain

$$\frac{dC}{d\tau} = N(1 - C) - 2\epsilon e^{3\tau} \left(S_2 + \frac{1}{N} \frac{dS_2}{d\tau} \right) \quad (6a)$$

and

$$\lim_{\tau \rightarrow \infty} \frac{dC}{d\tau} = N(1 - C) - 8\epsilon e^{-\tau}$$

$$\lim_{\tau \rightarrow 0} \frac{dC}{d\tau} = N \left(1 - \frac{\epsilon N}{6} + \dots \right) \quad (6b)$$

Thus, the limit of a first order reaction with a rate constant equal to $k_1 N$ is approached for $\tau \rightarrow \infty$. The initial rate ($\tau \rightarrow 0$) is proportional to the initial molecular weight for sufficiently large kinetic chain length and small initial molecular weight. This result is intuitively clear. Since initiation can

(17) See equation (14) of reference 3.

occur anywhere along the chain, the initial rate of production of monomer must be proportional to the number of monomers initially present in the chain.

These results may be compared with the corresponding ones for very small kinetic chain length, when the process reduces to a random splitting of bonds, with a rate constant $k = k_1(1 + \sigma)$.¹⁸

Introducing $\alpha = 1 - e^{-kt} = 1 - e^{-\tau}$, the fractional number of bonds broken at time t , we have⁴

$$1 - C = (1 - \alpha)^{L-1} \left[1 + \alpha \frac{(N - L)(L - 1)}{N} \right] \quad (7)$$

L is the number of groups, for instance methylene, in the smallest chain which does not evaporate before being further degraded. This quantity was introduced for the case of polyethylene because of the small cohesive energy density of this polymer. The rate of conversion is

$$dC/d\tau = (L - 1)(1 - C) - (1 - \alpha)^L \frac{(N - L)(L - 1)}{N} \quad (7a)$$

$$\lim_{\tau \rightarrow 0} \frac{dC}{d\tau} = \frac{(L - 1)L}{N} \quad (7b)$$

The important feature of equation (7a) is the existence of a maximum rate. This occurs when the fraction of bonds broken is

$$\alpha_{\max} = (N - 2L + 1)/L(N - L) \quad (8)$$

It can be shown that at the point $\alpha_{\max}$ the total number of molecules between the sizes L and N reaches a maximum. This extreme is characteristic of random processes with short kinetic chain length. Furthermore

$$C_{\max} = 1 - \left(\frac{L - 1}{L} \times \frac{N - L + 1}{N - L} \right)^{L-1} \left(1 + \frac{L - 1}{L} \frac{N - 2L + 1}{N} \right) \quad (9)$$

$$\left. \begin{aligned} \text{for } N \gg L, C_{\max} &\doteq 1 - \left(\frac{L - 1}{L} \right)^{L-1} \times \\ &\quad \frac{2L - 1}{L}; \quad \alpha_{\max} \doteq \frac{1}{L} \\ \left(\frac{dC}{d\tau} \right)_{\max} &\doteq (L - 1) \left(\frac{L - 1}{L} \right)^{L-1} \end{aligned} \right\} \quad (9a)$$

For $L = 3$, that is, evaporation of monomer only, the maximum occurs at about 25% conversion. For $L \gg 1$

$$C_{\max} \doteq 1 - 2e^{-(L-1)/L} \doteq 1 - 2e^{-1} = 0.26$$

$$(dC/d\tau)_{\max} \doteq Le^{-1}$$

Thus the maximum shifts only insignificantly with increasing L . Its height increases proportionally with L , while the intercept, equation (7b) increases with L^2 . This is indicated in Fig. 1.

The initial rate equation (6b) differs from the same quantity equation (7b) by a factor N^2 , as it should. Random splitting of a molecule gives two monomers, while random initiation with subsequent rapid propagation leads to a number proportional to N times N . A comparison of the rate curves for these two extremes of large and short kinetic chain length is shown in Fig. 2. For small values of ϵN , the rate is practically linear in C with an intercept given by (6b). As ϵ increases,

(18) The factor 2 in the definition of the K_i in equation (2a) arises from the definition of $Q_i = P_i + P_{i-1}$.

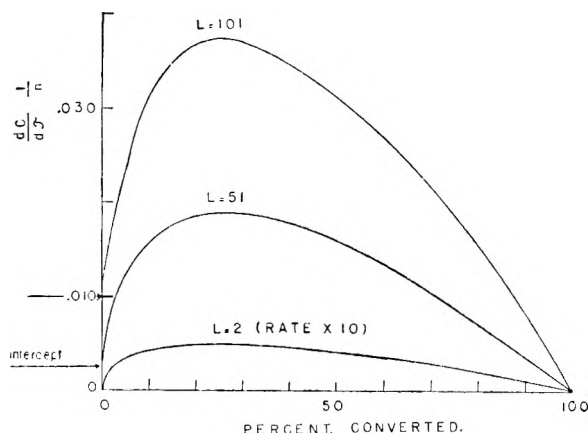


Fig. 1.—Rate $dC/d\tau$ as function of conversion for random depolymerization, equations (7) and (7a) for various values of evaporating limit L and for $N = 1000$.

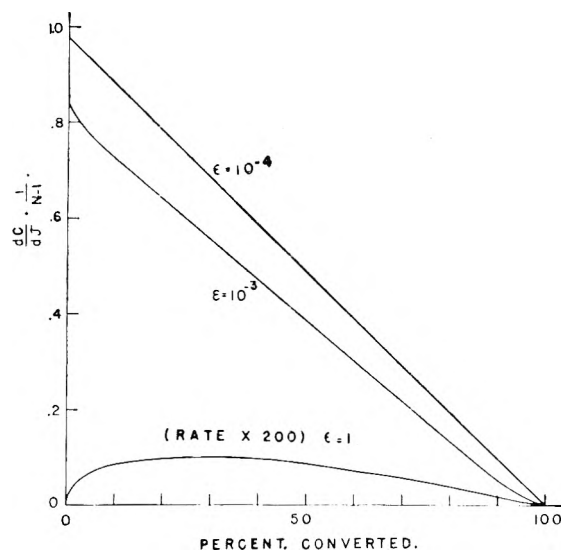


Fig. 2.—Rate $dC/d\tau$ as function of conversion and kinetic chain length, random initiation, equations (6), (6a), (7) and (7a) for $L = 2$.

curvature appears. Measurements of Madorsky¹⁰ on the rates of pyrolysis of polystyrene at 350° are of interest in this connection. Figure 3 shows the results. There is a definite maximum, however at a conversion of about 40% rather than 25% as the theory predicts for random decomposition. This is in qualitative agreement with the conclusion

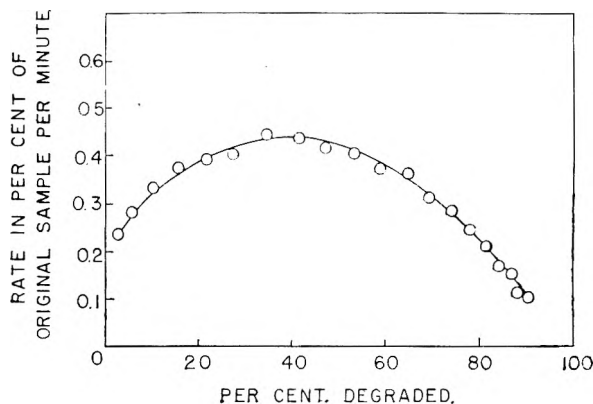


Fig. 3.—Experimental rate of decomposition as function of conversion for polystyrene at 350°: $\bigcirc$, experimental points.

drawn previously from the monomer yield. In polystyrene the kinetic chain length is small but differs sufficiently from unity to make the process non-random. One should expect a similar maximum at lower conversion in polyethylene. This is not observed,¹⁰ the rate decreasing monotonously between 5 and 95% conversion. We should like to suggest tentatively the following reason. The work of Oakes and Richards⁷ indicates a dual mechanism for the degradation, a fast reaction through tertiary hydrogen atoms, and a slow one through secondary hydrogen atoms. The superposition of two rate curves, one with a maximum at lower conversion and of greater height than the second, can give a resultant with a maximum at very low conversion which escapes observation, and a monotonous decrease in the experimental range. A decisive answer can be obtained through studies on a linear polymethylene.

From equation (2') we find the initial rate for any value of ϵ and σ , viz.

$$\lim_{t \rightarrow 0} \frac{dC}{d\tau} = -(1 + \sigma) \left(1 - \frac{8}{N-1} \right) + \frac{4(2 + \sigma)}{(N-1)\epsilon} \left(1 - \frac{3}{4}\epsilon \right) \left[\frac{N-1}{2} - \frac{1}{\epsilon} + \frac{1-2\epsilon}{\epsilon} (1 - \epsilon)^{(N-1/2)} \right] + \frac{\sigma(N-3)}{2(N-1)} \quad (6b')$$

Since ϵ is a function of σ , the rate is not in general, linear in σ . Two special cases have already been discussed. A third one is of interest when $N/2 \gg 1/\epsilon \gg 1$. Then it is very improbable that a molecule is completely eliminated in one stage. On the other hand, the production of monomer by initiation is negligible. Thus the initial rate of reaction should be proportional to $1/\epsilon$, as in polymerization. Indeed (6b') gives

$$\lim_{t \rightarrow 0} \frac{dC}{dt} \doteq k_1 4/\epsilon(1 + \sigma/2) = 4k_1 \frac{k_2}{k_4 R} = 4k_2 \left(\frac{k_1}{k_4} \right)^{1/2} \frac{1}{[2(N-1)Q_{N-1}(O)]^{1/2}}$$

For large kinetic chain length and small molecular weight the energy of activation of the reaction is essentially that of the initiation step. As the molecular weight increases under fixed external conditions, we have

$$E_{act} = \frac{1}{2} E_1 + E_2 - \frac{1}{2} E_4$$

and the rate is now independent of molecular weight. Actually, Madorsky¹⁰ found for two polystyrene fractions of molecular weight 106,000 and 584,000 the same activation energy. At 350° the initial rate for the former is only about 10% smaller than for the latter.

When $1/\epsilon \rightarrow 1$, the rate is dominated again by initiation and by transfer. Thus E_{act} must vary with molecular weight, unless $E_1 + E_3 = 2E_2$. No specific rate in terms of an invariant reaction order can be defined at finite conversions, except in special cases. Hence, a meaningful activation energy can, in general, be derived only for $C \rightarrow 0$ or 1.

From (6b), the previous value of $1/\epsilon$ derived from the monomer yield, and Fig. 3, one obtains for polystyrene at 350°

$$\lim_{t \rightarrow 0} \frac{dC}{dt} = \frac{1}{3} \times 10^{-4} \text{ sec.}^{-1} \doteq 2k_1 (2 + \sigma) \left(\frac{1}{\epsilon} - 1 \right)$$

Hence $k_1 (\sigma + 2) = 5.4 \times 10^{-6} \text{ sec.}^{-1}$. In equation (1) which defines ϵ , $k_2/k_4 R$ represents the true length of the kinetic chain. The number of transfer acts occurring during the life of a kinetic chain is given by $\sigma/2$. Now in thermal polymerization, the kinetic chain lengths for styrene and methyl methacrylate are of the same order of magnitude.¹⁹ We assume that this carries over into depolymerization, i.e., that the ratios $k_2/k_4 R$ are similar. In methyl methacrylate this quantity is of the order of several thousands,^{3,8} and equal to $1/\epsilon$, $\sigma \ll 1$ being assumed. Thus the small value of $1/\epsilon$ in polystyrene is ascribed to a large value of σ . Hence, the above reduces to $k_1 \sigma = k_3 R = 5.4 \times 10^{-6} \text{ sec.}^{-1}$.

This is as far as we can go without additional information. However, it is of interest to introduce the absolute value of the rate constant for transfer with monomer in the thermal polymerization of styrene, determined by Bamford and Dewar,¹⁹ although we are concerned with transfer to polymer. Extrapolating their results to $T = 620^\circ \text{K.}$ by means of the Arrhenius expression, one estimates $k_3 \approx 1.5 \times 10^2 \text{ l. mole}^{-1} \text{ sec.}^{-1}$, and hence $R = 3 \times 10^{-8} \text{ mole l.}^{-1}$. This is about 200 times as large as in thermal polymerization at 25°. Writing equation (1) as $1/\epsilon - 1 = (2k_2/k_4 R) \times (k_1/k_3 R)$ and introducing the expression for the steady state concentration of radicals, R , one has finally, $k_2 = 1.07 \times 10^4 \rho \text{ sec.}^{-1}$ where ρ is the density (g./cc.) of the polymer. This gives

$$k_2 = \rho 1.3 \times 10^{12} e^{(-23,100/RT)}$$

The activation energy, E_2 , is the sum of the heat of polymerization energy, 16.6, kcal. mole⁻¹, and the energy of activation for the propagation step in polymerization, 6.5 kcal. mole⁻¹.¹⁹ The pre-exponential factor is of the expected magnitude. Dainton and Ivin²⁰ obtained reasonable values for the ceiling temperature of polymerization by assuming a factor of 10^{13} . In addition one derives from R the ratio

$$\frac{k_1}{k_4} = \frac{1}{\rho} \times 2.4 \times 10^{-17}$$

The dubious assumption that k_4 can be calculated from polymerization data, i.e., $k_4 \approx 3.2 \times 10^7$, gives $k_1 = 1/\rho 7.4 \times 10^{-10} \text{ sec.}^{-1}$. Hence: $\sigma = k_3 R/k_1 = 6 \times 10^3 \rho$. This would mean that two to three thousand transfer acts occur in one kinetic chain at 350°. Its length, $k_2/k_4 R \approx 1.1 \rho \times 10^4$, is of the same order as is observed for $1/\epsilon$ in methyl methacrylate, which was our starting assumption.

Finally some conclusions can be drawn about the activation energies involved. Since $E_{act} = 60 \text{ kcal./mole}^{-1}$ one has $E_1 - E_4 = 2(60 - 23.1) = 73.8 \text{ kcal.}$, or $E_1 \geq 74 \text{ kcal.}$ If polymerization values are assumed, $E_1 = 76.6$, which is close to the energy of a C—C bond.

In previous publications^{3,4} we have given expressions and graphs for the molecular weight as function of conversion, corresponding to equa-

(19) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc. (London)*, **A192**, 350 (1948); **A197**, 358 (1949).

(20) Dainton and Ivin, unpublished.

tions (6) and (7). Here we reproduce only an experimental curve, Fig. 4, for polystyrene.¹⁰ It is radically different from those characteristic of methyl methacrylate which are discussed below and those calculated from equation (6). On the other hand, equation 7 would predict a steeper decrease, and this discrepancy is again in qualitative agreement with our previous conclusions about polystyrene.

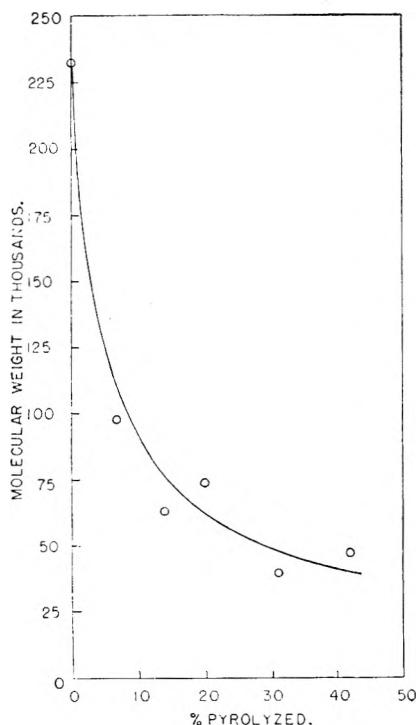


Fig. 4.—Experimental number average molecular weight of residual polymer as function of conversion for polystyrene: O, experimental points.

It remains to summarize the corresponding relations for the case where initiation occurs exclusively at the molecule ends and transfer is negligible. Equation (2b) yields when N is large²¹

$$1 - C = e^{-z} \left[1 + \frac{\epsilon N}{4} z - \frac{(\epsilon N)^2}{24} \left(z - \frac{z^2}{2} \right) + \frac{(\epsilon N)^3}{192} \left(z - z^2 + \frac{z^3}{6} \right) + \dots \right] \quad (10)$$

$$\frac{dC}{dz} = (1 - C) - e^{-z} \frac{\epsilon N}{4} \left[1 - \frac{\epsilon N}{6} (1 - z) + \frac{(\epsilon N)^2}{48} \left(1 - 2z + \frac{z^2}{2} \right) + \dots \right] \quad (11a)$$

and

$$\left. \begin{aligned} \lim_{z \rightarrow \infty} \frac{dC}{dz} &= (1 - C) \\ \lim_{z \rightarrow 0} \frac{dC}{dz} &= 1 - \frac{\epsilon N}{4} \left[1 - \frac{\epsilon N}{6} + \frac{(\epsilon N)^2}{48} + \dots \right] \end{aligned} \right\} \quad (11b)$$

The initial rate is independent of the initial molecular weight when $\epsilon N \ll 1$. This is realized in methyl methacrylate.¹⁵

For $\epsilon N \rightarrow \infty$, we revert to the case of exclusive breaking of terminal bonds. Equation (2a, 2') of reference⁵ leads for all practical purposes to

$$C = 2z/N \quad (12)$$

(21) See equation (13') of reference 3.

until the completion of the reaction, when dC/dz drops to zero. Thus, the reaction is of zero order. Figure 5, the analog of Fig. 2, shows the rates for the two extremes just discussed. Equations (10)

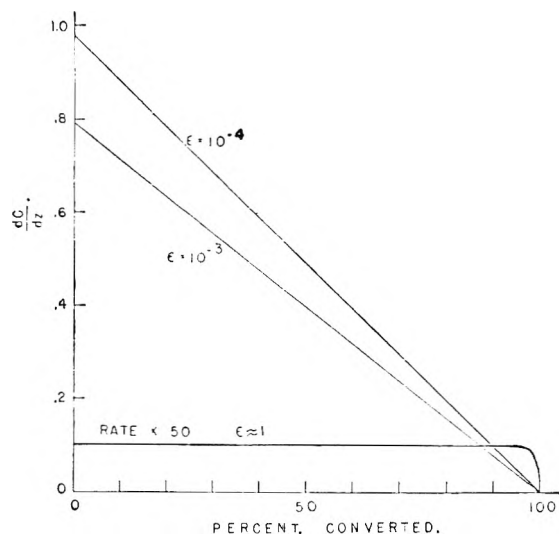


Fig. 5.—Rate dC/dz as function of conversion and kinetic chain length, terminal initiation, equations (10), (11a) and (12).

and (11a) again yield straight lines with the intercept being given by equation (11b). Such a straight line relationship has been observed in a methyl methacrylate, azodinitrile-catalyzed polymer by Grassie and Melville.⁸ It is presumed that the diphenyl cyanomethyl radical both initiates and terminates the chain and that hence the molecule ends are identical. We can use equation (11b) to obtain the rate of initiation k_1 and ϵ . Grassie and Melville have measured the initial rates for various molecular weights with the result exhibited in Fig. 6. The polymer was prepared with benzoyl peroxide as catalyst. Assuming that quadratic and higher terms are negligible in (11b), the initial rate should vary linearly with $N^{1/2}$. For ϵ is proportional to the radical concentration R and hence, in the present case, inversely proportional to the square root of the molecular weight. Thus $\epsilon = \epsilon_1 N^{-1/2}$ where ϵ_1 is independent of N . The straight line indicated in Fig. 6, yields on conversion to fraction of monomer evolved, $k_1 = 3.9 \times 10^{-5} \text{ sec.}^{-1}$ and $\epsilon_1 = 1.73 \times 10^{-2}$. For $M = 94,000$, $\epsilon = 4.1 \times 10^{-4}$ which is in close, although somewhat fortuitous agreement with the value previously estimated from molecular weight data of the same authors.³ For $M \approx 179,000$, $\epsilon = 2.9 \times 10^{-4}$.

The general expression for the limiting rate is now

$$\lim_{z \rightarrow 0} \frac{dC}{dz} = 2 - \sigma \left(1 - \frac{8}{N-1} \right) - \frac{4}{(N-1)} \left[\frac{N-1}{2} - \frac{1}{\epsilon} + \frac{(1-2\epsilon)}{\epsilon} (1 - \epsilon)^{(N-5)/2} \right] + \frac{4\sigma}{(N-1)\epsilon} \left(1 - \frac{3}{4}\epsilon \right) \left[\frac{N-1}{2} - \frac{1}{\epsilon} + \frac{(1-2\epsilon)}{\epsilon} (1 - \epsilon)^{(N-5)/2} \right] + \frac{\sigma(N-3)}{2(N-1)} \quad (11b')$$

For $N/2 \gg 1/\epsilon \gg 1$, this leads again to

$$\frac{dC}{dt} = \frac{k_1}{4} \frac{[1 + \sigma/2](N-1)}{(N-1)\epsilon}$$

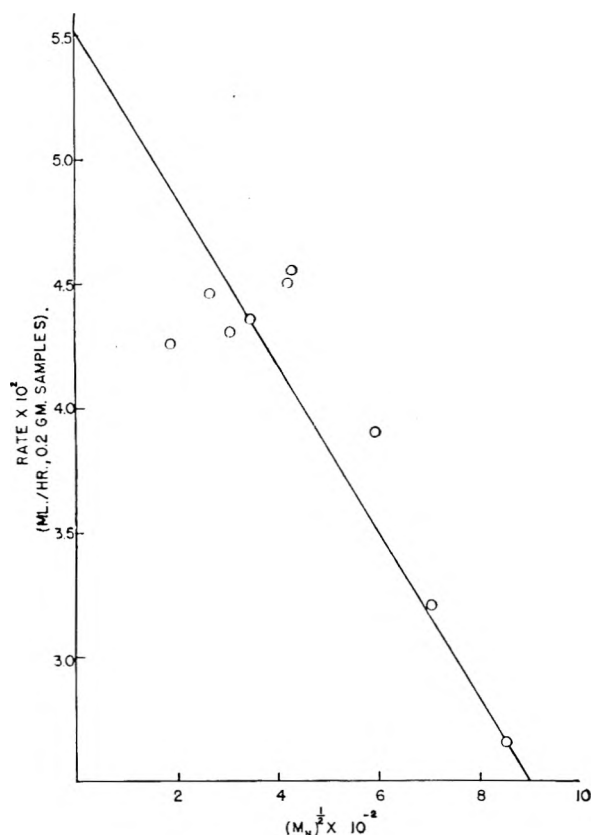


Fig. 6.—Initial rates as function of initial D.P. for methyl methacrylate: $\circ$, experimental points, reference 8.

The radical concentration R is now proportional to $[Q_{N-1}(0)]^{1/2}$. Hence, when σ is small the initial rate is inversely proportional to the square root of the initial molecular weight. As in the case discussed previously, equation (6b'), the activation energy varies with molecular weight. From (6b') or (11b') one can obtain the values of k_i , ϵ and σ by making suitable rate measurements over a range of molecular weights for small conversions.

The molecular weight curves were previously not analyzed in detail, but merely the conversion determined, at which the original D.P. had been decreased by 10%.³ We now make a more detailed analysis by using measurements on two polymers of osmotic molecular weights 94,000 and 177,000, respectively. In reference⁸ results on a small molecular weight (44,000) and two large ones (650,000 and 775,000) are also included. The former gives, within the error of measurement, no change up to 60% conversion, indicating that $\epsilon N \ll 1$. The latter two give more or less the linear decrease, equation (3), which should be characteristic of terminal initiation and very small kinetic chain length. We revert later on to this point. Figures 7 and 8 indicate the situation. The experimental data can be fitted by assuming values of ϵ in the range between 1 and 4×10^{-4} in the region of low conversion. It must be noted that the osmotic pressure data may not be accurate enough for precise indication of the slight changes in molecular weight occurring at the beginning. This is particularly noticeable for the smallest fraction considered in reference 8. However, at higher

conversions the experimental drop is much more pronounced than our theory indicates. Unfortunately the expression (5) becomes inadequate at conversions of 50% and above, where the higher terms of the expansion become important. These would tend to enhance the D.P. drop.

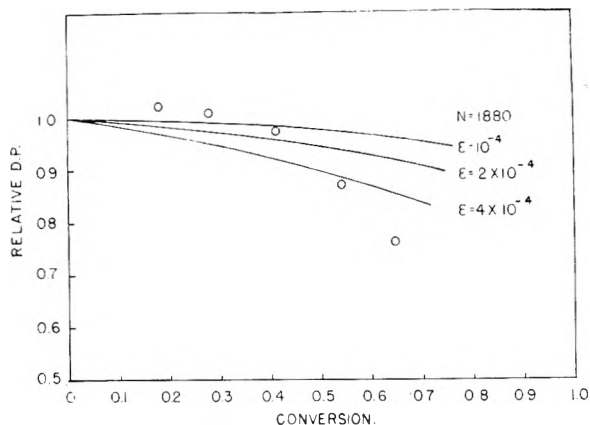


Fig. 7.—Comparison of data for methyl methacrylate ($N = 1880$) with theoretical curves; plots of mol. wt. decrease as function of conversion: $\circ$, experimental points, ref. 8.

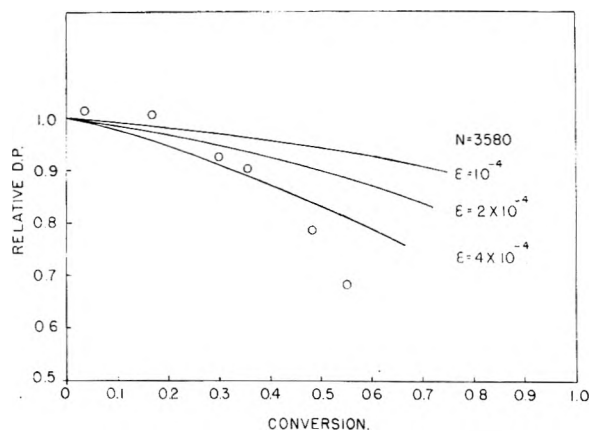


Fig. 8.—Comparison of data for methyl methacrylate ($N = 3580$) with theoretical curves; plots of mol. wt. decrease as function of conversion; $\circ$, experimental points, ref. 8.

It is doubtful that this suffices to explain the discrepancy. The differences between calculated and experimental values at higher conversions may be related to the following. The activation energy increases in the course of the reaction from 31 to 42 kcal. mole⁻¹.⁸ This would mean a decrease of the rate of initiation k_i . Thus, the transfer rate which we neglected in our calculations may become significant in reducing the kinetic chain length. Another cause for this reduction might be the inverse of the viscosity effect on the rate of termination, observed in polymerization. The early approach to the diagonal in the plots of molecular weight *versus* conversion obtained for $N = 13,000$ and 14,500 [8] is also indicative of a shortening in the kinetic chain length. The data are not sufficient to decide the shape of the curves. Clearly, measurements at higher conversions and on samples of larger initial molecular weight are needed.

The preceding analysis was based on the assumption that initiation of the chain process occurs ex-

clusively at the molecule ends. This was supported by two experimental facts. First the limiting rate dC/dt for $t = 0$ is almost independent of initial molecular weight in agreement with equation (11b). Second, the use of special catalysts in the preparation of the polymer produces significant differences in the initial rate of degradation.⁸ This difference has been ascribed to the catalyst fragments at the chain ends. Strictly, however, the observed behavior is merely indicative of a few initiating points independent of molecular size, some of which can also be located in the interior. A recent study by Arnett²² suggests that the termination of two

(22) L. M. Arnett, paper presented at the 119th Meeting of the American Chemical Society, Cleveland 1, Ohio, April 8-12, 1951.

radicals occurs by combination in the polymerization of methyl methacrylate. This may create an additional initiating site in the interior of the polymer. In such a case we would have to introduce additional terms in equation (2b) similar to those in (2a) with an effective rate of initiation depending on the size of the parent molecule, since the probability of finding a weak point at a particular location is inversely proportional to the chain length. At higher conversions this effect should actually tend to decrease the molecular weight drop. However, for the range under consideration this is insignificant. Furthermore, many of these weak points would be consumed by the propagation step.

DETERMINATION OF DIFFUSION COEFFICIENTS FROM RATES OF EVAPORATION

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Received July 31, 1951

Diffusion coefficients were measured for water vapor in combination with air, methane, ethane, ethylene, propane and sulfur dioxide as well as for heavy water vapor in air. The measurements were made at several temperatures and mean molecular diameters were computed from the results.

Introduction

Accurately determined values of diffusion coefficients of gases are of interest for several reasons. First, they serve to indicate how rapidly mixing by the diffusion process will occur. Second, it is possible by use of theoretical results obtained by Chapman and Cowling^{2a} to calculate mean molecular diameters of the gas pairs from their mutual diffusion coefficients.³ This calculation gives information related to the van der Waals dimensions and in some instances an insight regarding the force fields between molecules. From a more practical standpoint, diffusion data are of great value in designing columns for thermal separation of isotopes.

In this investigation, the diffusion constant for water vapor-air was checked; in addition the diffusion constants for water vapor going into methane, ethane, ethylene, propane and sulfur dioxide were determined. Of the latter combinations, the diffusion of water vapor into methane and ethylene has been investigated at somewhat different temperatures by Schwertz and Brow.⁴ The present research was also concerned with the measurement of the diffusion coefficients of heavy water vapor moving into air. The temperature dependence of diffusion was also investigated for the systems heavy water vapor-air and water-methane.

Theory

When a gas contains two or more different kinds of molecules whose relative concentrations vary

from point to point, a process called diffusion is observed to occur in such a way as to diminish the inequalities of composition. The net flow of each kind of molecule will obviously occur in the direction of its negative density gradient.

Let us consider a mixture of two gases confined to a cylindrical tube parallel to the x direction, and let us assume that the composition is a function only of x and of the time, t . If n_1 and n_2 are the number concentrations of the two gases, then the net number of a given kind of molecule crossing a unit area perpendicular to the x direction will in unit time be equal to

$$\Gamma_1 = -D_{12}(\partial n_1/\partial x); \quad \Gamma_2 = -D_{12}(\partial n_2/\partial x) \quad (1)$$

where D_{12} is the coefficient of mutual diffusion.

According to the mathematical theory of non-uniform gases^{2a} a first approximation to the coefficient of mutual diffusion is given by

$$D_{12} = \frac{3}{8n\sigma_{12}^2} \left\{ \frac{kT(m_1 + m_2)}{2\pi m_1 m_2} \right\}^{1/2} \quad (2)$$

Equation (2) was derived on the assumption that the molecules are rigid elastic spheres of masses m_1 and m_2 with diameters σ_1 and σ_2 . The mean diameter, $(\sigma_1 + \sigma_2)/2$, is defined as σ_{12} and the total concentration, $n_1 + n_2$, is denoted by n . Higher approximations show that D_{12} depends to some extent upon the composition of the gas mixture, but this dependence is very slight and is usually neglected.

Experimental

A convenient way of determining the diffusion coefficient of a pair of gases is the measurement of the rate of evaporation of one of the components into an atmosphere of the other. When applicable (one of the components must of necessity be in the liquid state) this method is rapid and accurate.

- (1) Anderson Physical Laboratories, Champaign, Ill.
- (2) Chapman and Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge Press, 1939. (a) p. 245, (b) p. 229.
- (3) Wall and Kidder, *This Journal*, **50**, 235 (1946).
- (4) Schwertz and Brow, *J. Chem. Phys.*, **19**, 640 (1951).

The apparatus and experimental method used were very similar to that described by Winkelmann⁵ and more recently by Gilliland.⁶ Briefly, the experiment consisted of placing one of the two components in the liquid state in a small glass tube and filling the tube within 1 to 5 cm. of the top (Fig. 1). The tube and liquid were held at constant temperature, and the second gas was passed over the top of the tube. The rate of diffusion was obtained by measuring the rate of fall of liquid in the tube.

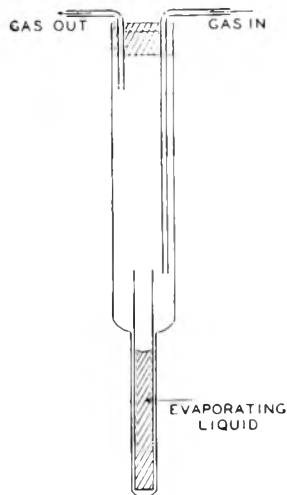


Fig. 1.—Diffusion apparatus.

Previous investigators have found that between rather wide limits the rate of evaporation is independent of the rate of flow of the gas stream. The gas stream must be fast enough to keep the concentration of the vapor effectively zero at the mouth of the evaporation tube, but it must not be so rapid as to cause excessive turbulence. As a conservation measure, it was advisable to keep the gas rate as slow as possible and still meet the above conditions. Hence a rate of 5 to 10 liters per hour was chosen for most of the runs.

This rate of flow of non-corrosive gases was measured by a wet test meter. Corrosive gases and gases more than slightly soluble in water were metered by a kerosene manometer which was previously calibrated against the wet test meter.

The gases were dried by passing them through a tube filled with anhydrous (magnesium perchlorate). Gases inert to sodium hydroxide were also passed through a tube of ascarite (sodium hydroxide on asbestos) to remove traces of carbon dioxide. In order to bring them to the desired temperature, the gases were passed through a coil of copper tubing which was immersed in a thermostated water-bath. The coil was about 2 meters long and 7 mm. in diameter.

The procedure used in making a run was as follows. The evaporation tube was carefully cleaned with sodium chromate-sulfuric acid "cleaning solution" and rinsed several times with the liquid to be used. It was then filled to the desired level and placed in position in the constant temperature bath.

The flow of gas was then started and after waiting for several hours so that the system would attain a steady state, the distance from the liquid surface to the top of the tube was measured. These measurements were made with a cathetometer which had a scale calibrated in millimeters attached to it. The scale was equipped with a vernier and a magnifying lens which allowed readings to be made to ± 0.02 mm. Readings of the liquid level and the barometric pressure were then taken at convenient time intervals.

Stefan⁷ has shown that the following equation applies to an experiment of this sort.

$$v = \frac{D}{h} \ln \frac{P}{P-p} \quad (3)$$

where

v = volume of vapor measured at the pressure and temperature of the experiment which goes through a unit cross-section in unit time

D = diffusion coefficient at the pressure P

h = distance from top of tube to surface of evaporating liquid

P = barometric pressure

p = vapor pressure of evaporating liquid

The vapor volume vdt which is evolved in the time dt corresponds to a lowering of the level of

the liquid by an amount dh . If S is the density of the liquid and d the density of the vapor it follows that

$$d \times v \times dt = Sdh$$

or

$$v = \frac{Sdh}{d \, dt} \quad (4)$$

Substituting (4) into (3) and integrating, the following is obtained

$$D_{12}^{\circ} = \frac{(h_1 + h_0)(h_1 - h_0)}{2} \times \frac{S}{d_1} \times \frac{T'}{273} \times \frac{1}{(t_1 - t_0) \left(\ln \frac{P}{P-p} \right)} \quad (5)$$

where

D_{12}° = diffusion coefficient corrected to 760 mm.

h_0 and h_1 = distances from liquid surface to top of evaporation tube at times t_0 and t_1 , respectively

d_1 = density of the vapor at 0° and 760 mm.

T' = temperature of the experiment

The other symbols have the same significance as before. Equation (5) was used for calculating the diffusion coefficients from the experimental data, after which equation (2) was used to compute mean molecular diameters.

Results and Conclusions

Table I gives a summary of the results obtained in this investigation.

TABLE I

Gas pair	Temp., $^{\circ}\text{C}$.	D_{12} , cm. ² /sec.	σ_{12} , Å.
H ₂ O-air	24.8	0.257	3.32
H ₂ O-CH ₄	24.8	.251	3.60
H ₂ O-CH ₄	40.0	.278	3.55
H ₂ O-CH ₄	50.0	.297	3.52
H ₂ O-CH ₄	60.0	.313	3.50
H ₂ O-C ₂ H ₆	24.8	.177	3.99
H ₂ O-C ₂ H ₆	24.8	.178	4.01
H ₂ O-C ₃ H ₈	24.8	.156	4.12
H ₂ O-SO ₂	24.8	.124	4.51
D ₂ O-air	24.8	.247	3.41
D ₂ O-air	40.0	.277	3.27
D ₂ O-air	45.0	.288	3.25
D ₂ O-air	60.0	.314	3.22

The value of 0.257 cm.²/sec. found for H₂O-air at 24.8 $^{\circ}$ is in good agreement with the value of 0.258 cm.²/sec. found by Gilliland.⁶

The mean molecular diameters of water and the various hydrocarbons show an increase as the molecular weight of the hydrocarbons increases, a result which would be expected. However, a discrepancy appears in the result for H₂O-C₂H₆ as compared to H₂O-C₂H₄, since C₂H₄ is known to have the smaller molecular diameter. This may be due to the fact that the C₂H₆ used was only 95% pure, while all the other hydrocarbons employed were of 99% purity. If the impurity in the C₂H₆ consisted largely of lower molecular weight materials such as H₂ and CH₄, the low result obtained would be expected.

It is interesting to note that the mass effect alone is not sufficient to account for the difference in the diffusion coefficients of H₂O-air and D₂O-air. The mean molecular diameter of H₂O-air at 24.8 $^{\circ}$ was calculated to be 3.32 Å. and that of D₂O-air 3.41

(5) Winkelmann, *Ann. Physik*, **22**, 1, 154 (1884); **23**, 203 (1884); **26**, 105 (1885); **33**, 445 (1885); **35**, 93 (1889).

(6) Gilliland, *Ind. Eng. Chem.*, **26**, 681 (1934).

(7) Stefan, *Ann. Physik*, **41**, 723 (1890).

Å. This is in qualitative agreement with results obtained by viscosity measurements reported by Chapman and Cowling.^{2b} They give the molecular diameter of H₂ as 2.63 Å. and that of D₂ as 2.76 Å., and hence D₂O would be expected to have a slightly higher molecular diameter than H₂O.

The diffusion coefficients for the system H₂O-CH₄ appeared to be proportional to T^2 for the four temperatures investigated. For the system D₂O-air no proportionality could be established between the diffusion constant and a power of the temperature. The values obtained for the diffusion constants at 24.8, 40 and 45° are nearly proportional to

T^3 , but the value obtained at 60° is much less than this proportionality would predict. The peculiar behavior of the system D₂O-air may be due in part to the fact that D₂O tends to exchange with water vapor in the atmosphere. Hence, the determinations involving D₂O are somewhat less reliable than those involving ordinary water.

For both H₂O-CH₄ and D₂O-air the value of the mean molecular diameter decreased with increasing temperature. This is to be expected since as the temperature increases the kinetic energy increases and hence the distance of closest approach decreases.

ELECTROPHORETIC ANALYSIS OF PROTEIN INTERACTION. II. EXPLANATION OF A BOUNDARY ANOMALY IN THE SYSTEM BOVINE SERUM ALBUMIN-METHYL ORANGE^{1,2}

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A pronounced anomaly in the descending Tiselius electrophoresis pattern for the system serum albumin-methyl orange is shown to be described by the equation $(\partial c/\partial x)_t = Kc(dr/dA_t)(\partial A_t/\partial x)_t$, where c and A_t are the total concentration of protein and the concentration of free dye, respectively, at any point, x , and time, t , and r is the average number of dye anions bound per protein molecule for that value of the free dye concentration. Consequently, it is demonstrated that the symmetry in such patterns must depend on variations in the protein concentration, on the constants of the adsorption isotherm which describes the dye protein interaction, and on the total concentration of dye anion. In particular, it is emphasized that reproducible, distinct inflections in such Tiselius patterns are not always due to the presence of additional distinct components. The importance of this restriction for the interpretation of such patterns is indicated.

It is generally recognized that pronounced lack of enantiography in the complete Tiselius patterns for the rising and descending boundaries is *a priori* evidence of interaction between the components of the system.⁴⁻⁸ However, there have been only a few qualitative attempts to relate the shapes of the patterns to processes occurring within the solution. The purpose of this report is to explain a marked anomaly in the patterns obtained for the simple interacting system bovine plasma albumin and methyl orange. Its possible importance for the interpretation of patterns of more complex mixtures is indicated.

In general, anomalous Tiselius patterns may be arbitrarily grouped as follows: (I) The first group includes those patterns in which the number of peaks and/or the relative distribution of areas under them vary between the ascending and de-

scending legs of the cell. Longworth and MacInnes⁵ laid the basis for the interpretation of such patterns in their analysis of the interaction of ovalbumin and yeast nucleic acid. They demonstrated that the shape of the resultant electrophoretic patterns in such systems depends on the rate of formation and decomposition of the complexes and they classified the possible patterns into five groups. Essentially, these groups differ in the relative magnitudes of the velocity constants, k_1 and k_2 of the forward and reverse reactions for establishment of the equilibrium, in comparison with the rate of electrophoretic separation of the components. Recently Smith and Briggs⁹ and Alberty and Marvin¹⁰ have discussed quantitatively the case where k_1 and k_2 are both large and comparable in magnitude. In particular Smith and Briggs showed that a correct analysis of these asymmetric patterns gave the constants of interaction of the components in the equilibrium state. Their equations were confirmed by application to the systems, plasma albumin-methyl orange and ovalbumin-yeast nucleic acid. Their analysis is restricted to conditions where (a) at least one of the components bears an electric charge; (b) the rate of attainment of equilibrium in the system is rapid compared to the time required for development of the electrophoretic boundaries. This type of asymmetry will not be considered further here.

(II) The second major group of boundary anomalies is that in which the lack of enantiography

(1) Paper No. 2683, Scientific Journal Series, Minnesota Agricultural Experiment Station. The contents of this paper constitute a part of the thesis submitted by J. R. Colvin to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, January, 1951.

(2) This investigation was supported in part by a research grant from the National Institutes of Health, Public Health Service.

(3) Division of Applied Biology, National Research Council, Ottawa, Ontario.

(4) E. Goldwasser and F. W. Putnam, *THIS JOURNAL*, **54**, 79 (1950).

(5) L. G. Longworth and D. A. MacInnes, *J. Gen. Physiol.*, **25**, 507 (1942).

(6) L. G. Longworth and C. F. Jacobsen, *THIS JOURNAL*, **53**, 126 (1949).

(7) L. G. Longworth, R. K. Cannan and D. A. MacInnes, *J. Am. Chem. Soc.*, **62**, 2580 (1940).

(8) G. W. Schwert, F. W. Putnam and D. R. Briggs, *Arch. Biochem.*, **4**, 371 (1944).

(9) R. F. Smith and D. R. Briggs, *THIS JOURNAL*, **54**, 33 (1950).

(10) R. A. Alberty and H. H. Marvin, *ibid.*, **54**, 47 (1950).

between Tiselius patterns for the two legs of the cell arises from the skewing of single peaks within an otherwise symmetrical distribution.¹¹ In such cases, the distribution of dn/dx with x departs strongly from the usual bell-shaped curve (or superposition of such curves) so that the whole pattern appears asymmetrical. This too is generally attributed to interaction^{5,6,12,13} although to the writers' knowledge no quantitative interpretation of this type of asymmetry has yet appeared. Systems of the type under the present discussion have been excluded, by assumption, in the latest careful studies of the shapes of single Tiselius curves.^{11,14,15}

A recent example of the type of boundary anomaly which is to be discussed in the present paper was reported by Smith and Briggs⁹ when they extended their experiments to the higher methyl orange concentrations. Progressive deviation from linearity was found with increasing methyl orange concentration in the conventional plot of A_f/r versus A_f ¹⁶ and this discrepancy was accompanied by a marked anomaly in the dye-protein peak in the pattern for the descending boundary. Examples of these very reproducible anomalies are illustrated in Fig. 1. Clearly, such abnormal inflections are important in the interpretation of Tiselius patterns for analogous mixtures of proteins and it therefore seemed worthwhile to investigate their cause.

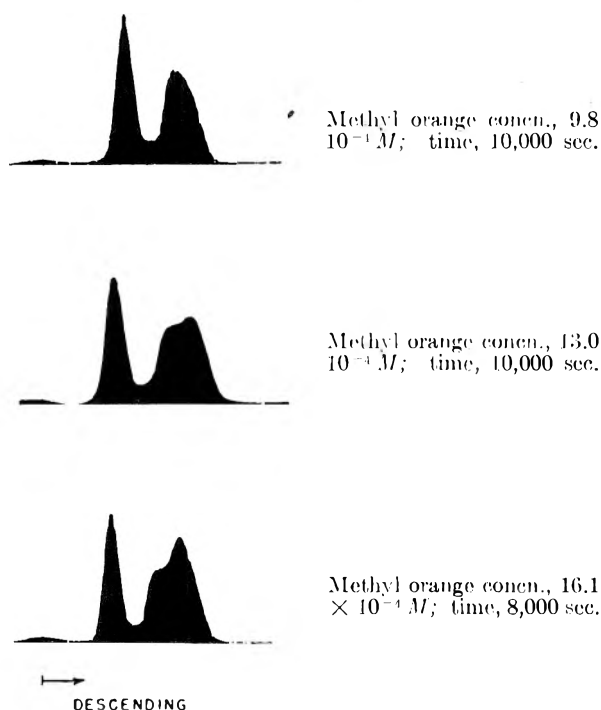


Fig. 1.—Illustration of the boundary anomaly, in the pattern for the descending boundary in the system serum albumin-methyl orange, which becomes more pronounced with increasing dye concentration: protein concn., 0.68%; pH 5.5; ionic strength, 0.05; field strength, 5.1 volts/cm.

(11) R. L. Baldwin, P. M. Laughton and R. A. Alberty, *This Journal*, **55**, 111 (1951).

(12) R. A. Alberty, *ibid.*, **53**, 114 (1949).

(13) M. L. Karon, M. E. Adams and A. M. Altschul, *ibid.*, **54**, 56 (1950).

(14) R. A. Alberty, *J. Am. Chem. Soc.*, **70**, 1675 (1948).

(15) R. A. Alberty, E. A. Anderson and J. W. Williams, *This Journal*, **52**, 217 (1948).

(16) G. Scatchard, *Ann. N. Y. Acad. Sci.*, **51**, 660 (1949).

Theory

The general methods of MacInnes and Longworth¹⁷ may be used to develop an approximate description of this system as follows. Consider the descending boundary in an ordinary Tiselius cell of constant cross section in which pure buffer is above a mixture of protein, methyl orange and buffer. Diffusion is assumed to be negligible and the concentration of buffer salts is such that we may assume the field strength in all parts of the cell to be approximately equal and constant. Moreover, let the adsorption isotherm describing the interaction between the protein of concentration P , bound dye anion of concentration A_b , and free dye anion of concentration A_f be expressed by the relationship $A_b/P = f(A_f)$, where $f(A_f)$ is some function of the free dye anion concentration only. Finally, let μ_A be the mobility of free anion and $\bar{\mu}_P$ be the constituent mobility of the protein,¹⁸ both of which are chosen to be positive.

Under these conditions, the equation of continuity for the anion takes the form

$$\left(\frac{\partial A_T}{\partial t}\right)_x = \mu_A \left(\frac{\partial A_f}{\partial x}\right)_t + \left(\frac{\partial \bar{\mu}_P}{\partial x}\right)_t A_b + \left(\frac{\partial A_b}{\partial x}\right)_t \bar{\mu}_P \quad (1)$$

where A_T is the total concentration of dye anion.

Similarly for the protein constituent of the system

$$\left(\frac{\partial P}{\partial t}\right)_x = \bar{\mu}_P \left(\frac{\partial P}{\partial x}\right)_t + P \left(\frac{\partial \bar{\mu}_P}{\partial x}\right)_t$$

Moreover, remembering that $A_T = A_f + A_b$, that $(\partial A_f / \partial t)_x$ must have a negative sign, and that for the special case in which we are interested⁹

$$f(A_f) = \frac{A_b}{P} = \frac{n_1 K_1 A_f}{1 + K_1 A_f}$$

we can obtain from (1) after some rearrangement

$$-\frac{(\partial A_f / \partial t)_x}{(\partial A_f / \partial x)_t} = \left(\frac{\partial x}{\partial t}\right)_{A_f} = \mu_A = \frac{P n_1 K_1 (\mu_A - \bar{\mu}_P)}{(1 + K_1 A_f)^2 + P n_1 K_1} \quad (2)$$

Obviously, the term $(\partial x / \partial t)_{A_f}$ represents the mobility of a point of constant free anion concentration. Therefore, it will, when A_f is taken at the point of the first moment of the pattern peak corresponding to the boundary in which the anion disappears, represent the constituent mobility, $\bar{\mu}_A$, of the anion-protein boundary provided our initial assumptions are fulfilled.

As P approaches zero equation (2) reduces to the familiar form of Kohlrausch's equation for an ion in an electric field. Likewise if it is rearranged to the form

$$\left(\frac{\partial A_f}{\partial t}\right)_x \left[1 + \frac{n_1 K_1 P}{(1 + K_1 A_f)^2}\right] = \left(\frac{\partial A_f}{\partial x}\right)_t \left[\mu_A + \frac{n_1 K_1 \bar{\mu}_P P}{(1 + K_1 A_f)^2}\right] \quad (3)$$

it can be shown that the solutions must be discontinuous, which is in agreement with experiment if diffusion could be minimized. Further, it will be shown later that equation (2) describes the

(17) D. A. MacInnes and L. G. Longworth, *Chem. Revs.*, **11**, 171 (1932).

(18) A. Tiselius, *Nova. Acta Regiae Soc. Sci. Upsalensis*, [4] **7**, No. 4 (1930).

system adequately at low anion concentrations although there is a progressive deviation of the predicted and observed values of the constituent mobility of the anion at higher concentrations. It will also be shown that these discrepancies are a direct result of the boundary anomalies mentioned earlier.

Initially, as suggested in the earlier paper of this series by Smith and Briggs, it was assumed that the anomalies observed in the anion-protein peak in the pattern for the descending boundary at high equilibrium dye concentrations were due to the increasing importance of a second group of reacting sites on the protein. Although this hypothesis was consistent with some features of the deviations from expected behavior it had to be abandoned for the following reasons. (I) If this were true, there should occur a large progressive deviation of the average number of anions bound per protein molecule as determined by equilibrium dialysis from that predicted by Klotz's equation (see reference 9). This is because the constants of this equation were determined at lower dye concentrations where, by assumption, the greater part of the anions bound are held by a first group of sites. Furthermore the appearance of this deviation should be simultaneous with the appearance of the boundary anomalies. A series of combined dialysis equilibrium and electrophoretic experiments (described later) gave no support to this.

(II) In addition, Smith and Briggs had shown that when the average mobility of the protein-dye complexes in the presence of the original concentration of free anion is plotted as a function of the average number of anions bound per protein molecule, a linear relation is obtained. However, if the additional anions were being bound for the most part on a new series of sites at the higher total dye concentrations, it is considered improbable that the mobility increment for the two series would be the same. As a result there should be a progressive alteration in the increment of $\bar{\mu}_P$ per anion added as the dye concentrations are increased. No indication of such a shift up to r values as high as twenty was found. Thus, no positive evidence for the existence of more than one type of interaction site is afforded on the basis of this argument.

The explanation of the anomaly was found as follows: It is an implicit assumption in all electrophoretic work that there exists a function F of the independent variables time, t , and position in the cell, x , such that $F(x, t) = c$ where c is the concentration of any substance the migration of which is being studied. (In the present instance, it is the protein, serum albumin.) Therefore

$$\left(\frac{\partial c}{\partial t}\right)_x = - \left(\frac{\partial x}{\partial t}\right)_c \left(\frac{\partial c}{\partial x}\right)_t$$

Experience shows that in such experiments $(\partial x / \partial t)_c$ is approximately constant (i.e., all peaks or recognizable inflections in the patterns move with constant mobility) and consequently

$$\left(\frac{\partial c}{\partial t}\right)_x = K \left(\frac{\partial c}{\partial x}\right)_t \quad (4)$$

under these conditions. Now for any such system the time rate of decrease of protein concentration

at a given point must be proportional to the total protein concentration at that point and to the electrophoretic rate of spreading apart of the individual protein particles. That is

$$\left(\frac{\partial c}{\partial t}\right)_x = K' c \frac{\partial(\Delta x_{mol})}{\partial t}$$

where $\partial(\Delta x_{mol}) / \partial t$ represents the rate at which the average distance between two unequally charged protein molecules in the cell is increasing with time. For the system under consideration, since $\bar{\mu}_P$ is linear with r as shown by the data of Smith and Briggs, then $\partial(\Delta x_{mol}) / \partial t$ is directly proportional to the difference in the average number of dye anions bound by each protein molecule. Consequently over a time which is long with respect to the time required to dissociate an anion

$$\left(\frac{\partial c}{\partial t}\right)_x = K'' c \left(\frac{\partial r}{\partial x}\right)_t$$

Since, however, r is a function of A_f only and A_f is itself a function of x and t in the boundary during electrophoresis, it is convenient to write the foregoing equation in the form

$$\left(\frac{\partial c}{\partial t}\right)_x = K'' c \frac{dr}{dA_f} \left(\frac{\partial A_f}{\partial x}\right)_t \quad (5)$$

Equating the right-hand sides of (4) and (5) gives

$$\left(\frac{\partial c}{\partial x}\right)_t = K''' c \frac{dr}{dA_f} \left(\frac{\partial A_f}{\partial x}\right)_t \quad (6)$$

However, $(\partial c / \partial x)_t$ is directly proportional to the quantity plotted against distance in the cell in all Tiselius patterns and therefore equation (6) is a fundamental relationship from the point of view of describing the shape of the boundaries observed. Clearly, if the protein concentration and the gradient of free dye concentration are known at a given point for a specified instant, we may calculate the gradient of protein concentration since a reasonably good value of dr / dA_f can be obtained from the adsorption isotherm. Unfortunately, as will be shown, accurate values of the free anion gradient through the boundary region in which the dye disappears cannot be determined but this does not detract from the theoretical interest of equation (6). The important idea which this equation summarizes is that the shape of the Tiselius pattern for the boundary in which the anion disappears is the product of three factors: (a) the protein concentration; (b) the constants of the adsorption isotherm describing the interaction; (c) the free anion concentration gradient. Each of these plays a role in determining the observed contour of the pattern. Because of this, the shape of these boundaries in such patterns may be far from symmetrical. This is apparent from the fact that the product of c , dr / dA_f and $(\partial A_f / \partial x)_t$ need not follow closely the distribution of any one of the factors but it will reflect, in some degree, variations in any of them. If, for instance, the increment in one of these factors over an interval in the cell is roughly compensated for by a decrement in one of the other factors, then $(\partial c / \partial x)_t$ will reflect the variations in the third factor over that same interval. Equally, if the concentration of anion is so adjusted that the change in c over an interval in the cell is just balanced by a change of opposite sign in the product

dr/dA_t ($\partial A_t/\partial x$)_i over the same interval, there will be an approximately horizontal portion in the $(\partial c/\partial x)_i$ versus x curve (*i.e.*, the boundary pattern). The relationship to the patterns in Fig. 1 is obvious. Thus, the partial mutual compensation of c , dr/dA_t and $(\partial A_t/\partial x)_i$ over limited regions in the cell is the primary cause of the anomalies in the observed distribution of $(\partial c/\partial x)_i$ in this system.

This may be seen more clearly, perhaps, from the following point of view. At low relative total dye concentrations, both c and dr/dA_t vary little throughout the anion-protein boundary region and therefore may be regarded as constants to a first approximation. Consequently, $(\partial c/\partial x)_i$ reflects the approximate Gaussian distribution of $(\partial A_t/\partial x)_i$ in this region and the familiar symmetrical peak for this boundary is recorded. However, as the total dye concentration rises, c will increase throughout the boundary region while dr/dA_t will decrease. In general, these variations will not cancel each other everywhere simultaneously throughout the boundary interval. As a result, the distribution of $(\partial c/\partial x)_i$ will be distorted from the approximate Gaussian distribution of $(\partial A_t/\partial x)_i$ and the instrument records the observed anomaly. The exact form taken by the curve for a given initial value of c and a given mobility difference between the constituents will be a function of the constants of the adsorption isotherm and the initial concentration of the dye anion.

Experimental Verification

By means of equation (2) it should be possible to predict the value of the constituent mobility of the anion from experiment. Using the methods described by Smith and Briggs⁹ a series of combined dialysis equilibrium-electrophoresis experiments were carried out in such a way as to obtain experimental values of μ_A , P and $\bar{\mu}_P$. It was therefore possible to compare the observed value of $\bar{\mu}_A$, taken as the first moment of the observed gradient curve for the boundary in which the anion disappears, with the value predicted by equation (2). The results of such a series of experiments are summarized in Fig. 2. Clearly, the agreement of $\bar{\mu}_A$ observed is within experimental error of the expected value at low concentrations of the dye but there is a progressive deviation at increasing total dye concentrations.

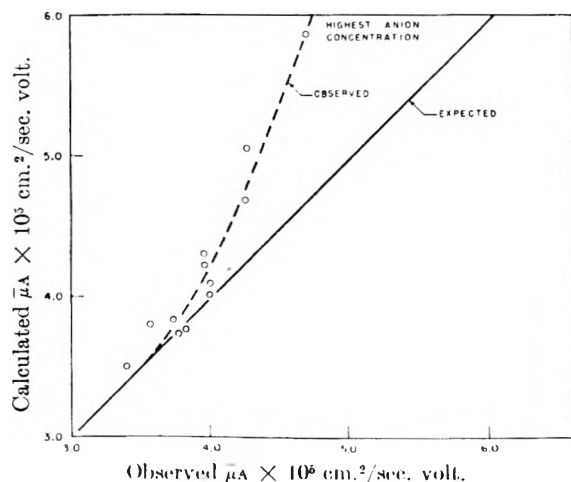


Fig. 2.—Comparison of observed $\bar{\mu}_A$ with that predicted from equation (2); $\bar{\mu}_A$ calculated from $\left(\frac{\partial x}{\partial t}\right)_{A_t} = \bar{\mu}_A = \mu_A - \frac{Pn_1K_1(\mu_A - \bar{\mu}_P)}{(1 + K_1A_t)^2 + Pn_1K_1}$.

Therefore, an adequate description of the system is provided only at low total dye concentrations. This deviation is related subsequently to the boundary anomalies.

It was emphasized above that $(\partial r/\partial x)_i$ cannot be precisely estimated. If this were possible, the ideas which have been presented could be easily tested, since from equation (6) $C(\partial r/\partial x)_i/(\partial c/\partial x)_i$ must be a constant throughout the boundary region. Crude and approximate estimates of $(\partial r/\partial x)_i$ in the boundary region can be obtained, however, by a combination of Tiselius electrophoresis patterns and light absorption measurements. In using this combination it is necessary to assume that the equilibrium between protein and anion is established instantaneously and that either (a) the change in absorption coefficient of the anion on adsorption by the protein is negligible, or (b) the change in the coefficient can be corrected for accurately by reference to a series of standard solutions. Neither of these conditions is apt to be fulfilled with exactness. Nonetheless, it is still of interest to see how even approximate data fit the equation. Accordingly simultaneous electrophoresis and light absorption measurements were made on the anion-protein boundary in a Tiselius cell for a solution in which the total initial concentration of anion and protein were 15×10^{-4} and $12 \times 10^{-5} M$, respectively.

These measurements were made as follows: The protein plus methyl orange solution in acetate buffer of pH 5.5, ionic strength 0.05, was placed below buffer in the Tiselius cell and the boundary developed electrophoretically to the desired point. The pattern for the descending boundary which contained the anomalous peak was then recorded. An arrangement of small mirrors and a 0.2-mm. slit had been devised by which it was possible to allow light of 436 mμ wave length from a AH-4 mercury lamp to pass through the small dimension of the leg of the cell and thus record the intensity photometrically without removing the cell from its original position in the bath. By this means, the optical density of the solution in successive small volumes along the length of the cell could be measured as the whole Tiselius U-tube was moved carefully up or down from its original position. Reference marks on the cell made it possible to identify the positions in the cell corresponding to the two types of measurement (*i.e.*, the Tiselius pattern and the light absorption measurements). Thus the variation in the concentration of total dye could be estimated in the anion-protein boundary by using the first assumption mentioned above. From the total dye concentration at any point within this boundary, its refractive index contribution to the dn/dx curve at that point, and the total dn/dx value obtained from the scanned pattern, it was possible to estimate the protein contribution to the dn/dx curve. From this was calculated the protein concentration, c , at that point in the boundary. Knowing c and the estimate of the total dye concentration at that point in the boundary, it was possible to calculate the value of r from the adsorption isotherm. From the resultant plot of r versus x the value of $(\partial r/\partial x)_i$ was obtained while the value of $(\partial c/\partial x)_i$ was estimated from the analogous plot of c versus x .

Some of these data are given in Fig. 3. It will be noticed that the anomaly in the anion-protein peak is very marked at this anion concentration. Table I summarizes these data and the last column records the value of the calculated con-

TABLE I

In this table the units of all quantities are arbitrary because only relative values are involved in the comparison

Position in cell	$(\partial c/\partial x)_i$	c	$(\partial r/\partial x)_i$	$c(\partial r/\partial x)_i/(\partial c/\partial x)_i$
2.52	3.0	28.0	2.70	2.5×10
2.65	4.1	28.9	6.05	4.2
2.77	7.0	30.0	6.05	2.6
2.90	11.5	32.5	6.05	1.7
3.02	13.2	36.0	6.05	1.7
3.15	13.0	39.5	6.05	1.8
3.30	12.8	43.0	6.05	2.0
3.40	12.7	46.5	6.05	2.2
3.52	12.4	50.0	6.05	2.4
3.64	11.0	52.7	4.68	2.2
3.77	8.8	55.0	3.87	2.4
3.90	5.5	57.2	3.00	3.1

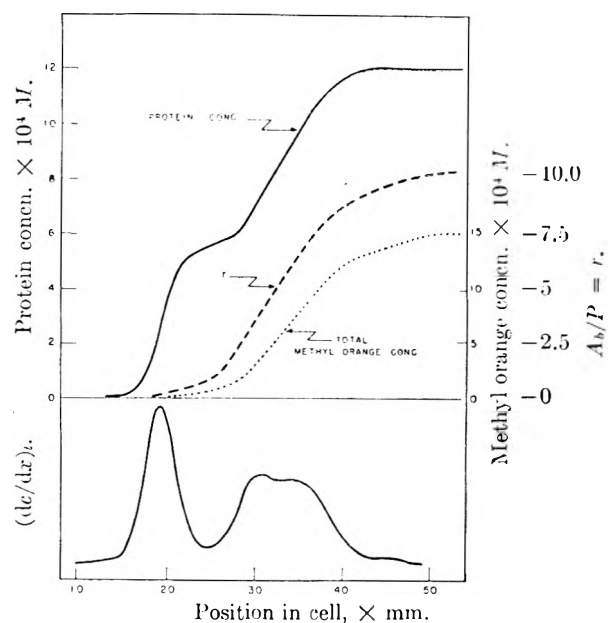


Fig. 3.—Curves describing the variations in the gradient of the protein concentration $(\partial c/\partial x)_t$, r , and total dye concentration with distance, x , in the cell for the descending boundary of a serum albumin-methyl orange mixture containing 15×10^{-4} molar methyl orange and 12×10^{-5} molar serum albumin; time of electrophoresis, 10,000 sec. at 6.6 volts per cm.; pH 5.5; ionic strength, 0.05; no dye in overlying buffer.

stant. Because of the drastic approximations and the simplifications made in treating these data, only the first digit of the product has significance, and therefore the constancy of $c(\partial r/\partial x)/(\partial c/\partial x)_t$ is considered reasonably good. Its value, which is obtained in arbitrary units, fluctuates around twenty within experimental error over the whole boundary region. The apparent tendency for deviation at both ends of the boundary is the result of very high relative errors in estimating the value of $(\partial c/\partial x)_t$ from the electrophoresis patterns. As a result the hypothesis on which the explanation of the anomaly is based is strengthened.

Equation (6) may, perhaps with more clarity, be tested in another way. At constant time, equation (6) becomes, after integration

$$\log c = K''r + f(t)$$

where $f(t)$ is an arbitrary function of time. That is, at any given time, t , there should be a linear relationship throughout the boundary between the logarithm of the protein concentration c , and r , the number of dye anions bound per protein molecule. The data from Table I provide the opportunity of making an approximate test and the results are shown in Fig. 4.

Obviously, within the experimental limitations imposed by the data and this approximate analysis, Fig. 4 is consistent with the assumption made in deriving equation (6).

The hypothesis also explains the deviation from linearity of the plot of A_t/r versus A_t in the data of Smith and Briggs, as shown in Fig. 2. As pointed out by these authors, at higher anion concentrations their plot breaks down and they suggested tentatively that this was due to the increasing importance of a new series of binding sites on the protein molecules. It may now be seen, however, that this deviation from linearity is a result of the progressive underestimation of the magnitude of $\bar{\mu}_A$ as the total dye concentration increases. As we have seen, at low total dye concentrations the value of $(\partial c/\partial x)_t$ is largely determined by the value of $(\partial A_t/\partial x)_t$ since under these conditions c and dr/dA_t are approximately constant. Moreover, since A_t is almost directly proportional to A_t under these conditions, the position of the first moment of the peak due to the protein gradient is a very good approximation to the position of the constituent anion boundary and will yield a dependable value of $\bar{\mu}_A$. However, as the total anion concentration increases, a larger proportion of the total anion is in the free state. As a result, the true position of the $\bar{\mu}_A$ boundary tends to be shifted

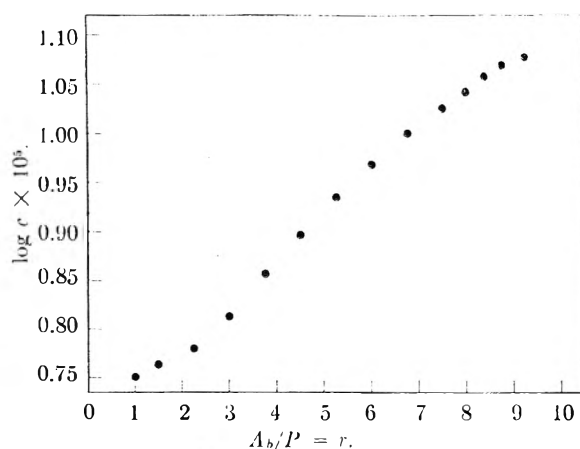


Fig. 4. $-\log c (\times 10^5)$ versus r taken at points throughout the descending dye anion-protein boundary.

forward toward the leading edge of the anion-protein boundary as total dye concentration rises. In practice, however, we continue to estimate its position by the first moment of the $(\partial c/\partial x)_t$ versus x distribution and as a result the value of $\bar{\mu}_A$ is progressively underestimated as the total dye concentration increases. In brief, the values of $\bar{\mu}_A$ used by Smith and Briggs, while very good approximations to the true values at lower total dye concentrations, are increasingly too low as total anion concentration increases. It follows from their equations (see equation 8, reference 9) that this will result in too low an estimate of free anion concentration and therefore too high an estimate of the average number of anions bound. As a consequence, at higher free dye concentrations the estimate of A_t/r will be too low, which is the result observed. Clearly, these ideas explain the deviation of $\bar{\mu}_A$ observed from that expected on the basis of equation (2).

In brief it is concluded that the hypothesis is generally supported by limited experimental evidence, and that therefore the boundary anomalies observed may be attributed to the interplay of the described factors in the boundary region.

Discussion

From the point of view of further application of the method of electrophoretic analysis of protein-anion mixtures, the explanation advanced above has obvious importance. If, for a particular system under study, the descending boundary in which the component of higher mobility disappears, shows any marked departure from symmetry, it immediately suggests that the first moment of the entire peak cannot be used to estimate the position of the boundary and the constituent mobility of that component and that therefore the method is invalid. Fortunately such boundary anomalies seem to be the exception rather than the rule. Out of a total of eight different anions studied in mixtures with serum albumin, only one other substance, phenol red, showed any indication of abnormalities similar to those observed with methyl orange and then only at such high concentrations that interpretation was difficult.

On the basis of this analysis it would be expected that the best agreement of $\bar{\mu}_A$ with the first moment of the descending peak in which the faster component disappears will be attained under the following conditions. (a) High absolute concentrations of the slow component since then the variation in c throughout the peak in which the faster component disappears will be minimized. (b) At a ratio of concentrations of the components where r is low,

for under these conditions one is working in the approximately linear portion of the isotherm where dr/dA_f is approximately constant. (c) The lower the value of interaction constants, K_1 and n_1 , the greater will be the possible variation in the total concentration of the fast-moving component before dr/dA_f will diverge greatly from its value at very low free anion concentrations. (d) The difference in mobilities of the two components should be at least compatible with the attainment of actual separation of the descending peaks, in order to promote resolution of the boundary.

The results emphasize the fact that, in systems composed of mixtures the components of which interact in solution, the mere presence of a shoulder

or inflection point in the Tiselius pattern, no matter how reproducible it may be, is not in itself sufficient evidence for postulating the existence of an additional component nor is it necessarily evidence for the existence of more than one type of site at which interaction can occur. It appears that great caution must be exercised in the interpretation of such patterns.

Acknowledgments.—The authors wish to thank Dr. R. F. Smith, for his kindness in supplying part of the data from which Fig. 4 was constructed.

Our thanks are given to the Saskatchewan Agricultural Research Foundation for a fellowship awarded to one of us (J. R. C.) during the early part of this study.

ENZYME MODELS. II. THE KINETICS OF AN ARTIFICIAL CARBOXYLASE CATALYSIS¹

BY RALPH E. SCHACHAT, ERNEST I. BECKER^{2a} AND A. D. McLAREN^{2b}

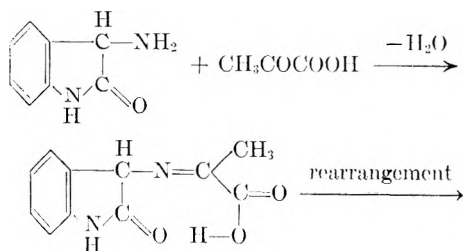
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Received August 7, 1951

The thermal, catalyzed decarboxylation of phenylglyoxylic acid by 3-amino- α -naphthoxindole at 70° has been studied by measurement of the rate of evolution of carbon dioxide. A mechanism for the reaction has been proposed and the resulting rate equations give a satisfactory fit of the theoretical rates with the measured rate.

The kinetics and mechanism of the catalytic action of model substances having enzyme-like activity may be of considerable interest if eventually the information acquired can be applied to the mode of action of natural enzymes. A previous paper³ dealt with the preparation of some artificial carboxylase models. The present work is concerned with a partial elucidation of the action of these catalysts.

The decarboxylation of a keto acid (*e.g.*, pyruvic acid) by a carboxylase model (*e.g.*, 3-amino α -naphthoxindole) may be considered to take place by the following scheme (*cf.* Langenbeck⁴)

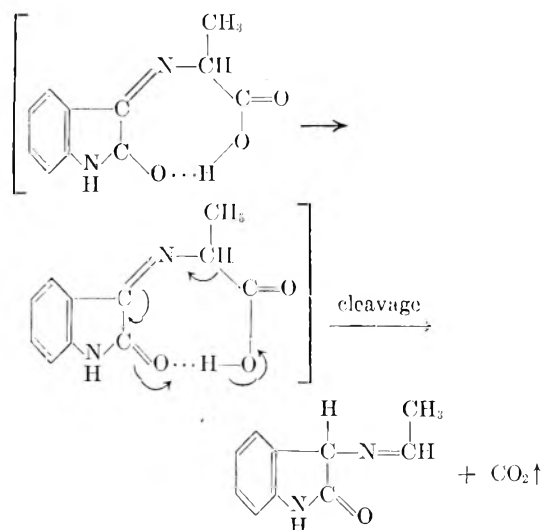


(1) For detailed paper (or extended version or material supplementary to this article) order Document 3184 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$1.50 for photocopies (6 × 8 inches) readable without optical aid. Taken from the dissertation submitted by R. E. Schachat in partial fulfillment of the requirements for the Ph.D. degree at the Polytechnic Institute of Brooklyn, June, 1950. Fellow of the National Institute of Health 1949-1950.

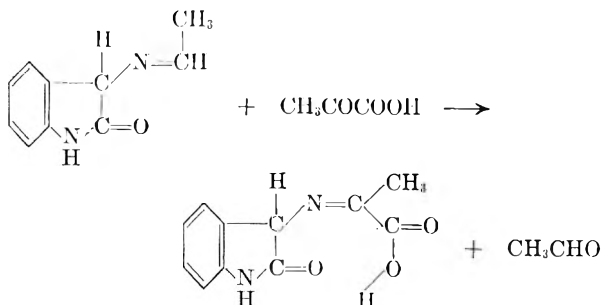
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(3) R. E. Schachat, E. I. Becker and A. D. McLaren, *J. Org. Chem.*, **16**, 1349 (1951).

(4) W. Langenbeck, "Die organischen Katalysatoren," 2nd ed., Springer Verlag, Berlin, 1949.



The formed Schiff base is then ready to react with additional pyruvic acid, regenerating the Schiff base of the acid and repeating the cycle



Inasmuch as the reaction stops far short of completion, there is, in addition, a termination step which will be described below.⁵ Figure 1 is a photograph of a model of the Schiff base of pyruvic acid and 3-aminoöxindole ("PC" in reaction 2, below). Note the proximity between the carbonyl oxygen in the 2-carbon and the carboxyl hydrogen, making hydrogen bonding possible. As proposed in the above scheme, hydrogen bonding between the oxygen and hydrogen atoms probably precedes decarboxylation.

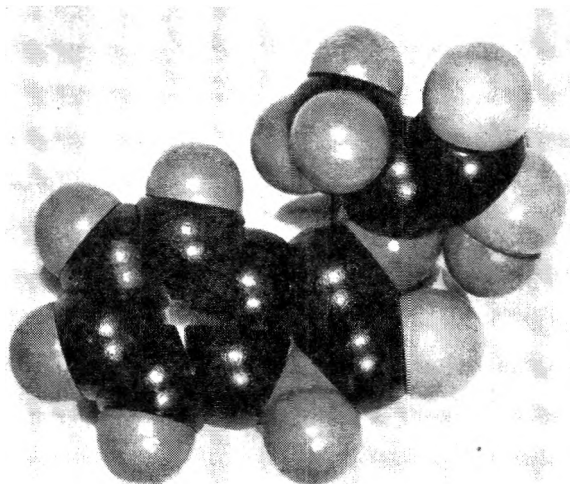
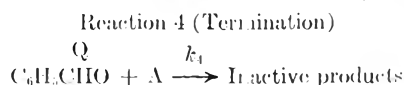
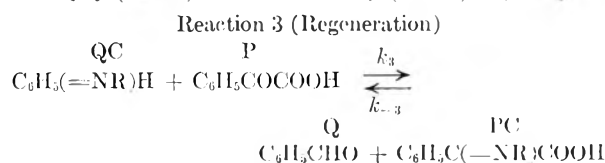
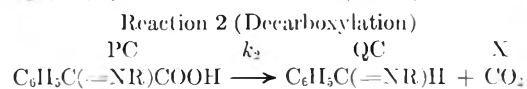
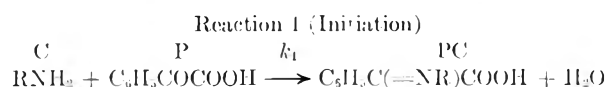


Fig. 1.—Model of 3-amino- α -naphthoxindole showing necessary configuration of molecule for decarboxylation by method described in text of article.

A discussion of the kinetics of these steps with phenylglyoxylic acid as a substrate and 3-amino- α -naphthoxindole as catalyst follows:

Proposed Mechanism. (a).—The decarboxylation of phenylglyoxylic acid takes place by the following four reaction steps with no other appreciable side reactions.



The symbols are (all concentrations are in gram moles per liter of solvent, *i.e.*, phenol)

A = concentration of all active forms of catalyst, *e.g.*,
 $A = C + PC + QC$
 C = catalyst in uncombined form, *i.e.*, concentration of RNH_2

C_0 = initial concentration of catalyst
 $K = k_3/k_{-3}$
 P = phenylglyoxylic acid concentration (substrate)
 P_0 = initial concentration of phenylglyoxylic acid
 PC = concentration of $\text{C}_6\text{H}_5\text{C}(=\text{NR})\text{CO}_2\text{H}$
 Q = concentration of benzaldehyde
 Q_0 = initial concentration of benzaldehyde added to substrate, if any
 QC = concentration of $\text{C}_6\text{H}_5\text{C}(=\text{NR})\text{H}$
 X = moles of CO_2 evolved per 1000 ml. of phenol

- (b) Reaction 1 goes forward only as water produced by the reaction is carried off by a stream of hot dry nitrogen (water is known to inhibit the reaction³).
- (c) One mole of benzaldehyde is produced per mole of carbon dioxide (*i.e.*, $Q = X$).
- (d) The catalyst in its active forms reacts irreversibly with benzaldehyde to form inactive products and that each of the active forms (C, PC and QC) react with it at approximately the same rate. It is further assumed that this bimolecular reaction is the only terminating step operating.
- (e) We assume that 99% of the catalyst is destroyed in 140 minutes (see Fig. 2) by reaction 4.

Mathematical Treatment.—Data from Table I are plotted in Fig. 2. The concentration of substrate

TABLE I
RATE OF REACTION OF 3-AMINO- α -NAPHTHOXINDOLE ON PHENYLGLYOXYLIC ACID

Elapsed time, min.	Interval mg. CO ₂ collected per 3.27 ml. phenol	Elapsed time, min.	Interval mg. CO ₂ collected per 3.27 ml. phenol
5.0	0.548	65.0	2.786
10.0	2.816	75.0	2.005
17.5	5.852	85.0	1.510
25.0	5.606	105.0	1.785
32.5	4.838	125.0	0.657
40.0	4.020	155.0	.268
47.5	3.369	215.0	.271
55.0	2.842	275.0	.002

was $P_0 = 1.18$ molar, and the catalyst concentration was $C_0 = 2.77 \times 10^{-3}$ molar.

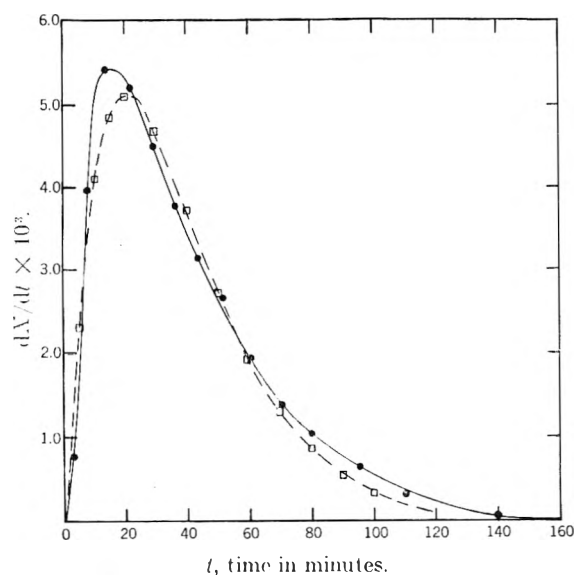


Fig. 2.—Plot of rate of evolution of CO_2 versus time. (Catalyst, 2.77×10^{-3} molar 3-amino- α -naphthoxindole; substrate, 1.18 molar phenylglyoxylic acid; temperature, 70° ; —●—, observed data; —□—, calculated data.)

(5) A marked resemblance can be found between this scheme and the mechanism proposed by Baddar for a quite different reaction, the Strecker degradation (F. G. Baddar, *J. Chem. Soc. (Supp. No. 1)* S169 (1949)).

From reaction 2 and the equilibrium constant, $K = k_3/k_{-3} = (PC)(Q)/(QC)(P)$ we have

$$dX/dt = k_2(PC) \quad (1a)$$

and

$$dX/dt = k_2 K (A - C) / \left(\frac{X}{P_0 - X} \right) + K \quad (1b)$$

Equation 1b is the general rate equation, where k_2 and K are constants. A may be evaluated from

$$-dA/dt = k_1 Q/dt = k_1(X)/dt \quad (2a)$$

as

$$A = C_0 e \exp \left[-K_1 \int_0^t X dt \right] \quad (2b)$$

By assumption (e) and equation 2b, $k_1 = 0.169$ (cf. Fig. 2). C may be evaluated from

$$-dC/dt = k_1(P)(C) = k_1(P_0 - X)(C) \quad (3a)$$

via

$$C = C_0 e \exp \left[-k_1 \int_0^t (P_0 - X) dt \right] \quad (3b)$$

A solution of equation 1b requires a knowledge of k_2 and K . To evaluate K and k_2 we use a special case of equation 1b; namely, when t is large C is small (for a justification of this see below).

$$\left(\frac{dX}{dt} \right)_{C \rightarrow 0} = k_2 K A / \left(\frac{X}{P_0 - X} \right) + K \quad (1c)$$

For examples, with $t = 60$ minutes, $dX/dt = 19.4 \times 10^{-4}$, $X/(P_0 - X) = 0.226$ and $A = 8.70 \times 10^{-4}$; with $t = 120$ minutes, $dX/dt = 1.50 \times 10^{-4}$, $X/(P_0 - X) = 0.294$ and $A = 0.693 \times 10^{-4}$. Solving the two examples in equation 1c simultaneously $K = 2.00$ and $k_2 = 2.48$.

With these figures it is also possible to determine k_1 and hence C . Thus, when t is small, A is nearly

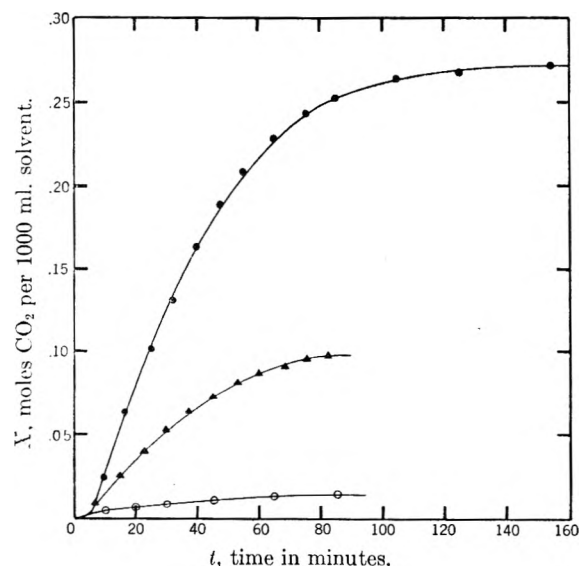


Fig. 3.—Plot of moles of CO_2 per 1000 ml. solvent versus time (temperature, 70°): ●, catalyst, 2.77×10^{-3} molar 3-amino- α -naphthoxindole; substrate, 1.18 molar phenylglyoxylic acid; solvent, phenol; ▲, catalyst, 2.42×10^{-3} molar benzal-3-amino- α -naphthoxindole; substrate, 1.18 molar phenylglyoxylic acid; solvent, phenol; ○, catalyst, 2.60×10^{-3} molar 3-amino- α -naphthoxindole; substrate, 1.20 molar phenylglyoxylic acid; solvent, water.

equal to C_0 , X is virtually zero, and equation 1b may be written as

$$\left(\frac{dX}{dt} \right)_{t \rightarrow 0} = k_2 C_0 \left(1 - e \exp \left[-k_1 \int_0^t (P_0 - X) dt \right] \right) \quad (1d)$$

From initial slope of Fig. 2 and equation 1d by differentiation

$$\left(\frac{d^2 X}{dt^2} \right)_{t \rightarrow 0} = (k_1 k_2) P_0 C_0 = 6.3 \times 10^{-1} \quad (1e)$$

and $k_1 = 0.193/k_2 = 0.0778$. Making use of this approximate evaluation of k_1 , equation 3b may be solved for C (cf. Fig. 4). At $t = 60$ minutes, $C = 1.91 \times 10^{-5}$ and at $t = 120$ minutes, $C = 2.52 \times 10^{-7}$. Summary results are presented in Table II.

TABLE II
SUMMARY OF CALCULATED DATA

Time Min.	$(dX/dt) \times 10^4$	$\frac{X}{(P_0 - X)}$	$A \times 10^4$	$C \times 10^4$	$\frac{(A - C)}{A} \times 10^4$
60	19.4	0.226	8.7	0.19	8.51
120	1.5	0.294	0.693	0.003	0.690

Equation 1b may now be solved simultaneously at 60 and 120 minutes to give better values for the constants; namely, K , 1.17; k_2 , 2.72; k_1 , 0.0709. With these constants the rate of CO_2 evolution was calculated from equation 1b to give the dotted line, Fig. 2. It should be observed that theoretical and observed curves are in reasonable agreement.

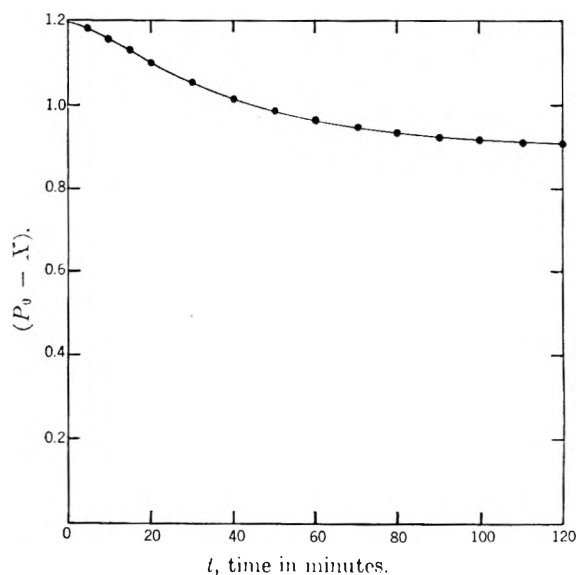


Fig. 4.—Plot of unreacted substrate versus time. (Catalyst, 2.77×10^{-3} molar 3-amino- α -naphthoxindole; substrate, 1.18 molar phenylglyoxylic acid; temperature, 70° .)

Several experiments were carried out to test the validity of the steps in the proposed mechanism. Water inhibits the reaction (see Fig. 3) as would be expected in a condensation in which water is formed (reaction 1). That the benzal Schiff base of 3-amino- α -naphthoxindole also behaves as a catalyst (see Fig. 3) for the decarboxylation is in agreement with the formulation of reactions 2 and 3. It would be predicted from reactions 3 and 4 that benzaldehyde would slow the reaction by decreasing the concentration of PC and by inactivation of the catalysts, A . It was found by Lan-

genbeck⁶ that benzaldehyde does markedly inhibit the reaction. Inhibition by benzaldehyde is calculable. Using a modified form of equation 1b, namely

$$dX/dt = k_2K(A - C)/Q_0/P_0 + K$$

From the constants obtained in the present work, and the quantities given by Langenbeck, it was calculated that 1.21×10^{-3} mole of CO_2 /liter of phenol should be evolved in 15 minutes (see Fig. 7). Langenbeck found experimentally 1.69×10^{-2} which is somewhat larger but not too far in disagreement. Benzoin does not inhibit the decarboxylation (Fig. 6), although Langenbeck states that it does inhibit the aniline-catalyzed decarboxylation of phenylglyoxylic acid.

When a new portion of catalyst was added after the reaction had essentially stopped, the rate picked up quickly and then fell again as in the initial phase of the experiment (see Fig. 5). This shows that the catalyst is consumed by a termination step, feasibly as in reaction 4.

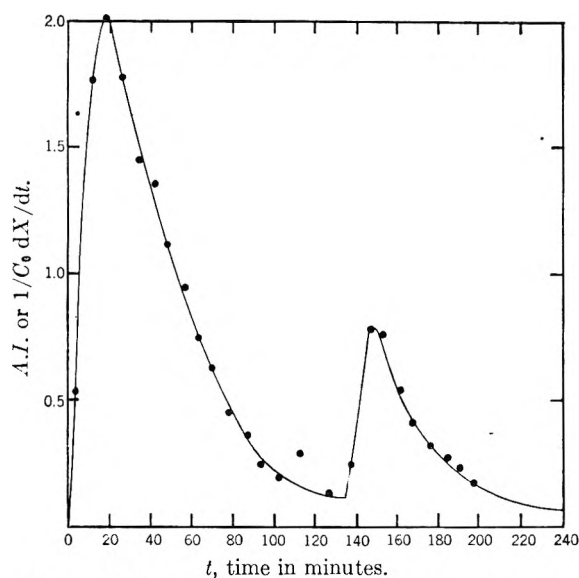


Fig. 5.—Plot of rate of evolution of CO_2 versus time, showing effect of introduction of fresh catalyst after 135 minutes. (Initial catalyst, 8.48×10^{-6} mole; supplementary catalyst added at 135 min., 1.96×10^{-6} mole; substrate, 1.18 molar phenylglyoxylic acid; temperature, 70° .) A.I. = activity index.

Finally, the curves of Figs. 2 and 3 are strikingly like those observed for the action of yeast carboxylase on pyruvic acid as observed by Akamatsu,⁷ Hägglund and Rosenquist,⁸ Albers and Schneider⁹ and others. The percentage of substrate decomposed in such experiments as the rate approached zero was about 0.1%.

An attempt was made to prepare synthetic polymers containing carboxylase model moieties as functional groups in the hope of studying the effect of colloidal size of catalyst particles on catalyst activity. The polymers used were a copolymer of

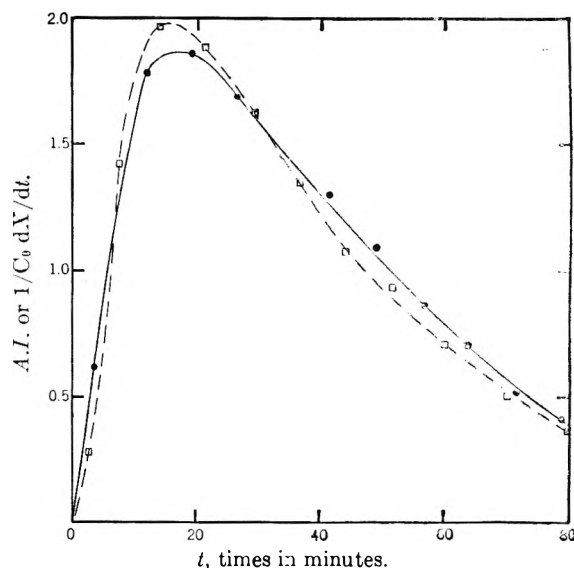


Fig. 6.—Plot of rate of evolution of CO_2 per mole of catalyst versus time, showing effect of introduction of benzoin. (—●—, with benzoin added; catalyst, 8.25×10^{-6} mole 3-amino- α -naphthoxindole plus 2.16×10^{-6} mole benzoin; —□—, without benzoin; catalyst, 9.05×10^{-6} mole 3-aminonaphthoxindole; both cases, substrate, 5.1 ml. of 1.18 molar phenylglyoxylic acid; temperature, 70° .)

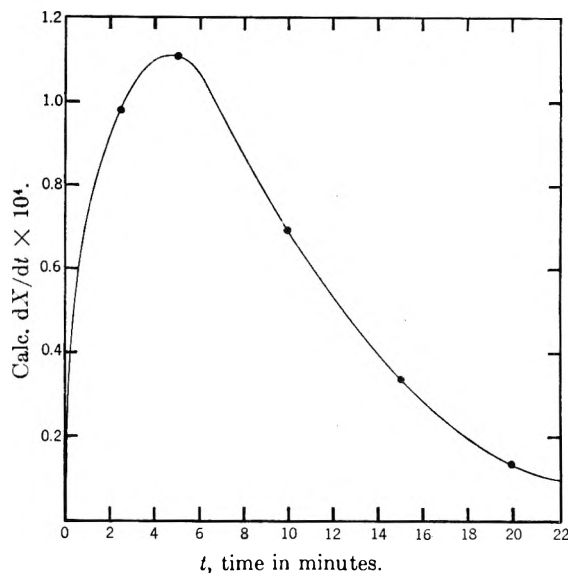


Fig. 7.—Plot of theoretical rate of CO_2 evolution versus time in the presence of benzaldehyde. (Assumptions: catalyst, 1.128×10^{-3} molar 3-amino- α -naphthoxindole; substrate, 0.525 molar phenylglyoxylic acid; benzaldehyde, 1.12 molar; temperature, 70° ; rate constants, see text.)

styrene and maleic anhydride (SYHM resin) and a copolymer of 2-vinylpyridine and methacrylyl chloride. No clear-cut positive results were obtained as an examination of the polymers by absorption spectrophotometry indicated that the model moiety was altered chemically during the coupling of it to the polymer.

Experimental

The apparatus used for the carbon dioxide determination is illustrated in Fig. 8. The various parts are lettered and may be described as follows: A is a pressure regulator adapted from one developed by Furter and Steyermark¹⁰

(6) W. Langenbeck, "Die organischen Katalysatoren," 2nd ed., Springer Verlag, Berlin, 1949, p. 91.

(7) S. Akamatsu, *Biochem. Z.*, **137**, 369 (1923).

(8) E. Hägglund and T. Rosenquist, *ibid.*, **181**, 296 (1927).

(9) H. Albers and A. Schneider, *Naturwissenschaften*, **24**, 794 (1936).

(10) M. F. Furter and A. Steyermark, *Anal. Chem.*, **20**, 257 (1948).

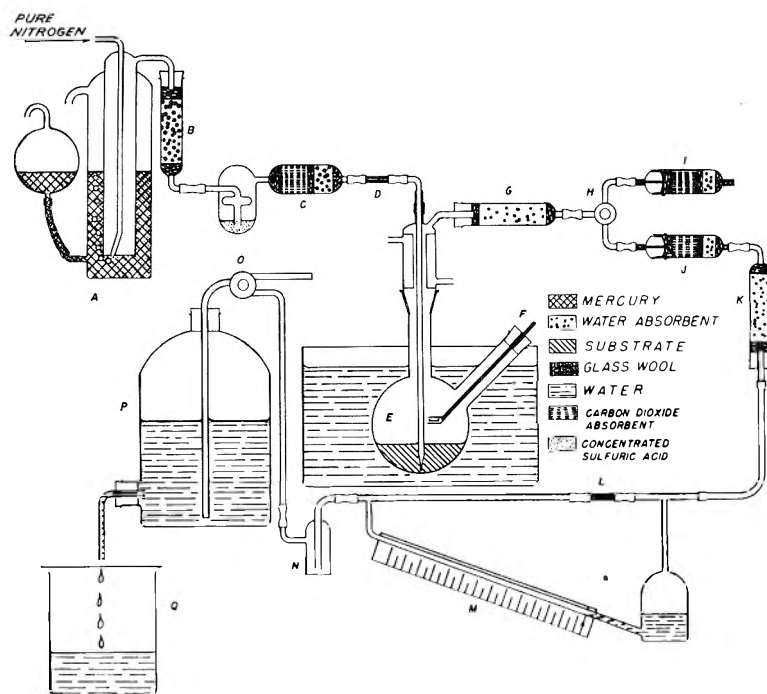


Fig. 8.—Apparatus for measurement of micro amounts of carbon dioxide.

for use in micro-combustion analysis. The fluid used is mercury in order to have a sufficient head of nitrogen without an overly large regulator. The mercury level and hence the nitrogen pressure can be adjusted by raising or lowering the leveling bulb. B, G and K are drying tubes. C is a combination bubble counter and carbon dioxide absorber.

D is a capillary tube having an air-flow resistance of about 5 or 6 times the resistance of any of the changeable absorption tubes (I and J). E is the reaction vessel containing the substrate and is kept immersed in a thermostat maintained at the desired temperature. The enzyme model is weighed into a micro-porcelain boat which is placed at the start of a determination at the lower end of movable arm F. Both H and O are two-way stopcocks, while I and J are standard micro-absorption tubes charged with a carbon dioxide absorbent (such as Ascarite) plus some drying agent. Inasmuch as these tubes are to be weighed to 10^{-6} gram, they must be carefully prepared and handled. See, for example, the recommendations of Pregl.¹¹

M is a flowmeter calibrated directly in liters per hour. The fluid used is colored water. L is a capillary tube of such a resistance that when the gas is flowing at its maximum rate, a reading will be obtained on the scale about three-fourths of the way up. N is a trap. P is a two-liter Mariotte bottle containing water. Q is a two-liter beaker which may be replaced by a graduated cylinder when calibrating flowmeter M.

The procedure is as follows: six micro-absorption tubes are wiped and weighed in the standard micro-analytical manner and two of these tubes are connected to the apparatus (I and J in Fig. 8). The substrate is weighed into vessel E. The usual substrate consists of a mixture of 4.5 g. of phenol, 0.5 g. of phenylglyoxylic acid and 0.1 g. of potassium phenylglyoxylate. About 10^{-6} mole of catalyst is weighed

on a micro-balance into a micro-porcelain boat which is inserted into the lower end of holder F. The apparatus is then assembled as in Fig. 8 and the flow of nitrogen started. While the apparatus is coming to equilibrium, the flow rate is adjusted to 2.00 ± 0.05 liters per hour using the coarse adjustment leveling bulb on A and the fine adjustment side arm on P. Usually, about 5 minutes is allowed for the apparatus to come to equilibrium, after which arm F is tipped, causing the boat containing the catalyst to slide from the holder and fall into the substrate. A stopwatch is started and after a predetermined time interval (usually 7.5 min.) drying tube K is disconnected from J and hooked to I and stopcock H turned to permit the gas to flow through tube I. Tube J is wiped and weighed and a new tube inserted in its place. After another time interval, the gas is allowed to pass through the new tube and the cycle repeated until a number of tubes have been used. Then tube No. 1 can be re-used, etc., until the desired number of points have been taken. In practice, due to the fact that it takes approximately 20 minutes to wipe and weigh a tube, it has been found that the optimum number of tubes is 6, and the number of points taken varies between 6 and 12, depending upon the activity of the catalyst. A second stopwatch is used in order to ensure that the tube wiping and weighing follows a definite schedule. Inasmuch as some of the tube weight increments were very small (less than 1 mg.), it was necessary to take a zero reading or rest point after each weighing and make the necessary correction. After such a series of readings had been taken, a plot was made of the moles of carbon dioxide evolved per minute per liter of solvent *versus* total elapsed time to the middle of the interval. Characteristic curves were thus obtained (Fig. 2 and Table I).

Acknowledgment.—The authors wish to extend their thanks to Dr. H. Morawetz for many helpful suggestions in connection with this paper.

(11) J. Grant, "Quantitative Organic Microanalysis," 4th ed., The Bakiston Co., Philadelphia, Penna., 1945, p. 50.

THE DISSOLUTION OF METALS OVER THE TEMPERATURE RANGE OF 25 to -60° . III.¹ THE DISSOLUTION OF ZINC IN HYDROCHLORIC ACID-METHYL ALCOHOL-WATER SOLUTIONS²

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Data have been obtained for the rates of depolarized dissolution of polished and pre-etched zinc in hydrochloric acid-methanol-water solutions under dynamic conditions. The rate is found to be first order with an activation energy in the order of 4000 cal./mole. A quantitative relationship appears to exist between the relative change in viscosity of the solvent-electrolyte system and the relative change in the dissolution rates in those systems. The activation energy of the liquid flow at the low temperatures is in the order of 3000 cal./mole which is similar to that for the dissolution process. A linear relationship for $\log k_1$ vs. $\log T/\eta$ of slope = 1.0 was obtained. This is further evidence that the rate determining step in dissolution of zinc is a diffusion process.

Purpose of the Investigation

The purpose of this research is to extend the data on the dissolution of zinc in acid solutions to cover the temperature range of 25 to -60° . Such data are essential in the study of zinc as an anodic element for primary cells; they also aid in elucidating the mechanism of the dissolution process. The solvent-electrolyte system, hydrochloric acid-methyl alcohol-water, was chosen for this study because it not only has a very low freezing point, but it also has a relatively low viscosity and good electrical conductivity over this temperature range. Nitroethane was used as a depolarizer; earlier work with magnesium¹ indicated that this gave consistent and reproducible dissolution rates.

Historical

The dissolution of zinc at room temperature in dilute acid media has been studied in detail by King⁴⁻⁶ and his co-workers. Their findings can be summarized as follows: Suitable depolarizers increase the dissolution rate to a maximum at each acid concentration and excess depolarizer has little additional effect.⁵ The dissolution rate with excess depolarizer is first order with respect to acid concentration, in aqueous media and in ethyl alcohol-water mixtures.⁶ The rate follows the diffusion coefficients of the acids very closely,^{4,5} in the mixed solvents as well as in water.⁶ The rate of stirring has a large effect on the dissolution rate,⁵ and the temperature coefficient is much lower than would be expected for a chemically controlled process.

Experimental

Apparatus.—The apparatus described in paper I, Fig. 1, was used, with a single hook to support the metal plates.

Materials.—Chemically pure cold rolled zinc sheet (*anal.* 0.00002% as arsenic; substances oxidized by KMnO_4 , as iron, 0.017%; and material insoluble in H_2SO_4 , 0.5%) from the Coleman and Bell Company was used. The zinc sheet (0.06 cm. thick) was cut into plates 1.5 by 1.5 cm. on a side.

The hydrochloric acid-methyl alcohol-water solutions used contained 90% methyl alcohol and 10% water by

weight. The acidity was adjusted to approximately 0.01 N and then standardized against a standard sodium hydroxide solution. The nitroethane (0.05 molar) used as a depolarizer throughout the investigation, was purified by treatment with anhydrous aluminum chloride followed by distillation from boric acid.

Procedure.—From 500 to 750 ml. of the prepared hydrochloric acid solution was measured into the reaction vessel at 25° and the solution made 0.05 molar with nitroethane. The solution was precooled to the desired temperature in an acetone-Dry Ice-bath and brought to thermal equilibrium in the cryostat. All of the dissolution studies were made in an atmosphere of dry nitrogen.

Measuring the zinc plates, weighing them and timing the runs, were the same as described in paper I.¹

The errors involved were almost identical with those reported in paper I.¹ At 20° the values obtained for the reaction velocity constant for two determinations deviate from the mean by an average of 2.1%, the maximum deviation being 5.5%. Corresponding values at -20 and -60° for average and maximum deviation from the mean are, respectively, 2.1 and 3.9%; 1.4 and 2.6%.

Data

To find a suitable depolarizer concentration range, increasing concentrations of nitroethane were added to 0.05 M hydrochloric acid at 25° . As shown in Fig. 1 there is no further effect on the dissolution rate above 0.02 M . A concentration of 0.05 M nitroethane was chosen for all further experiments since it was obvious that this would ensure maximum rates.

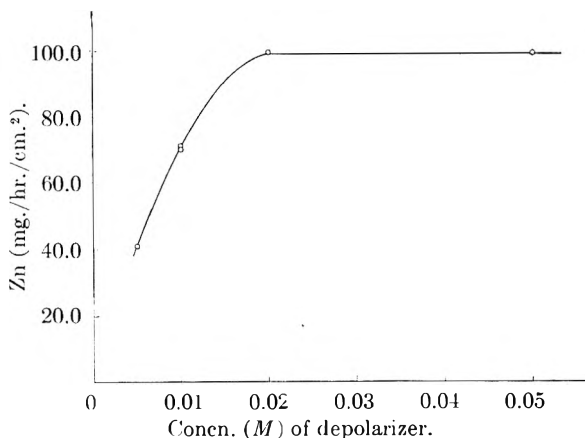


Fig. 1.—Dissolution of zinc in 90% methyl alcohol-10% water containing 0.05 M hydrochloric acid; (mg./hr./cm.²) vs. depolarizer concentration: acid concentration constant; temperature, 25° .

The effect of the change of the surface of the zinc during reaction on the dissolution rate at -60° was studied by running a series of short determinations on zinc plates that had been polished with emery cloth, without altering the surface of the plates between determinations (see Table II).

(1) Paper I, Garrett and Cooper, *THIS JOURNAL*, **54**, 437 (1950); paper II, Garrett and Heiks, *ibid.*, **56**, 449 (1952).

(2) This work was initiated and is supported by the Battery Branch of the Signal Corps Engineering Laboratories at Fort Monmouth, New Jersey.

(3) Research Division, Olin Industries, New Haven, Conn.

(4) King and Braverman, *J. Am. Chem. Soc.*, **54**, 1744 (1932).

(5) King and Schack, *ibid.*, **57**, 1212 (1935).

(6) Roehl, King and Kipness, *ibid.*, **63**, 284 (1941).

The dissolution rate of zinc plates that had been polished and then lightly pre-etched in 6.0 molar hydrochloric acid were examined also (see Table II). It was found that the rate of dissolution of the polished plates increased with the quantity of zinc dissolved up to a certain value, and then remained constant and that the pre-etched plates gave the same initial rate as that ultimately reached by the polished plates. On this basis, pre-etching was adopted throughout the entire investigation.

TABLE I

DETERMINATION OF ORDER OF REACTION OF ZINC IN HYDROCHLORIC ACID-METHYL ALCOHOL-WATER, TEMP., -60°

Original quantity of acid in milliequivalents (a in Eq. 1)	Milliequivalents of metal lost (x in Eq. 1)	Time of run, min.	Surface area, cm. ²	R.p.m.	Volume of soln., ml.	k_1 (average)
12.30	0.371	20.0	8.60	1300	645	0.115
11.56	.351	20.0	8.60	1300	645	.116
9.25	1.08	60.0	8.52	1300	461	.113
8.20	0.177	10.0	8.88	1300	461	.113
7.93	.177	10.0	9.04	1300	461	.115

TABLE II

EFFECT OF SURFACE TREATMENT ON THE RATE OF DISSOLUTION OF ZINC IN HYDROCHLORIC ACID-METHYL ALCOHOL-WATER

Polished Zinc Surface; Temp., -60°						
Original quantity of acid in milliequivalents (a in Eq. 1)	Milliequivalents of metal lost (x in Eq. 1)	Time of run, min.	Surface area, cm. ²	R.p.m.	Volume of soln., ml.	k_1 (average)
12.95	0.0658	5.2	8.60	1300	645	0.073
12.88	.0719	5.0	8.60	1300	645	.082
12.73	.0811	5.0	8.60	1300	645	.095
12.65	.171	10.0	8.60	1300	645	.101
12.47	.176	10.0	8.60	1300	645	.109
13.20	.371	20.0	8.60	1300	645	.115
11.93	.371	20.0	8.60	1300	645	.118
11.56	.351	20.0	8.60	1300	645	.116
Pre-etched surface; Temp., -60°						
Original quantity of acid in milliequivalents (a in Eq. 1)	Milliequivalents of metal lost (x in Eq. 1)	Time of run, min.	Surface area, cm. ²	R.p.m.	Volume of soln., ml.	k_1 (average)
8.20	0.177	10.0	8.88	1300	461	0.113
7.93	.177	10.0	9.04	1300	461	.115

The effects of the following factors on the dissolution rate were studied; (1) acid concentration at -60° ; (2) stirring speed at 20, -20 and -60° ; (3) temperature, from -60 to 20° , at a stirring speed of 1300 r.p.m.; (4) viscosity, which varies with solvent composition at constant temperature, and with temperature at constant solvent composition.

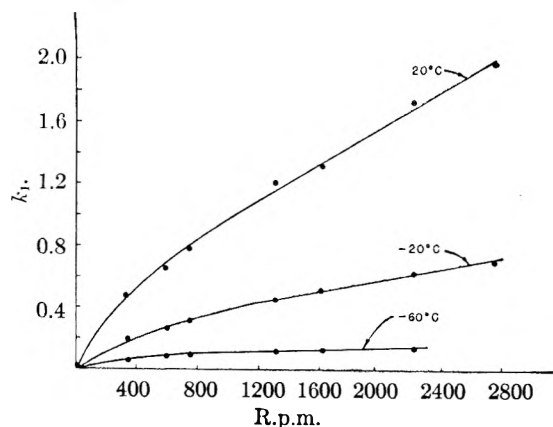


Fig. 2.—Dissolution of zinc in 90% methyl alcohol-10% water solutions containing hydrochloric acid. Reaction velocity constant plotted against stirring speed at several temperatures.

The viscosities of 90% methyl alcohol-10% water solutions of 0.1 *M* hydrochloric acid over a suitable temperature range are available.⁷

Dissolution rate data in hydrochloric acid at -60° (Tables I and II) are compared on the basis of the first order equation

$$\frac{dx}{dt} = k_1 A \frac{(a-x)}{V} \quad (1)$$

Satisfactory rate constants k_1 are obtained when polished zinc samples are used in longer runs or when the samples are pre-etched (Table II), and also when the acid concentration is varied over a considerable range (Table I). Experiments not reported here⁸ show that the reaction follows the same equation at room temperature. Since the first order law is valid at both extremes of temperature, it is assumed to hold at intermediate temperatures.

Effect of Stirring Speed on Rate of Dissolution.—Plots of k_1 vs. stirring speed have been drawn to show the profound effect of stirring speed on the rate of dissolution (Fig. 2). Above 700 r.p.m. (9,200 cm./min.) the velocity constant appears to vary linearly with stirring speed.

Activation Energy.—A plot of $-\log k_1$ vs. $1/T$ has been drawn (Fig. 3) for the dynamic depolarized dissolution process at a stirring speed of 1300 r.p.m., in order to determine the activation energy (Arrhenius) of the dissolution process.

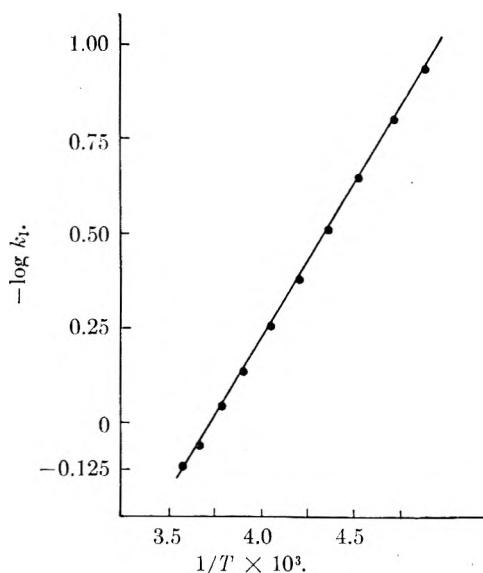


Fig. 3.—Dissolution of zinc in 90% methyl alcohol-10% water solutions containing hydrochloric acid: $-\log k_1$ vs. $1/T$; stirring speed 1300 r.p.m.; activation energy 3600 cal./mole.

A simple plot of k_1 vs. T was drawn and used to prepare Table III, showing the temperature coefficients of the reaction over the temperature range covered.

TABLE III

THE TEMPERATURE COEFFICIENT FOR THE RATE OF DISSOLUTION OF ZINC IN HYDROCHLORIC ACID-METHYL ALCOHOL-WATER; DEPOLARIZER, NITROETHANE 0.05 *M*; r.p.m., 1300

Temperature, $^{\circ}\text{C}.$	$(k_1)T$	$(k_1)T + 10^{\circ}$	Temp. coeff. per 10° -interval
10 to 20	0.954	1.210	1.269
0 to 10	.750	0.954	1.272
-10 to 0	.588	.750	1.275
-20 to -10	.454	.588	1.296
-30 to -20	.340	.454	1.335
-40 to -30	.246	.340	1.380
-50 to -40	.174	.246	1.415
-60 to -50	.118	.174	1.475

(7) A. B. Garrett and Samuel Woodruff, *THIS JOURNAL*, **55**, 477 (1952).

(8) Jay Welsh, Ph.D. Thesis, The Ohio State University, 1949.

Relationship between Viscosity and Rate of Dissolution.

To show the relationship between viscosity and dissolution rates, the data have been treated as follows: (a) The ratio of the dynamic dissolution rate (1,300 r.p.m.) of zinc, in a given alcohol mixture at 20° , to its dissolution rate in pure water at 20° , has been plotted as a function of alcohol percentage. The data for both acetic acid and hydrochloric acid are shown on the same graph (Fig. 4). For comparison the ratio of the viscosity of pure water to that of the mixture at 20° , has also been plotted against the alcohol percentage, on Fig. 4. (b) A plot of $-\log (1/\text{viscosity})$ vs. $1/T$ has been made for the 90% methyl alcohol-10% water (0.1 molar with respect to hydrochloric acid) (Fig. 5). This gives the activation energy of the flow process. And (c) a plot of $\log k_1$ vs. $\log T/(\text{viscosity})$ has been made, using temperature as the parameter (Fig. 6).

Discussion

The following generalizations can be made from the data obtained. (1) The depolarized dissolution process appears to be first order with respect to the acid concentration. (2) The rate of stirring has a profound effect on the dissolution rate. This is an indication that diffusion is an important factor in determining the rate of reaction. (3) The energy of activation of the dynamic depolarized dissolution process is in the order of 4,000 cal./mole. This low energy of activation is further evidence that a mechanical process, probably diffusion, is the predominant factor in determining the rate of reaction. (4) The rate of dissolution of zinc at -60° is faster for an etched surface than for a freshly polished one. It does not seem to matter whether the surface becomes etched in the course of the determination or whether it is lightly pre-etched in a strong acid solution before the determination begins. (The use of the word "etched" in this instance (at -60°) may be misleading since the resulting reaction surface was mirror-like. Because of this feature it is believed that the change in reaction rate may not be entirely due to a change in surface area.) (5) A qualitative relationship appears to exist between the relative change of viscosity of various alcohol mixtures referred to water and the relative change in the dissolution rate in those mixtures (referred to its value in pure water) (Fig. 4). Roehl, King and Kipness⁶ have pointed out that much better correlation exists between the diffusion coefficients of the acid in these mixtures and the dissolution rates, than between the viscosities and the dissolution rates. They suggest that this is the case because the type of solvation changes with the percentage of alcohol. The data obtained in this investigation for methyl alcohol-water mixtures appear to correlate rather well with King's data obtained in ethyl alcohol, except that the tendency for the dissolution rates of this investigation to follow the viscosity curve is much more pronounced, especially at high alcohol concentrations. King⁶ did not observe a minimum in the dissolution rate values, with either acetic acid or hydrochloric acid, although such a minimum was theoretically predicted for the former on the basis of diffusion coefficient data. The dissolution rates in both acetic acid and hydrochloric acid in this investigation show minima. This may be due to the fact that the similarity between methyl alcohol and water, is closer than that between ethyl alcohol and water.

The plot of $\log (1/\text{viscosity})$ vs. $1/T$ (Fig. 5)

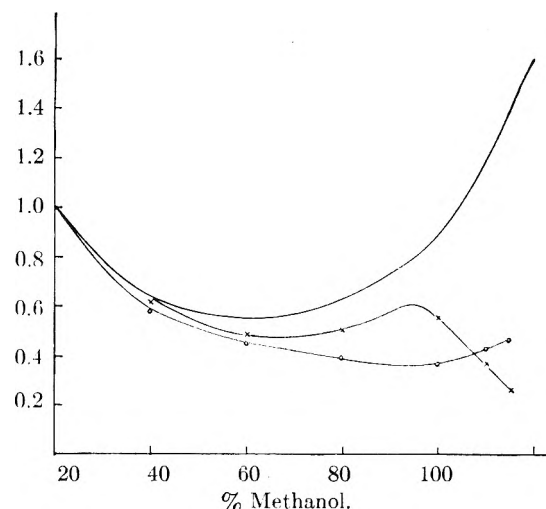


Fig. 4.—Dissolution rate of zinc vs. methyl alcohol concentration, compared with the viscosity of methyl alcohol-water mixtures; temperature, 20° ; stirring speed, 1300 r.p.m.; K is k_1 of mixture, K_0 is k_1 in pure water; (η_0/η) ("Int. Crit. Tables"); $\times$, (k/k_0) of Zn in 0.01 M acetic acid-0.05 M $C_2H_5NO_2$; $\circ$, (k/k_0) of Zn in 0.01 M HCl -0.05 M $C_2H_5NO_2$.

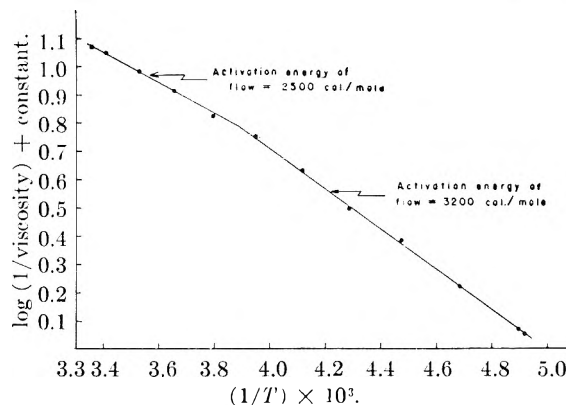


Fig. 5.— $\log (1/\text{viscosity})$ vs. $1/T$: solution, 90% CH_3OH -10% H_2O (0.1 molar HCl).

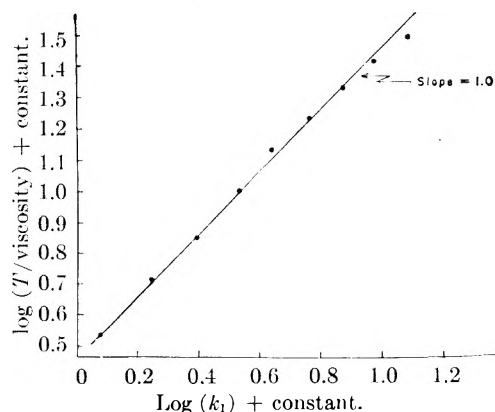


Fig. 6.— $\log (T/\text{viscosity})$ vs. $\log (k_1)$: solution, 90% CH_3OH -10% H_2O (0.1 molar HCl); stirring speed, 1300 r.p.m.

shows two well-defined linear portions with a break occurring at about -15° . The activation energy of liquid flow is about 3,200 cal./mole for the high temperature portion. The activation energy of the flow process over the low temperature portion of the curve is of the same order of magnitude as the ac-

tivation energy of the dissolution process. This is significant in itself; if one goes farther, however, and accepts the Einstein equation for the diffusion coefficient

$$D = K'(T/\eta)$$

where

$$K' = R/N6\pi r, \eta = \text{viscosity}, T = \text{temperature}$$

as applicable to the process under consideration, and assumes that the dissolution process is diffusion controlled, then

$$k_1 = KD = k''(T/\eta)$$

or

$$\log k_1 = \log (T/\eta) + C$$

It follows, therefore, that a plot of $\log k_1$ vs. $\log (T/\eta)$ should give a straight line of slope 1.0. Figure 6 shows good agreement with this prediction. It should be noted that Van Name⁹ was able to treat the dissolution of cadmium in iodine in an analogous manner.

In order for K and K'' , in the above equation, to be a true constant the effective thickness of the diffusion layer must remain the same over the entire temperature (viscosity) range. King¹⁰ has shown, by a consideration of convection currents next to a solid interface, that this is a valid assumption provided density changes are not large.

(9) R. G. Van Name, *Am. S. Sci.*, [4] **43**, 449 (1917).

(10) C. V. King, *J. Am. Chem. Soc.*, **57**, 828 (1935).

PHASE RULE STUDIES IN ANHYDROUS ALUMINUM BROMIDE

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Pure, anhydrous aluminum bromide freezes at 97.5°. No phase transformation was found in solid aluminum bromide near 70°. Mixtures of bromine and aluminum bromide form only a simple eutectic system; this is also true of mixtures of bromoform with aluminum bromide and of bromobenzene with aluminum bromide. Pure ethyl bromide forms a 1:1 complex with aluminum bromide. Several other saturated aliphatic bromides, other than ethyl bromide, were found to evolve hydrogen bromide readily when mixed with aluminum bromide. Benzyl bromide and triphenylbromomethane form a stable system with aluminum bromide only in high mole fractions of aluminum bromide.

Because of the current interest in the mechanism

of reactions catalyzed by anhydrous aluminum halides, we became interested in investigating compound formation in binary systems composed of aluminum bromide and bromine and bromine derivatives of various types of hydrocarbons. Thermal analyses of the systems $\text{AlBr}_3\text{-C}_2\text{H}_5\text{Br}$, $\text{AlBr}_3\text{-C}_6\text{H}_5\text{Br}$, $\text{AlBr}_3\text{-CHBr}_3$ and $\text{AlBr}_3\text{-Br}_2$ are reported herein.

Experimental

Materials.—Aluminum bromide was prepared by the addition of redistilled bromine to aluminum pellets in a round bottom flask fitted with a reflux column (Fig. 1). After the reaction rate had decreased, the aluminum bromide was refluxed in the column until all the bromine had reacted. The column was then exchanged for a stillhead (Fig. 2) and pure, white aluminum bromide (m.p. 97.5°) was distilled into a reaction tube.

The bromine (Coleman and Bell) was purified by distillation; the middle fraction was used. The purified sample had a boiling point of 59.0° and a freezing point of -7.5°.

The bromoform was an Eastman Kodak Company sample with a boiling point of 149.0° and a freezing point of 7.0°.

The ethyl bromide was a Coleman and Bell, C.P. grade with a boiling point of 38.0° and a freezing point of -188.0°. It was purified by redistillation and recrystallization in various stages of this research.

The bromobenzene was an Eastman Kodak Company sample which was purified by redistillation and the middle fraction boiling at 156.0° was collected for use. The freezing point was -30.0°.

Procedure.—The systems were studied by the freezing point method. The freezing points were determined by means of cooling curves recorded by a Leeds and Northrup Micromax recorder. The iron-constantan thermocouple was calibrated, over the range of temperatures covered in this research, at the melting points of the following carefully purified substances: carbon tetrachloride, chloroform, ethyl acetate, toluene, mercury, water, *p*-toluidine and tin. It was also calibrated with a standard mercury thermometer calibrated at the National Bureau of Standards.

Samples were prepared for thermal analysis by first distilling the aluminum bromide into the reaction tube (S, Fig.

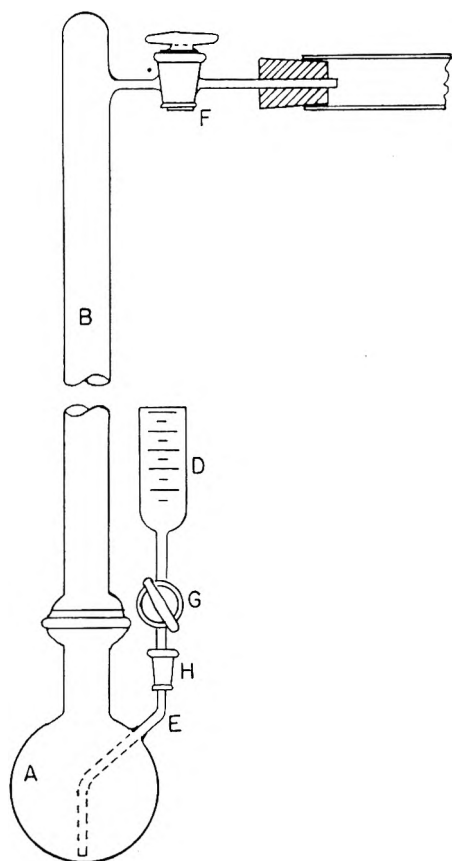


Fig. 1.—For the preparation for AlBr_3 .

(1) Mound Laboratory, Monsanto Chemical Co., Miamishburg, Ohio.

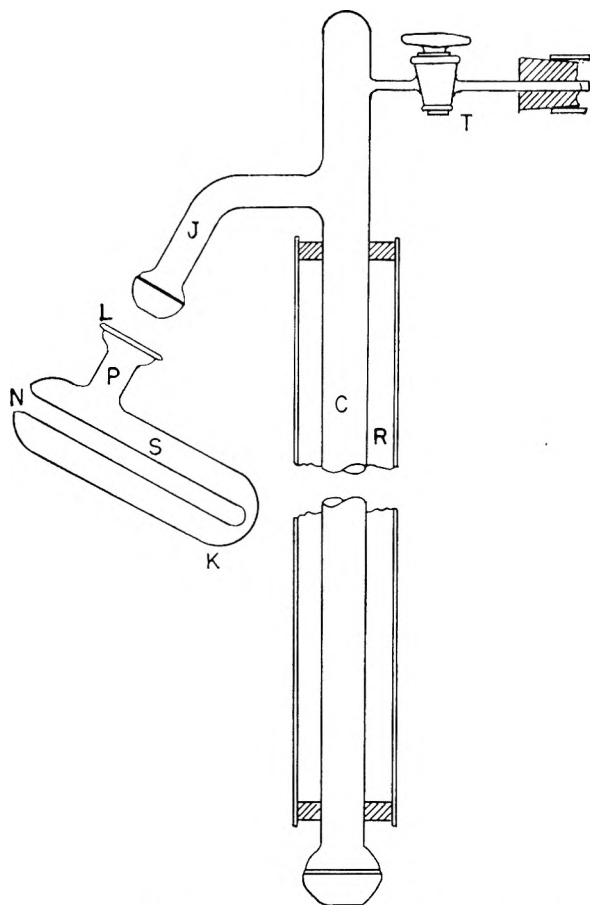


Fig. 2.—For the distillation of AlBr_3 into sample flask.

2) and weighing it. To this a sufficient amount of the second component was then added to give the mixture which was desired for analysis. This mixture was then heated until a completely homogeneous melt was obtained. The system was protected from atmospheric moisture by means of a drying train containing barium oxide and phosphorus oxide (P_4O_{10}). The calibrated thermocouple was inserted into a glass well (N in Fig. 2) which extended into the reaction tube in such a manner that it made intimate contact with the molten mixture. In practically all cases, 20 to 40 g. of material was used for each determination and the material was agitated continuously. Cooling curves were obtained over the entire range of compositions for each system studied. The data are believed to be accurate to $\pm 1.0^\circ$. All points were determined two or more times.

Results and Discussion

The freezing point-composition diagrams for the five systems studied in this research are given in Figs. 3, 4, 5 and 6.

The carefully purified anhydrous aluminum bromide gave a freezing point of 97.5° . We found no phase transformation in solid aluminum bromide near 70° , as reported by Kendall, Crittenden and Miller.² Our conclusions are in accord with those of Heldman and Thurmond³ who claim there is no convincing evidence of a phase transformation in aluminum bromide near 70° .

The aluminum bromide-bromine system has a eutectic at $-18.0 \pm 0.5^\circ$ but forms no compound.

The aluminum bromide-bromoform system has a

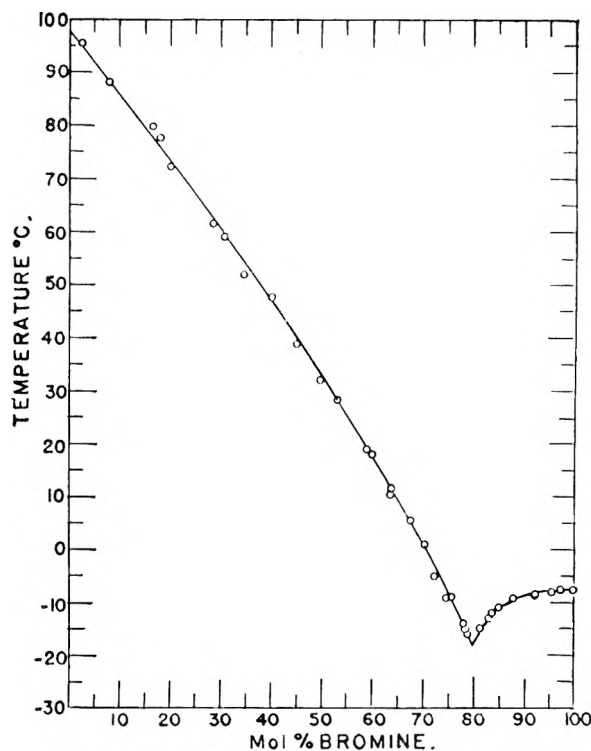


Fig. 3.—The bromine-aluminum bromide system.

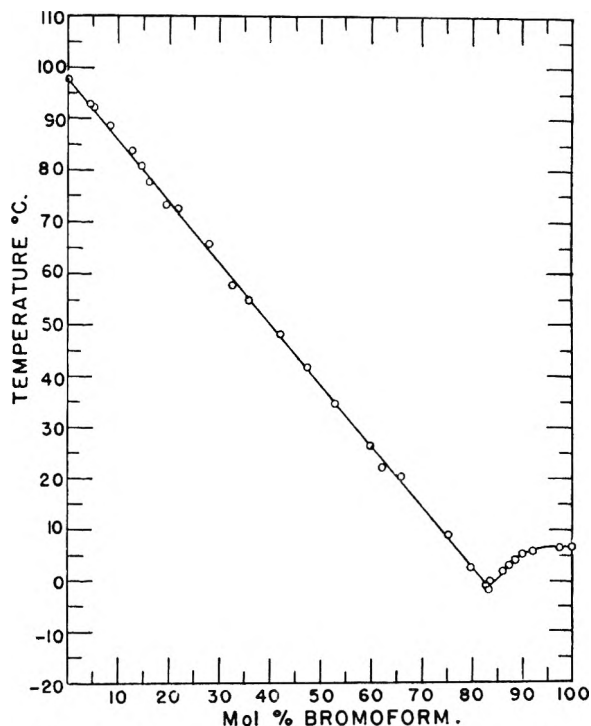


Fig. 4.—The bromoform-aluminum bromide system.

eutectic at -3.5 ± 0.5 and forms no compound. This is consistent with the conclusion of Ishekov⁴ who found no compound formation with carbon tetrabromide and of Kablukov and Khanov⁵ who found no compound formation with dibromo-methane. No data have been determined for methyl bromide because of its low boiling point.

(2) J. Kendall, E. D. Crittenden, and H. K. Miller, *J. Am. Chem. Soc.*, **45**, 963 (1923).

(3) J. D. Heldman and C. D. Thurmond, *ibid.*, **66**, 427 (1944).

(4) V. A. Ishekov, *J. Russ. Phys. Chem. Soc.*, **45**, 1792-8 (1913).

(5) I. Kablukov and A. S. Khanov, *ibid.*, **41**, 1755-62 (1909).

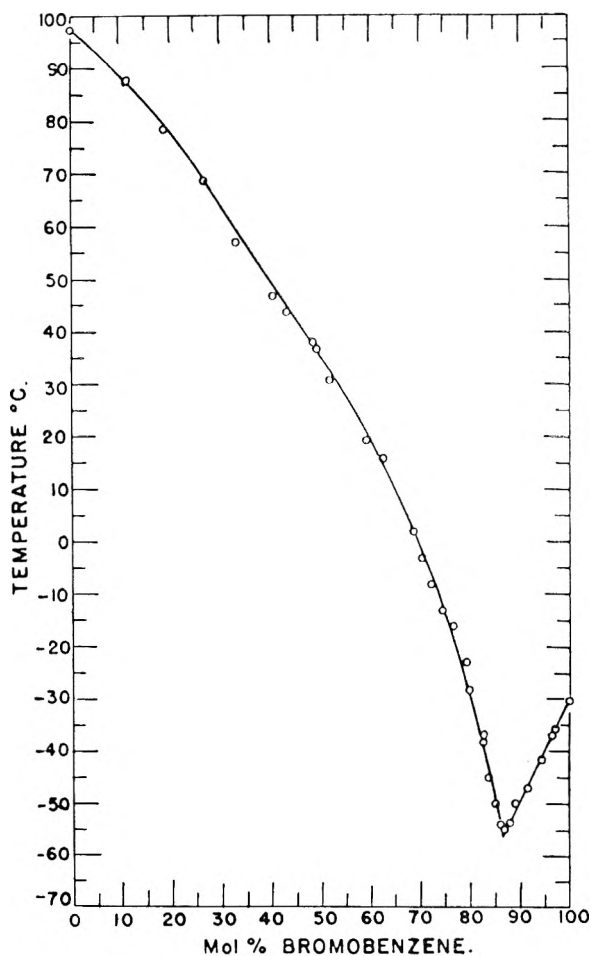


Fig. 5.—The bromobenzene-aluminum bromide system.

The aluminum bromide-bromobenzene system has a eutectic at $-56.0 \pm 0.5^\circ$ and forms no compound. This casts some doubt on the interpretation of Wohl and Wertyporoch⁶ of their electrical conductivity data on this system in which they assumed the formation of a complex.

The aluminum bromide-ethyl bromide system has eutectics at -68.5 and -132° and forms a compound having the empirical formula $\text{AlBr}_3 \cdot \text{C}_2\text{H}_5\text{Br}$. Considerable difficulty was encountered in obtaining this compound because of decomposition of the products with evolution of hydrogen bromide. Careful purification of the ethyl bromide by redistillation and recrystallization removed an impurity which seemed to catalyze the decomposition of the ethyl bromide. Recent evidence for the existence of a 1:1 compound of aluminum bromide-ethyl bromide has been obtained recently by Sheka and Sheka⁷ from dielectric constant data.

Attempts to study the aluminum bromide-butyl bromide system led to decomposition of the alkyl halide. When liquid *n*-butyl bromide was added to solid aluminum bromide, hydrogen bromide was split from the *n*-butyl bromide and the resulting gaseous butene-1 immediately added to the aluminum bromide, forming the scarlet, liquid addition complex. The liquid addition

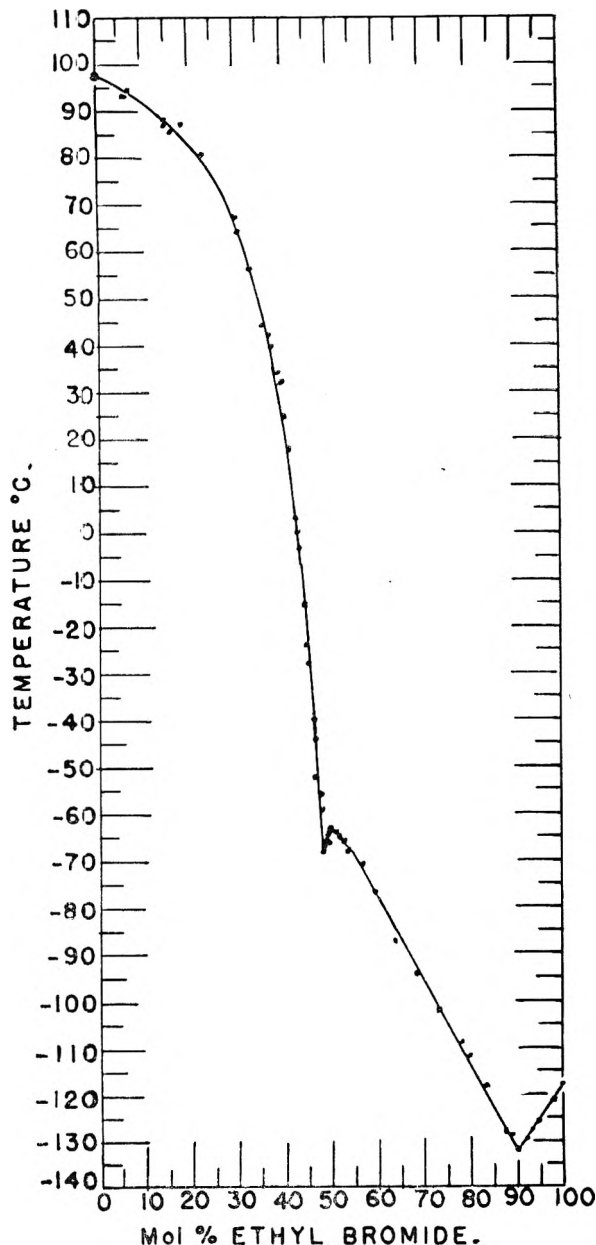


Fig. 6.—The ethyl bromide-aluminum bromide system.

complex, $\text{C}_4\text{H}_8 \cdot \text{AlBr}_3$, between aluminum bromide and butene-1 was isolated and analyzed quantitatively. This liquid complex is quite stable at room temperature in a closed system free of moisture. Conversely, direct addition of an olefin, hexene-1, to aluminum bromide resulted in the formation of a high molecular weight hydrocarbon and a mixture of by-products. The lower the temperature maintained during the addition, the greater the yield of hydrocarbon that was obtained.

Other bromide-bearing organic compounds were also investigated. Hydrogen bromide evolution was also noted when normal propyl and isopropyl bromides were added to aluminum bromide. Allyl bromide and vinyl bromide reacted violently with the aluminum bromide. The system triphenylbromomethane-aluminum bromide was stable to concentrations of 85 mole % of aluminum bromide.

(6) E. Wohl and E. Wertyporoch, *Ber.*, **64B**, 1357 (1931).

(7) I. A. Sheka and Z. A. Sheka, *Doklady Akad. Nauk S.S.S.R.*, **73**, 739 (1950).

Above 15 mole % of the triphenylbromobenzene decomposition occurred as was indicated by irreproducibility of the freezing points. The benzyl bromide-aluminum bromide system was stable up

to 34 mole % of benzyl bromide. Evidence of a eutectic was observed at 34.5 mole %. All mixtures above this value decomposed with evolution of copious quantities of gas.

THE SORPTION OF AMINES BY SILICA GELS¹

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Sorption isotherms of primary aliphatic amines and a few related compounds have been determined on silica gels, mostly at 25°. On one sample of silica (gel B) the lower amines (ethylamine, *n*-propylamine and ethylenediamine) show small but definite hysteresis loops whereas the higher amines (*t*-butylamine, *n*-amylamine, *n*-hexylamine and *n*-heptylamine) show no loop. On the other sample (gel D) all show large loops which, however, decrease in size as the molecular diameter (σ) increases. The point of hysteresis inception in all systems corresponds to a pore radius (calculated from the Kelvin equation) between 2σ and 3σ . The saturation volumes are roughly constant as required by Gurvitch's rule. The monolayer capacities correspond to the covering of a constant surface area, the number of moles adsorbed being inversely proportional to σ^2 . The gradual decrease in the size of the hysteresis loop as σ increases, and its ultimate disappearance on gel B, together with the location of the point of hysteresis inception, are in agreement with the predictions of the open-pore theory, which appears to offer a more satisfactory explanation of the experimental data than the rival "ink-bottle" theory.

A systematic examination of the sorption isotherms of the aliphatic alcohols on silica gel^{2,3} failed to reveal any marked decrease in the size of the hysteresis loop as the size of the adsorbed molecule increased, but later it was observed^{4,5} that triethylamine gave a hysteresis loop much smaller than those found with the alcohols. This suggested that an investigation of the aliphatic amines might be of interest since these compounds are considerably more volatile than the corresponding alcohols and it is therefore possible to examine a wider range of molecular size. The open pore theory of sorption hysteresis⁶ predicts that the loop should become smaller as the adsorbed molecule increases in diameter. This prediction has been confirmed in the present work, where it is shown that on one sample of silica gel the lower amines (ethylamine, *n*-propylamine and ethylenediamine) show definite loops whereas the higher amines (*t*-butylamine and *n*-amylamine upwards) show no loop. On other samples of silica gel and on ferric oxide gel⁷ all these amines show large hysteresis loops similar to those reported by Bartell and Dobay⁸ on a silica gel prepared by hydrolysis of silicon tetrachloride.

Experimental

The substance here designated "silica gel B2" is a commercial sample similar to, but not identical with, the "gel B" used in the earlier work with alcohols and triethylamine. After evacuation to constant weight at an activation temperature of 150° it lost a further 1% of water on ignition. Another commercial sample "silica gel D" was examined, which had a residual water content of 2.3% after evacuation at 200°. The experimental technique was similar to that used previously,² with minor modifications which, together with the methods used for purification of the amines, are described elsewhere.⁷ Data for ethylamine were obtained

by a modification of the method of Goldmann and Polanyi,⁹ which unfortunately enabled only desorption points to be determined.

Isotherms for water and ethyl alcohol were first determined for comparison with corresponding data obtained previously on other gels.² The following substances were investigated on both gel B2 and gel D: ethylamine, ethylenediamine, *n*-propyl-, *n*-butyl-, *n*-amyl-, *n*-hexyl- and *n*-heptylamine, *t*-butylamine (Me₃CNH₂), cyclohexylamine and pyridine. An oxygen isotherm was also determined at 90.3°K. in order to obtain surface areas by the B.E.T. method.

Results

Gel B2.—These results are illustrated in Figs. 1–3 which show all the isotherms obtained, except those for water and *n*-butylamine. The water curve is similar to that reported on gel B by Broad and Foster¹⁰ and shows a large hysteresis loop. The results obtained with *n*-butylamine were not reproducible but indicate the presence of a hysteresis loop. There seems to be some specific interaction between the amine and this particular gel since the volume adsorbed at saturation is abnormally high. Figures 1–3 show definite hysteresis loops with oxygen, ethyl alcohol, *n*-propylamine and ethylenediamine. It is reasonable to suppose that a loop would also have been detected with ethylamine had it been possible to determine the adsorption curve. The largest molecule to show a definite reproducible loop is *n*-propylamine; no loop is found with any of the straight chain amines above *n*-butyl or with *t*-butylamine, pyridine or cyclohexylamine.

Another feature of interest is that as the loop disappears, the linear middle portion of the isotherm becomes more prominent (*e.g.*, with *n*-amylamine and *t*-butylamine), but this linear region in turn diminishes and has practically vanished when *n*-heptylamine is reached. There is a perceptible flattening in the middle of the pyridine isotherm but cyclohexylamine gives a normal B.E.T. type 1 isotherm which follows the Langmuir equation over the entire range.

(1) Based on a thesis presented by Marjorie J. Brown for the degree of Ph.D. in the University of London, 1950.

(2) A. G. Foster, *Proc. Roy. Soc. (London)*, **A146**, 129 (1934).

(3) A. G. Foster, *ibid.*, **A150**, 77 (1935).

(4) D. W. Broad, Ph.D. Thesis, London, 1938.

(5) A. G. Foster, *THIS JOURNAL*, **55**, 638 (1951).

(6) A. G. Foster, *Trans. Faraday Soc.*, **28**, 645 (1932).

(7) M. J. Brown and A. G. Foster, *J. Chem. Soc.*, Feb., 1952.

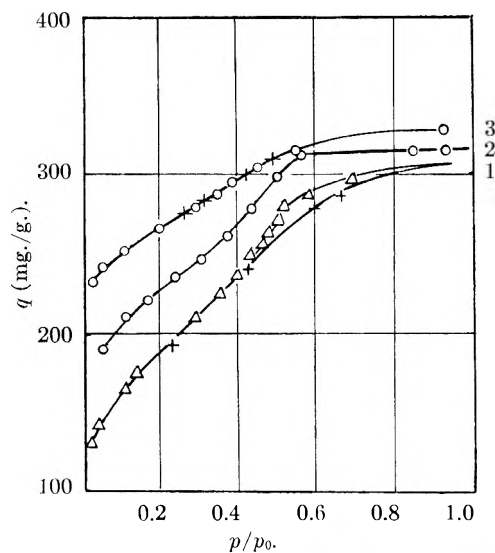
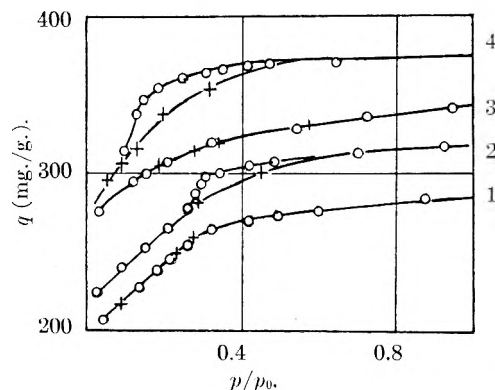
(8) F. E. Bartell and D. G. Dobay, *J. Am. Chem. Soc.*, **72**, 4388 (1950).

(9) F. Goldmann and M. Polanyi, *Z. physik. Chem.*, **132**, 321 (1928).

(10) D. W. Broad and A. G. Foster, *J. Chem. Soc.*, 372 (1945).

TABLE I
 SUMMARY OF DATA FOR SILICA GEL B2

Sorbate	Temp., °C.	q_s , mg./g.	V_s , cc. liquid/g.	V_m , mg./g.	V_m/M , millimoles/g.	Surface area, m. ² /g.	V_m/q_s , %
Water	25	398	0.399	196 ^a	10.9	806	49
Ethylamine	0	315	.446	187	4.12	709	59
<i>n</i> -Propylamine	0	320	.434	221	3.74	739	69
<i>n</i> -Butylamine	25	410	(.557)	228	3.12	715	56
<i>n</i> -Amylamine	25	330	.440	234	2.69	691	71
<i>n</i> -Hexylamine	25	338	.444	263	2.60	727	78
<i>n</i> -Heptylamine	35	346	.454	271	2.36	721	78
Ethylenediamine	25	375	.420	270	4.50	788	72
<i>t</i> -Butylamine	0	277	.388	194	2.65	624	69
Cyclohexylamine	25	320	.371	320	3.23	879	100
Pyridine	25	424	.433	337	4.25	848	80

^a Point of hysteresis inception.

 Fig. 1.—Silica gel B2: 1, EtOH; 2, EtNH₂; 3, *n*-C₃H₇NH₂; adsorption points +; desorption points ○, △.

 Fig. 2.—Silica gel B2: 1, Me₃C-NH₂; 2, *n*-C₃H₇NH₂; 3, *n*-C₇H₁₅NH₂; 4, (CH₂-NH₂)₂; adsorption points +; desorption points ○.

The more important data for gel B2 are summarized in Table I. The saturation volume V_s does not appear constant but shows no regular variation. The best method of testing the validity of Gurwitsch's rule is that of Broad and Foster¹¹ who showed that the plot of q_s/M (moles adsorbed at saturation) against d/M (reciprocal of molar volume) should be linear and pass through the origin.

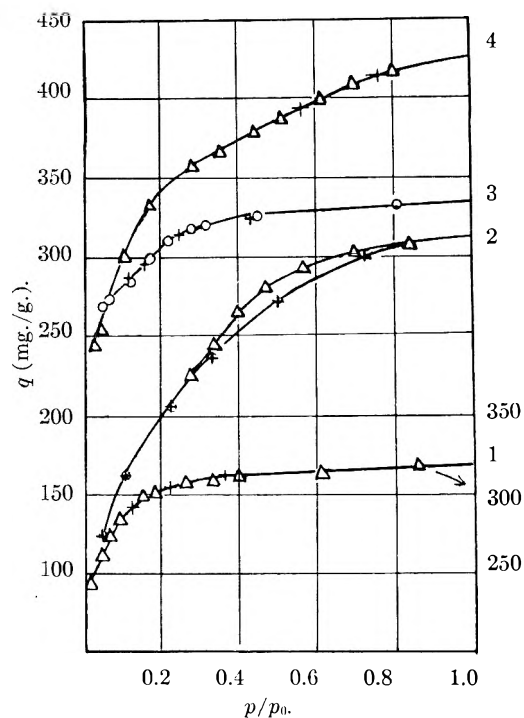
 (11) D. W. Broad and A. G. Foster, *J. Chem. Soc.*, 366 (1945).

 Fig. 3.—Silica gel B2: 1, cyclohexylamine; 2, oxygen; 3, *n*-hexylamine; 4, pyridine; adsorption points, +; desorption points, ○, △.

Figure 4 shows that this is true both for gel B2 and for gel D, the mean saturation volumes being 0.42 and 0.58 cc. per gram, respectively.

The amounts V_m required to form a complete monolayer, recorded in column 5, are calculated by the "point A" method of Emmett and Brunauer¹⁵ (except for cyclohexylamine, where the reciprocal slope of the Langmuir plot is given). The occurrence of a linear middle region in an isotherm which subsequently turns away from the concentration axis, is associated with small values of n (the number of adsorbed layers).¹² The usual B.E.T. graphical method for estimating V_m breaks down here, but the "point A" method (which for high values of the B.E.T. constant c is theoretically sound), has been applied successfully to other systems of this type.¹² The figures in column 6 which represent the number of millimoles required to form a com-

 (12) A. G. Foster, *ibid.*, 773 (1945).

TABLE II
 SUMMARY OF DATA FOR SILICA GEL D

Sorbate	q_s , mg./g.	V_s , cc./g.	V_m , mg./g.	V_m/M , milli- moles/g.	Surface area, m ² /g.	V_m/q_s , %	p_1/p_0	r_1 , Å.	r_2 , Å.	r_1/σ	$r_2 + D$ Å.
Water	555	0.557	150 ^a	8.33	618	27	0.30	8.8	32.2	2.5	35.7
Ethylamine	435	.617	166	3.68	630	38	...	...	...	...	...
<i>n</i> -Propylamine	438	.594	190	3.21	636	43	.32	15.5	28.7	2.7	40.1
<i>n</i> -Butylamine	454	.616	226	3.09	703	50	.28	14.7	30.4	2.4	42.3
<i>n</i> -Amylamine	476	.635	256	2.94	751	54	.28	18.5	26.6	2.9	40.1
<i>n</i> -Hexylamine	440	.577	282	2.78	776	64	.21	17.7	27.1	2.6	40.7
<i>n</i> -Heptylamine	439	.575	292	2.53	770	66	...	...	26.8	...	41.0
Ethylenediamine	470	.526	195	3.24	576	42	.12	10.6	28.1	2.0	38.9
<i>t</i> -Butylamine	412	.577	185	2.53	594	45	.32	16.8	27.7	2.7	40.1
Cyclohexylamine	468	.542	240	2.42	612	51	.18	17.0	31.8	2.6	44.8
Pyridine	529	.541	198	2.51	503	37	.24	16.7	29	2.9	40.5

^a Point of hysteresis inception.

plete monolayer clearly decrease with increasing molecular weight.

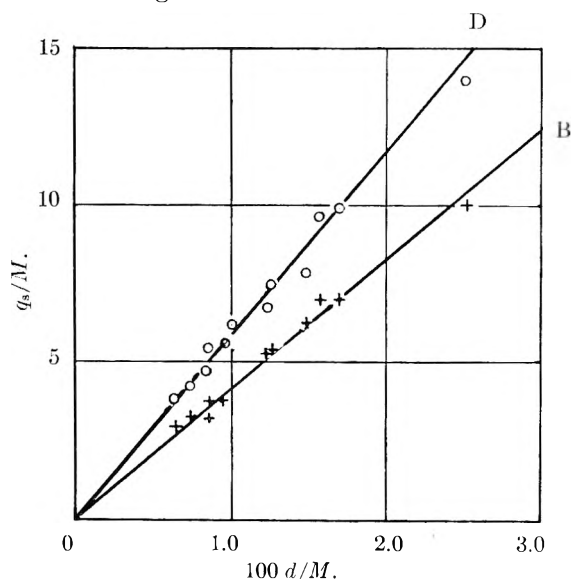


Fig. 4.— q_s/M vs. $100 d/M$.

It was first pointed out by Goldmann and Polanyi⁹ that the quantity $(V_m/M)(M/d)^{2/3}$ should be constant for the covering of a constant area, but, apart from their own data for charcoal and those of Broad and Foster¹¹ for silica gel B, there is little experimental evidence for this view. The latter workers obtained a linear plot of V_m/M against $1/\sigma^2$ where the molecular diameter σ was calculated by means of the equation¹³

$$\sigma \text{ (in } \text{\AA}.) = 1.33(M/d)^{1/3} \quad (1)$$

This relation, which has also been used in the present work, holds for an assembly of closely packed spheres in which N molecules occupy a volume $N\sigma^3/\sqrt{2}$ cc. and is a special case of the relation

$$\sigma^2 = F(M/Nd)^{2/3} \quad (2)$$

used by Livingston,¹⁴ in which F has the value 1.260 for square close packing. The equation used by Emmett and Brunauer¹⁵ which gives $\sigma^2 = 16.2 \text{ \AA}^2$

(13) E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," 2nd ed., Oxford, 1947, p. 7.

(14) H. K. Livingston, *J. Am. Chem. Soc.*, **66**, 571 (1944).

(15) P. H. Emmett and S. Brunauer, *ibid.*, **59**, 1553 (1937).

for nitrogen, using the liquid density, corresponds to $F = 1.091$ for hexagonal close packing. In column 7 the values of $V_m\sigma^2/M$ have been multiplied by N to convert to specific surface areas, which are seen to be roughly constant. Figure 5 shows the points for the aliphatic amines lying slightly below the best line through the other points, including those for oxygen and water. The slope of this line corresponds to a surface area of 780 sq. m. per gram. The use of the lower value of $F(1.091)$ would give an area of 675 sq. m. but would not alter the relative positions of the various points. The B.E.T. plot for oxygen is linear up to $p/p_0 = 0.3$ and from the slope and intercept $c = 37$ and $V_m = 180$ cc. (N.T.P.) or 8.04 millimoles g.

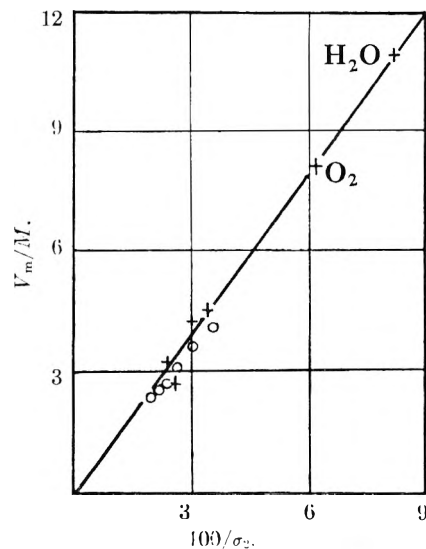


Fig. 5.—Silica gel B2: $\circ$, normal amines; +, other substances.

Gel D.—The same substances were investigated as on Gel B2 and at the same temperatures. All the systems examined showed large hysteresis loops. Three typical isotherms are illustrated in Fig. 6 and the more important data summarized in Table II. It is again found that the values of $V_m\sigma^2/M$ are roughly constant and although the experimental points of Fig. 7 are somewhat scattered, the best curve still runs close to the points for oxygen and water. The slope of this curve gives a specific sur-

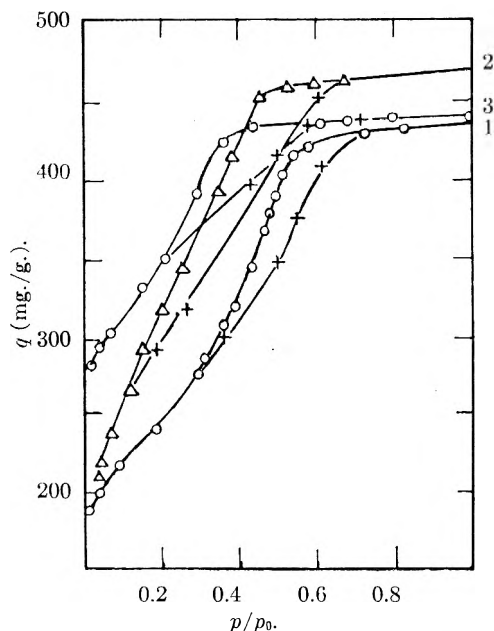


Fig. 6.—Silica gel D: 1, $n\text{-C}_3\text{H}_7\text{NH}_2$; 2, $(\text{CH}_3)_2\text{NH}$; 3, $n\text{-C}_6\text{H}_{13}\text{NH}_2$; adsorption points, +; desorption points, O, Δ .

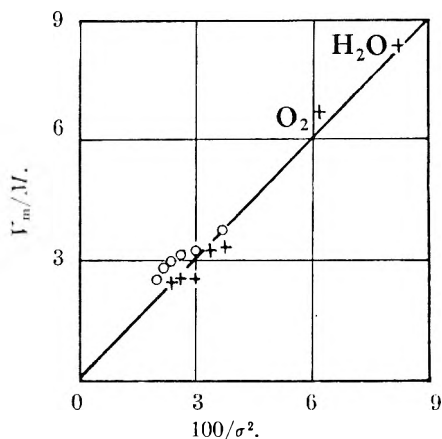


Fig. 7.—Silica gel D: O, normal amines; +, other substances.

face area of 610 sq. m. (or 526 sq. m. if $F = 1.091$). The oxygen isotherm was determined only up to $p/p_0 = 0.2$ and the B.E.T. plot gave $c = 33.5$ and $V_m = 149$ cc. or 665 millimoles g. Column 8 gives the values of P_h/P_0 , the relative pressure at the point of hysteresis inception.

Discussion

Saturation Volumes and Surface Areas.—As in the earlier work of Broad and Foster on silica gel B¹¹ and on ferric oxide gel,¹⁶ the saturation volumes are only roughly constant and show large variations ($\sim 10\%$) from the mean and there is no correlation between saturation volume and any particular property of the adsorbed molecule.

The absolute values of the surface areas depend, of course, on the values chosen for σ^2 , the cross-sectional area. The values used previously¹¹ for σ , calculated from equation (1) have been retained in this work although those generally used for the determination of surface areas by the B.E.T. method

are slightly lower, being based on the lower packing factor required for hexagonal close packing in equation (2). The chief feature of the gel B results is that the surface areas obtained from the isotherms for oxygen and water agree closely with those for the amines. Whereas on gel B the points for the normal straight chain amines lie rather below the best curve through the other points, the converse is true for gel D. Similar results for saturation volumes and surface areas were also obtained on a third sample (gel C) which is not described here because the data for the higher amines were not reproducible. The isothermal for water on this gel, which has already been described,¹⁷ shows no linear range below the hysteresis loop and runs straight back to the origin. It was therefore impossible to apply the "point A" method, but it was found that the point of hysteresis inception gave an area agreeing reasonably well with those derived from the "point A" values for the amines. The values of V_m/M tabulated for water on gel B2 and gel D have also been obtained in this manner, since the point A values are not very clearly defined, and are abnormally low (3.00 and 1.44 millimoles per gram, respectively). The extensive results of Broad and Foster¹¹ (who also found an abnormally low "point A" value for water) together with those of the present work are remarkable in providing almost the only independent evidence in support of the data of Goldmann and Polanyi⁹ for the constancy of the expression $(V_m/M)(M/d)^{2/3}$. It is noteworthy that most other workers who have examined a wide range of adsorbed molecules have found it necessary to use values for sectional area which are considerably larger than those calculated by equation (2) in order to get agreement with the surface areas derived from the nitrogen isothermals by the B.E.T. method.¹⁷

Capillary Radii.—Unfortunately neither the gel B2 nor the gel D isotherms show the clearly defined points of inflection on the descending branch of the hysteresis loop at which pore radii are usually compared.¹⁷ For gel D pore radii calculated from the Kelvin equation are recorded at two points on each isotherm (Table II), r_1 at the point of hysteresis inception, and r_2 at the point of maximum curvature (the "opacity point" of the Zsigmondy theory¹⁸). The most striking feature of these results is that r_1 clearly depends on σ , the value of r_1/σ being approximately constant with a mean value of 2.6, whereas r_2 varies only by ± 3 around the mean value of 29 Å. According to the original version of the open pore theory⁶ it is not the radius as calculated by the Kelvin equation which should be constant but the true pore radius or Kelvin radius plus thickness of adsorbed layer. The last column of Table II shows the values of $(r_2 + D)$, where D is taken as 2σ except for water where only one layer is allowed for. These show a variation of ± 4 around the mean value of 40 Å. According to Cohan's version of the open pore theory¹⁹ r_1 is equal to 2σ and Table III shows that the mean value of r_1/σ is 2.2 for gel B2.

(17) A. G. Foster, *Discuss. Faraday Soc.*, **3**, 48 (1948).

(18) E. Zsigmondy, *Z. anorg. Chem.*, **71**, 356 (1911).

(19) L. H. Cohan, *J. Am. Chem. Soc.*, **66**, 98 (1944).

(16) D. W. Broad and A. G. Foster, *J. Chem. Soc.*, 446 (1946).

TABLE III
RADII AT POINT OF HYSTERESIS INCEPTION ON GEL B2

	r_1 , Å.	r_1/σ
Water	9.1	2.6
Oxygen	8.6	2.1
Ethyl alcohol	11.2	2.2
Ethylenediamine	9.3	1.8
n-Propylamine	13.3	2.3

Emmett and Cines²⁰ compared their Kelvin radii with the values calculated from the equation $r = 2V/S$ where V is the saturation volume and S the surface area. Taking the specific surface area of gel B2 as 780 sq. m., based on equation (1), and $V = 0.42$ cc., from the slope of Fig. 5, gives 10.8 Å. for the pore radius, whereas taking $S = 675$ sq. m. based on equation (2) gives 12.5 Å. The mean Kelvin radius calculated from the water isothermal is 10.0 Å., to which 3.5 Å. must be added for the thickness of the unimolecular layer, making 13.5 Å. in all, so that the use of equation (2) for calculation of cross-sectional areas would seem to give the better agreement. On the other hand, this method is only approximate when σ is of the same order of magnitude as r and gives a value which is roughly the mean of the Kelvin radius and the true radius. An alternative procedure is to use the values of n ($= r/\sigma$) corresponding to different values of V_m/q_s tabulated by Foster.¹⁷ This is equivalent to calculating a value of r/σ which will give the observed ratio between monolayer volume and total volume. V_m/q_s for water is 49% (Table I) corresponding to $n = 3.5$ or $r = 12.25$ Å., whilst the values of V_m/q_s for the other adsorbates give 13 ± 2 Å., so that the Kelvin radii although very small would seem to be essentially correct.

The pore radius distribution in gel D is obviously very wide since the lowest r_1 value is 9 Å. and the highest r_2 value 32 Å., so that neither of the above simple methods are likely to be accurate¹⁷ when applied to this gel.

The Shape of the Sorption Isotherms.—According to the open-pore theory in its original version⁶ the limiting types of sorption isotherm are determined primarily by pore size, or rather by the ratio r/σ . Thus when $r/\sigma = 1$ or 2 the formation of a monolayer fills practically the entire available volume and the isotherm is of B.E.T. type I. When r/σ is large, say > 10 , the monolayer occupies only a small fraction of the total volume and the major portion of the adsorbed substance is held by multimolecular sorption or capillary condensation giving B.E.T. type IV isotherms. The gradual change of

type with increasing r/σ is apparent from Figs. 1–3. First the hysteresis loop decreases in size, then the linear middle range (predicted by the B.E.T. theory²¹ for certain systems where $n = 2$ or 3) becomes prominent and finally this in turn vanishes giving type I isotherms. The gradual rise in the ratio V_m/q_s with increasing σ also illustrates this point, i.e., the monolayer occupies an increasing fraction of the total pore volume.

Hysteresis.—In a discussion of the factors determining the size of the hysteresis loop, it has already been indicated⁵ that these results give strong support to the open pore theory. Both the pressure at the point of hysteresis inception and the size of the hysteresis loop vary with the molecular diameter in accordance with the predictions of this theory. The alternative ink-bottle theory does not enable any quantitative predictions to be made since, in attributing hysteresis to the presence of bottle necks, it makes this phenomenon a function solely of the structure of the adsorbent, independent of the nature of the adsorbed molecules except that ultimately the adsorbed molecule may become too large to enter the narrow necks, whereon both hysteresis and adsorption should vanish. Katz²² counters this argument by pointing out that the necks will not all be of the same size, so that there should be a gradual falling off in saturation volume as the loop decreases in size. This is contrary to the experimental evidence presented here, since even with the largest molecules the saturation volume shows no diminution although the loop has already vanished.

A further argument in favor of the open-pore theory is the reasonable agreement between pore radii calculated from the relation $r = 2V/S$ and the values obtained by application of the Kelvin equation to the desorption curve. In an assembly of ink-bottles with short necks of radius r_1 and long bodies of radius r_2 , the ratio $2V/S$ will give a radius approximating to r_2 , whereas application of the Kelvin equation to the desorption curve will give r_1 , hence the two methods would not in general agree. The extensive data of Emmett and Cines²⁰ on porous glass, however, show excellent agreement between the radii calculated by the two methods.

Acknowledgments.—The authors wish to thank the Department of Scientific and Industrial Research for a maintenance award and the University of London for a postgraduate scholarship (to M. J. B.) and also to acknowledge the financial assistance given by Imperial Chemical Industries Ltd. to the department, which has defrayed some of the expenses of this research.

(21) A. G. Foster, *J. Chem. Soc.*, 769 (1945).

(22) S. M. Katz, *Research*, 4, 93 (1951).

(20) P. H. Emmett and M. Cines, *This Journal*, 51, 1260 (1944)

D-FRUCTOSE DIHYDRATE

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The discovery, preparation and properties of a new crystalline dihydrate of β -D-fructose are described.

β -D-Fructose is most often crystallized from aqueous solutions as anhydrous crystals, although its separation as a metastable phase (possibly the hemihydrate) has also been described.^{2,3} During an investigation of the phase diagram of the fructose-water system, details of which will be reported later, we observed that fructose can also be crystallized as a dihydrate. The preparation and properties of fructose dihydrate are described here.

Preparation.— β -D-Fructose dihydrate may be obtained by seeding a 75% aqueous fructose solution with anhydrous fructose crystals at 0° and allowing it to stand at this temperature for several days. If the spherulites of fructose hemihydrate which ordinarily form first are vigorously stirred, they will usually transform in a few hours to large, well-formed prisms of fructose dihydrate like those shown in Fig. 1. At lower temperatures and concentrations (−10° and 50 to 60% fructose), seeding with anhydrous fructose sometimes results directly in the formation of fructose dihydrate.

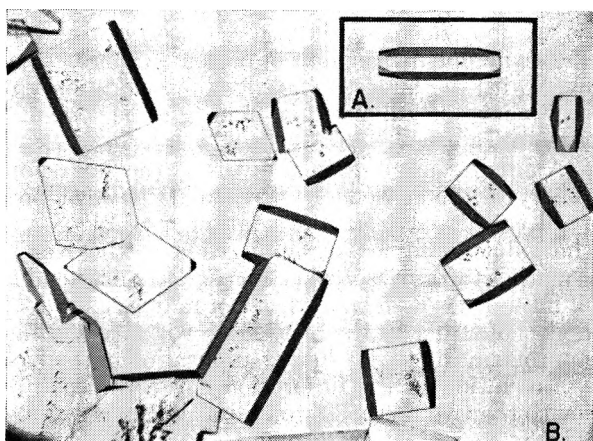


Fig. 1.—Fructose dihydrate: A, undistorted crystal; B, crystals flattened by growing against cover glass (100 ×).

After seed crystals of the dihydrate have been obtained, it is more conveniently crystallized at 0° from solutions containing about 65% fructose. Additional crops may be taken at lower temperatures.

Fructose dihydrate crystallizes rapidly, even in solutions saturated with glucose. The solubility of fructose dihydrate decreases rapidly and at −9°, which is probably its optimum crystallization temperature, its solubility is only about three-fifths the solubility of anhydrous fructose. Thus crystallization as the dihydrate rather than as anhydrous fructose results in a much more fluid mother liquor, and the crystals are therefore easier to filter and wash. These properties suggest that the crystallization of fructose dihydrate may be used advantageously in the purification of fructose. Preliminary experiments indicate that this is the case.

Composition.—Analyses of powdered fructose dihydrate dried to constant weight at −1° over anhydrous fructose

gave an average of $83.3 \pm 0.1\%$ fructose (theory, 83.33%). A large single crystal which had been air-dried at +1° was found to contain 83.45% fructose. These analyses were made by determining the refractive indices of solutions containing weighed amounts of fructose dihydrate and water. The results were calculated using the tables of Jackson and Mathews.⁴

Mutarotation.—The initial rotation and rate of mutarotation of fructose dihydrate were determined at $20.0 \pm 0.1^\circ$ using a quartz wedge saccharimeter and sodium light. The solution contained 5.18 g. of fructose dihydrate per 100 ml. of solution in 0.001 M potassium phthalate buffer at a pH of 4.59. The initial specific rotation, -124° , and the mutarotation coefficient, 52.2 min.^{-1} (using common logarithms), are in sufficiently good agreement with the accepted values of -132.2° and 59.2° to indicate that fructose is present in the β -pyranose form in this dihydrate.

Melting Point.—The melting point of a dry single crystal in a sealed capillary in a constant temperature bath was found to be $+21.3^\circ$. Complete melting at this temperature required three days, however. Under these conditions it is reasonable to assume that mutarotatory equilibrium was maintained during melting. This is obviously not the case when the melting point is determined by the conventional capillary melting point method. Because of the slowness with which fructose dihydrate melts, this method is very unsatisfactory. The apparent melting point appears to depend on the size of the sample and, with a warming rate of about $1/2^\circ$ per minute, ranges from about $+22^\circ$ for specks of powder on the walls of the capillary to about $+29^\circ$ for a sample in a thin-walled tube 2 mm. in diameter. On the other hand, samples in 4-mm. tubes melted completely at 25° in about 2 hours.

When the melting of a fructose dihydrate crystal, such as those shown in Fig. 1, is observed at 25° with a microscope, etch pits with angular outlines usually appear first. As melting progresses, these etch pits enlarge until they extend completely through the crystal and cause it to have a "honeycomb" structure which eventually collapses leaving slowly melting fragments. As a result, a crystal in a capillary tube may appear to be only slightly melted when in

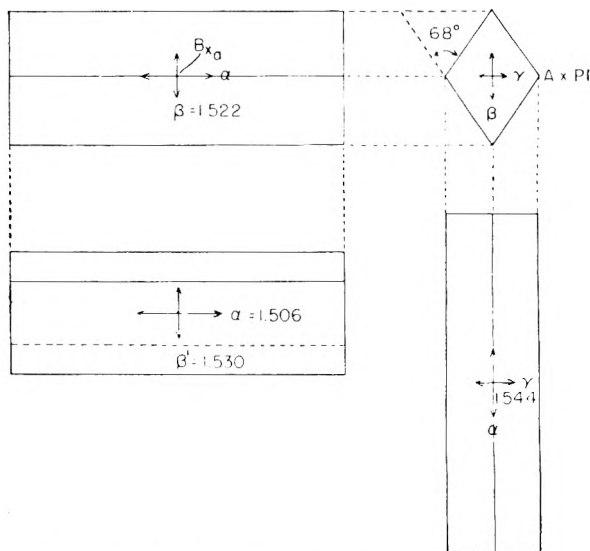


Fig. 2.—Fructose dihydrate: optic orientation.

(1) Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) M. Honig and L. Jessor, *Monatsh.*, **9**, 563 (1888).

(3) M. L. Wolfrom and Alva Thompson, *J. Am. Chem. Soc.*, **68**, 791 (1946).

(4) R. F. Jackson and J. A. Mathews, *J. Research Natl. Bur. Standards*, **8**, 412 (1932) (RP426).

(5) H. S. Isbell and W. W. Pigman, *ibid.*, **20**, 773 (1938) (RP1104).

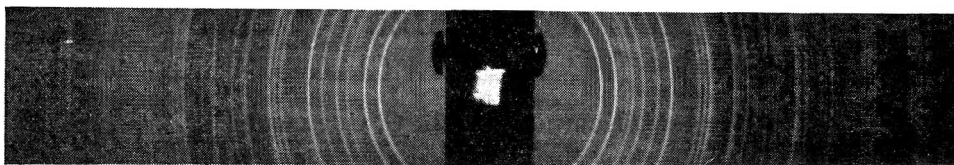


Fig. 3.—X-Ray powder photograph of fructose dihydrate.

reality, very little solid structure is left to hold the liquid within the framework of the original crystal. The high viscosity of the melt also helps to prevent collapse. This behavior was shown by a large single crystal which appeared to be only slightly melted after 48 hours at $+21.4^{\circ}$ but which crumbled to small fragments in a drop of solution when pressed lightly with a spatula.

Optical and Crystallographic Properties.—Fructose dihydrate somewhat resembles anhydrous fructose in crystal habit,⁶ although its crystals are usually two to five times longer than they are wide when they are not confined by the container walls during growth (Fig. 1a). The crystals shown in Fig. 1b are slightly flattened by growing against the cover glass which also has trapped a few air bubbles. The higher birefringence and lower melting point of fructose dihydrate clearly distinguish it from anhydrous fructose.

Fructose dihydrate crystals are prismatic with a rhomb shaped cross-section as shown in Fig. 1b. The dome is often absent. The hemimorphic character required by the optical activity of fructose was not apparent in any of the crystals examined.

Ordinary views such as Fig. 1a give an interference figure showing the axial plane tilted about half-way between the acute bisectrix and the optic normal. Such a view shows the refractive index α for lengthwise vibrations and an intermediate value β' for crosswise vibrations. End views show a centered obtuse bisectrix interference figure and pro-

vide the refractive indices β and γ . A few fragments in position to show an optic axis interference figure have occasionally been obtained. From these, the curvature of the isogyre indicates that the optic axial angle ($2V$) is about 80° ; the dispersion is faint with ($r > v$) and the optical character is (+).

Figure 2 shows the optic orientation and crystal morphology.

The optical properties (Table I) were determined in sodium light at 14° on crystals mounted on a hollow slide cooled by circulating tap water to avoid melting. The refractive indices of the immersion oils were determined on an Abbe refractometer at the same temperature.

The X-ray powder pattern of fructose dihydrate is shown in Fig. 3. The spacing and intensity data obtained from this figure are given in Table II.

TABLE II

X-RAY DIFFRACTION POWDER DATA FOR β -D-FRUCTOSE DIHYDRATE

d in Å.	Est. I ^a	d in Å.	Est. I ^a
8.10	VW	2.385	W
6.60	VS	2.346	M
5.83	VS	2.301	W
5.33	W	2.258	W
5.14	MS	2.219	W
4.77	S	2.183	M
4.36	S	2.145	MW
4.05	VS	2.114	VW
3.96	VW	2.077	W
3.51	MS	2.049	W
3.42	MS	2.004	MW
3.34	S	1.974	W
3.29	VW	1.947	MW
3.02	M	1.889	VW
2.984	MW	1.795	M
2.866	M	1.756	M
2.776	W	1.716	MW
2.662	M	1.640	VW
2.583	MW	1.612	VW
2.518	W	1.534	W
2.422	MS	1.449	W

^a VS, very strong; S, strong; MS, medium strong; M, medium; MW, medium weak; W, weak; VW, very weak.

TABLE I

OPTICAL AND CRYSTALLOGRAPHIC PROPERTIES OF β -D-FRUCTOSE DIHYDRATE

Crystal system: orthorhombic; Class 6: rhombic bisphe-noidal. Prismatic habit. Acute angle on rhomb-shaped end views = 68° .

Refractive indices ($5893 \text{ Å.}; 14^{\circ}$):

$$\alpha = 1.5061 \pm 0.0005$$

$$\beta = 1.5221 \pm 0.0005$$

$$\gamma = 1.5444 \pm 0.0005$$

Optic axial angle:

$$\text{Est. from curvature} \quad 2V = 80^{\circ}$$

$$\text{Calculated from } \sin^2 V = \frac{\alpha^2(\gamma^2 - \beta^2)}{\beta^2(\gamma^2 - \alpha^2)} \quad 2V = 81.5^{\circ}$$

$$\text{Calculated from } \sin E = \beta \sin V \quad 2E = 156^{\circ}$$

Optical character: (+)

Dispersion: ($r > v$) faint.

Optical orientation: see Fig. 5.

(6) Anhydrous fructose has been described by Bates⁷ and Winchell.⁸

(7) F. J. Bates and Associates, "Polarimetry, Saccharimetry and the Sugars," National Bureau of Standards Circular C 440, 1942, p. 543.

(8) A. N. Winchell, "Optical Properties of Organic Compounds," University of Wisconsin Press, 1943, p. 186.

The authors wish to thank Dr. Fred Stitt for valuable suggestions and criticisms and Dr. Kenneth Palmer and Mr. Dale Black for the X-ray diffraction measurements.

SORPTION OF GR-S TYPE OF POLYMER ON CARBON BLACK. III. SORPTION BY COMMERCIAL BLACKS¹

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The sorption capacities toward GR-S rubber of five commercial carbon blacks are in decreasing order: Spheron 6, Vulcan 1, Philblack 0, Sterling 105, Philblack A. Apparently, the sorption is not related to surface area. The sorption on Vulcan 1 of GR-S from its solutions in seven different solvents or mixtures of solvents increases with decreasing solvent power for the rubber. The sorption curves of two "cold rubbers," polymerized at -10 and $+5^{\circ}$, respectively, showed little difference from that of 50° GR-S. Previous heating of carbon black in nitrogen at 500 or 1100° increased the sorption by about 20% over unheated carbon. Air-heating of carbon black at 425° did not cause a difference in the sorption from benzene solution, but produced an increase in the sorption of rubber from *n*-heptane solution. In the range 75% butadiene-25% styrene to 5% butadiene-95% styrene there is practically no effect of the degree of unsaturation upon the sorption. Polystyrene of high intrinsic viscosity exhibits a peculiar behavior with furnace blacks. Vulcan 1 sorbed microgel as well as the sol fraction from *n*-heptane solutions of GR-S containing microgel (conversion 74.7 and 81.5%). There was no appreciable difference in the amount of sorption of rubber fractions having average molecular weights varying from 433,000 to 85,000. There is little change in the amount sorbed after two hours of shaking but the intrinsic viscosity of the residual rubber decreases with time. The low molecular weight rubber is sorbed more rapidly, but is slowly replaced by the more tightly sorbed high molecular weight fraction. Partial fractionation of a rubber sample can be achieved by allowing the rubber solution to flow through a column of weakly-sorbing carbon black. A large portion of the sorbed rubber can be recovered from the column by washing it with a "good" solvent such as xylene. "Bound rubber" is produced by intimate mixing of equal parts of carbon black and rubber swollen in chloroform, when the mixture is dried in vacuum at 80° or at room temperature. Milling is not essential to get "bound rubber."

The sorption of GR-S type polymers in solution on Graphon carbon black under different experimental conditions has been described in two previous papers.^{3,4} Graphon with its partially graphitized surface, is not a commercial type of black. For this reason, four commercial carbon blacks have been employed in an extension of previous studies. Following a comparison of the sorption capacities of the four blacks, the effects of solvent, degree of unsaturation, molecular weight and previous heat treatment of the carbon black are considered. Some experiments with rubber fractions of high and low molecular weight and with carbon columns are reported. The sorption of two low temperature rubbers is compared with the standard GR-S prepared at 50° . Finally, some results of a preliminary study of "bound" rubber, that portion of the rubber which is insolubilized in benzene by intimate mixing with carbon black, are given.

Materials.—Reagent grade benzene, chloroform and carbon tetrachloride, absolute ethanol, *n*-heptane (research grade, 99 mole % purity, from Phillips Petroleum Co.), and technical grade xylene and toluene were used as solvents.

The carbon blacks used and some of their properties supplied by the manufacturers are listed in Table I.

GR-S type rubber of different degrees of unsaturation, conversion approximately 60%, was prepared by the mutual recipe at 50° , a varying ratio of monomers being used in the charge. GR-S X-418 was obtained from the Government Pilot Plant, Akron, Ohio. Two samples of cold rubber, polymerized at $+5$ and -10° , respectively, were obtained through the courtesy of Dr. C. F. Fryling, Phillips Petroleum Company.

Procedure.—In general, 0.25% solutions of polymer in the various solvents were prepared. One hundred ml. of solution was shaken with a certain weight of carbon black at 30° , usually for a period of 40 hours. After centrifuging, 25-ml. aliquots of the supernatant liquid were evaporated to determine the amount of residual rubber.

In some experiments with chloroform solutions and other solvents, especially benzene, it was necessary to apply a correction for the amount of carbon black colloiddally suspended in the solution, and weighed with the non-sorbed rubber. Details of the procedure for the determination of black in rubber are contained in another publication.⁶

Experimental Results

Comparison of the Sorption Capacities of the Carbon Blacks.—The sorption of GR-S from chloroform and *n*-heptane solution by the various carbon blacks was determined, following the general procedure given above. The

TABLE I
SOME PROPERTIES OF THE CARBON BLACKS EMPLOYED

Carbon black	Type	Nitrogen surface area (sq. m./gram)	Electron microscope area (sq. m./gram)	Producer
Vulcan 1	Reinforcing furnace	109	98	Godfrey L. Cabot Inc.
Graphon	"	85		Godfrey L. Cabot Inc.
Sterling 105	Fine furnace	99	75	Godfrey L. Cabot Inc.
Philblack A	High modulus furnace	39	52	Phillips Petr. Co.
Philblack O	High abrasion furnace	82	84	Phillips Petr. Co.

* Graphon is prepared by induction heating of Spheron 6, a medium processing channel black, to 3200° over a period of two hours. The nitrogen area of Spheron 6 is given as 106 sq. m./gram, the electron microscope area as 120 sq. m./gram.⁵

(1) This work was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Synthetic Rubber Program of the United States Government.

(2) J. T. Baker Chemical Company, Phillipsburg, New Jersey.

(3) I. M. Kolthoff, R. G. Gutmacher and A. Kahn, THIS JOURNAL, **55**, 1240 (1951).

(4) I. M. Kolthoff and A. Kahn, *ibid.*, **54**, 251 (1950).

(5) W. D. Schaeffer, private communication.

sorption isotherms are plotted in Figs. 1 and 2. In both solvents, the arrangement of the carbon blacks in order of decreasing sorption is the same: Spheron 6 (Graphon), Vulcan 1, Philblack 0, Sterling 105, Philblack A. The low solvent power for rubber of *n*-heptane, which was previously

(6) I. M. Kolthoff and R. G. Gutmacher, *Anal. Chem.*, **21**, 1002 (1950).

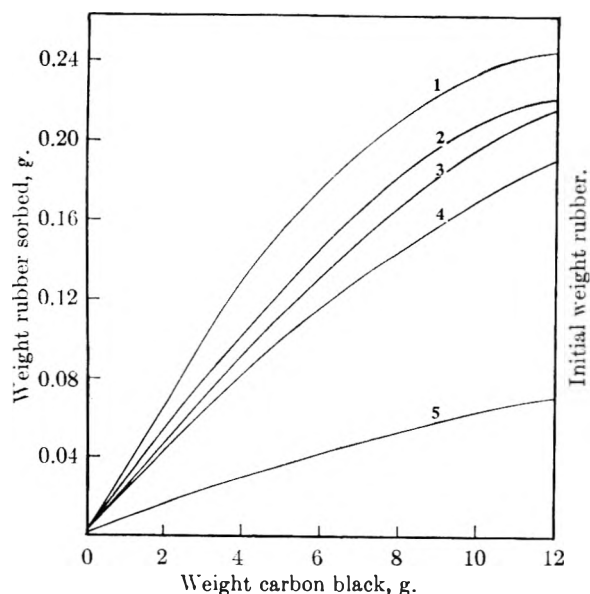


Fig. 1.—Sorption of GR-S from chloroform solution by various carbon blacks: (1) Spheron 6; (2) Vulcan 1; (3) Phlblack 0; (4) Sterling 105; (5) Phlblack A.

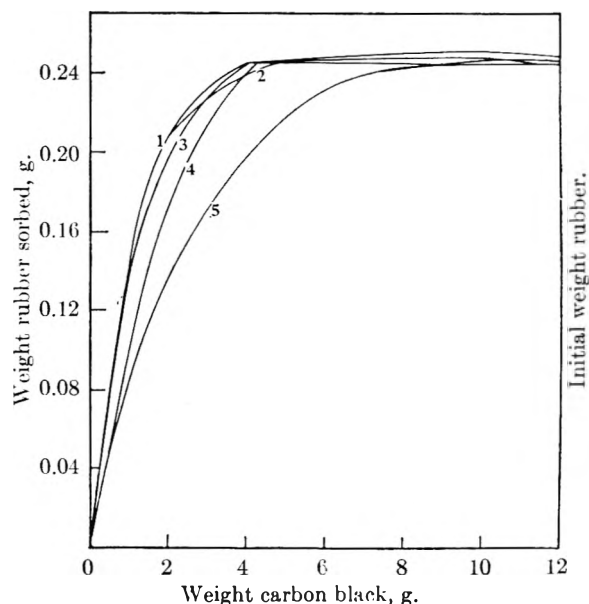


Fig. 2.—Sorption of GR-S from *n*-heptane solution by various carbon blacks: (1) Spheron 6; (2) Vulcan 1; (3) Phlblack 0; (4) Sterling 105; (5) Phlblack A.

noted in sorption studies with Graphon, decreases the relative differences in sorption characteristics of the carbon blacks. The sorption is found not to be directly related to surface area.

Sorption of Rubber from Various Solvents.—A sample of GR-S of 57.5% conversion was used to prepare 0.25% solutions in benzene, chloroform, *n*-hexane, chloroform-*n*-hexane (1:1 by volume), and benzene and chloroform with varying amounts of ethanol added. The sorption on varying amounts of Vulcan 1 was determined by the usual procedure. The results are plotted in Fig. 3. In Fig. 4 the weight of rubber sorbed per gram of Vulcan 1 is plotted against the final equilibrium concentration in solution. The curves represent sorption isotherms at room temperature.

The greatest amount of sorption is obtained from *n*-heptane solution, and thereafter, in decreasing order, from chloroform-*n*-heptane (1:1), chloroform-ethanol (8:2), benzene-ethanol (9:1), chloroform-ethanol (9:1), benzene and chloroform.

The addition of ethanol to benzene or chloroform, which

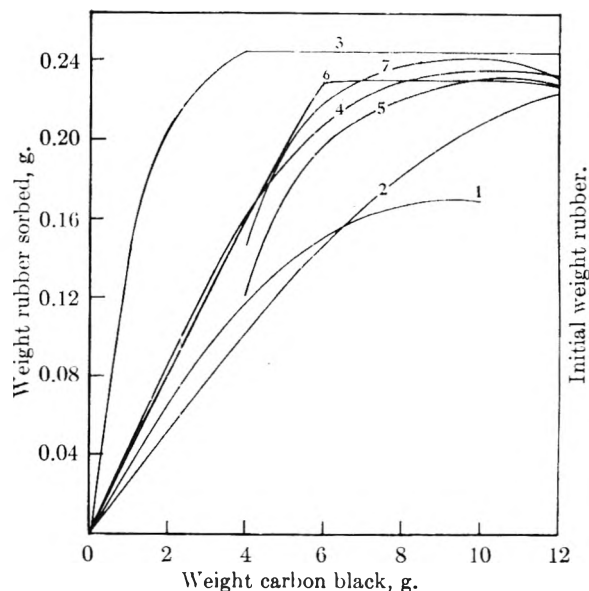


Fig. 3.—Sorption of GR-S from solution in various solvents by Vulcan 1: (1) benzene; (2) chloroform; (3) *n*-heptane; (4) chloroform-*n*-heptane (1:1); (5) chloroform-ethanol (9:1); (6) chloroform-ethanol (8:2); (7) benzene-ethanol (9:1).

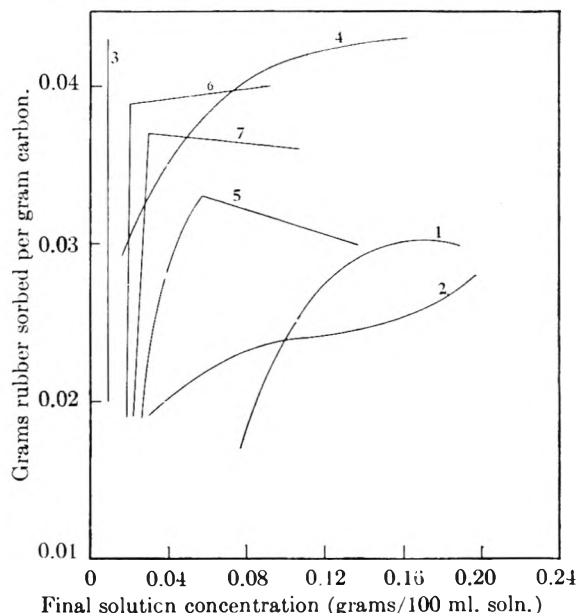


Fig. 4.—Variation of weight of rubber sorbed per gram carbon black with final concentration for different solvents: (1) benzene; (2) chloroform; (3) *n*-heptane; (4) chloroform-*n*-heptane (1:1); (5) chloroform-ethanol (9:1); (6) chloroform-ethanol (8:2); (7) benzene-ethanol (9:1).

decreases the solvent power toward rubber, gives an expected increase of the sorption.

Sorption of Low Temperature Rubbers.—The sorption of two samples of "cold rubber," polymerized at -10° and $+5^{\circ}$, respectively, from 0.25% solution in chloroform and 90% benzene-10% ethanol (by volume) by Vulcan 1 was studied. The two rubber samples were polymerized by the Phillips Petroleum Company "Custom recipe," and were stated to be gel-free. The sorption data, obtained after 40 hours of shaking various amounts of Vulcan 1 with 100-ml. portions of the rubber solutions are plotted in Fig. 5.

The sorption curves exhibit no striking differences. Twelve grams of Vulcan 1 sorb 84% of the -10° rubber, 75% of the $+5^{\circ}$ rubber, and about 86% of 50% GR-S from chloroform solution. The somewhat lower sorption of the

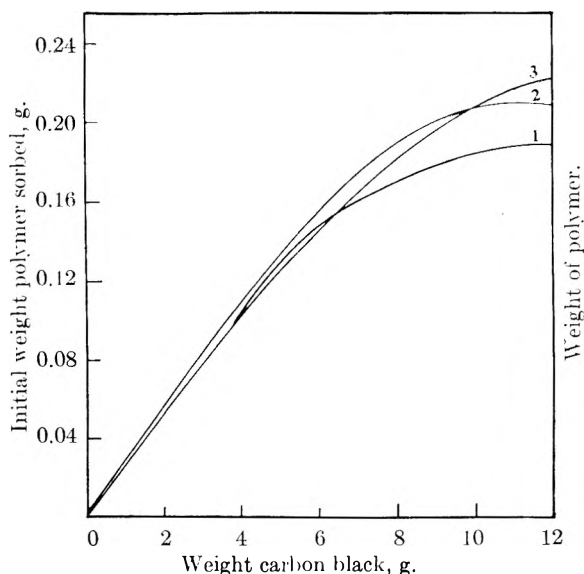


Fig. 5.—Sorption of low-temperature rubbers from chloroform solution by Vulcan 1: (1) R157 (polymerized at +5°); (2) R169 (polymerized at -10°); (3) GR-S (polymerized at 50°).

+5° rubber may be due to the fact that it contains about 9% of rosin acid, rosin soap and anti-oxidant.⁷

Effect of Previous Heat Treatment of the Carbon Black.—The manner of activation of carbon black determines the charge upon its surface and the gases which remain adsorbed. Air-heating at 950° gives a positively charged surface upon which oxygen is adsorbed; air-heating at 450° leaves the surface negatively charged.⁸ If the carbon black is heated in an atmosphere of nitrogen at 500°, physically adsorbed oxygen is removed; heating at 1100° should remove combined oxygen also.

To determine the effect of heating carbon black on its sorption of rubber from solution, samples of Philblack A, Vulcan 1 and Sterling 105 were heated at 500° and 1100° for eight hours in an atmosphere of nitrogen. After heating, they were allowed to cool under nitrogen and bottled.

Various amounts of the heated carbon blacks were shaken with 100 ml. of a 0.25% solution of GR-S (66% conversion) in benzene for 40 hours. The residual rubber in solution was determined.

By comparison with the sorption by the unheated carbon black of the same rubber solution, heating in nitrogen gave a 20% increase in sorption by Philblack A and Vulcan 1. A slight increase was also observed with Sterling 105. There was no significant difference between the sorption obtained on carbon black heated at 500 and 1100° in nitrogen (Fig. 6).

A sample of Vulcan 1 was heated in air in a loosely-covered nickel crucible for periods of one, three and five hours at 425–450°. The weight loss was, respectively, 1.9, 5.3 and 7.1%. The sorption of GR-S from benzene solution and from *n*-heptane solution was determined as before. It was found that the period of heating made almost no difference, and that the sorption by air-heated black from benzene solution was practically identical with that shown by unheated black. Air-heated carbon shows an increase in sorption from *n*-heptane solution; six grams of the heated carbon black give complete sorption of the GR-S, but with even 12 g. of the unheated Vulcan 1 about 3% of the rubber remains in solution. Of course, the over-all sorption from *n*-heptane is much greater than from benzene solution.

Sorption of Polymers of Various Degrees of Unsaturation and of Polystyrene.—Polymers of varying butadiene-styrene ratios ranging from 75% butadiene–25% styrene to pure polystyrene were prepared by the mutual recipe at 50°. The conversion in each case was approximately 60%. The sorption from 0.25% solution in chloroform was determined with Vulcan 1 and Sterling 105. The data, as given in Table II, show that in the range 75% butadiene–25% sty-

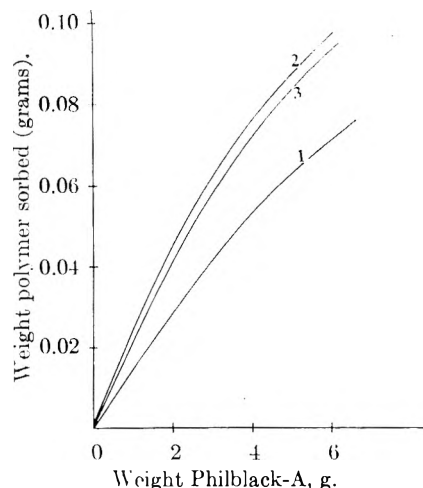


Fig. 6.—Sorption of GR-S on Philblack A heated in nitrogen: (1) unheated; (2) heated at 500°; (3) heated at 1100°.

rene to 5% butadiene–95% styrene there is little change in the amount of polymer sorbed by a given weight of carbon black; the same was found with Graphon.

TABLE II
SORPTION OF POLYMERS OF VARYING BUTADIENE-STYRENE RATIOS BY VULCAN 1

Wt. carbon black, g.	75 pt. Bu.–25 pt. Sty.		50 pt. Bu.–50 pt. Sty.	
	Residual rubber, g./100 ml. soln.	Rubber sorbed, g.	Residual rubber, g./100 ml. soln.	Rubber sorbed, g.
0	0.252	...	0.244	...
2	.198	0.054	.194	0.050
4	.148	.104	.149	.095
6	.108	.144	.110	.134
8	.075	.177	.078	.166
10	.052	.200	.058	.186
12	.036	.216		
	25 pt. Bu.–75 pt. Sty.		5 pt. Bu.–95 pt. Sty.	
0	0.252	...	0.263	...
2	.194	0.058	.214	0.049
4	.143	.109	.151	.112
6	.104	.148	.103	.160
8	.072	.180	.068	.195
10	.050	.202	.045	.218
12	.048	.204	.038	.225

Pure polystyrene behaves in a different and striking manner. With Graphon, a marked decrease in sorption of polystyrene was noted in comparison to the sorption of the copolymers with butadiene. Clear supernatant liquids could be obtained by centrifuging. When polystyrene was shaken with commercial carbon blacks such as Vulcan, very dark supernatant liquids resulted and reliable sorption data could be obtained. However, it was found that when 10 or 12 g. of Vulcan 1 and polystyrene of high inherent viscosity ($\eta = 12.2$) in chloroform solution were shaken, a clear supernatant liquid resulted and the carbon was in large, spherical, rubbery balls at the bottom of the bottle. About 6% of the polymer originally present remained in solution. Reagent grade chloroform, which contained about 0.7% ethyl alcohol, was used as the solvent. Removal of the alcohol or the addition of more alcohol to bring the total concentration up to 2.7% were found to make no difference. A more dilute solution of polystyrene in chloroform (0.065 g./100 ml. instead of the usual 0.25 g./100 ml. of solution) also gave no "bunching" effect with weights of Vulcan 1 less than 12 g. It did not matter whether the carbon was added all at once or in portions at long intervals, as long as the final quantity was 12 g. of black in 100 ml. of polymer solution.

(7) C. F. Fryling, private communication.

(8) F. O. K. Verstraete, *Natuurw. Tijdschr.*, **18**, 107 (1936).

A time study of the sorption of polystyrene ($\eta = 12.2$) from 100 ml. of 0.25% solution in chloroform on 12 g. of Vulcan 1 was made. The "bunching" effect was observed after 0.75 hour of shaking, but the liquid remained dark until after ten hours of shaking, after which time the supernatant liquid became perfectly clear. The time required for attainment of sorption equilibrium is fairly long in comparison with usual experience.

Experiments with high viscosity polystyrene ($\eta = 9.8$ and 3.8, respectively) and other carbon blacks showed that 10 or 12 g. of Philblack A, 18–20 g. of Philblack O or Sterling 105 are required to produce bunching. With low viscosity polystyrene ($\eta = 1.3$, and 0.26 (made with mercaptan)) and Vulcan or other blacks, no "bunching" is found; the supernatant liquids are dark but transparent, and sorption data can be obtained. Philblack A, which sorbs the smallest amounts of GR-S of any of the four furnace blacks, also sorbs the smallest amount of low viscosity polystyrene. Up to 30 g. of Spheron 6, the only channel black tested, gave no bunching under any conditions.

Sorption of Rubber Containing Microgel.—In previous experiments, GR-S samples of about 60% conversion were employed to avoid the complications caused by microgel, which is often present in polymer of 70% conversion or higher. In studies with Graphon and benzene solutions of GR-S, it was found that microgel was not sorbed on Graphon, but that the sol fraction could be completely sorbed. The nature and behavior of microgel has been discussed in detail by Baker.⁹

The sorption of two samples of GR-S of 74.7 and 81.5% conversion in *n*-heptane solution on Vulcan 1 was investigated. The sorption isotherms of the whole rubbers were obtained in the usual manner. The gel content was determined by the method of Medalia and Kolthoff.¹⁰ A portion of the rubber which had been milled and heated as required for gel determination was dissolved in *n*-heptane. The mixtures were filtered through glass wool and the usual sorption experiments were performed with the filtrates. Both with the whole rubber and the sol fraction, the supernatant liquids were clear after centrifuging.

From the results of Table III it appears that microgel is sorbed as well as the sol fraction on Vulcan 1 from *n*-heptane solution. The small amount of non-sorbed material may be the anti-oxidant, some fatty acid, or some very low molecular weight rubber.

TABLE III
SORPTION OF MICROGEL-CONTAINING GR-S ON VULCAN 1
FROM *n*-HEPTANE

Vulcan, g.	FROM <i>n</i> -HEPTANE	
	Residual rubber, g./100 ml. soln. Conversion 81.5%.	Rubber sorbed, % Gel content 52%
Whole rubber		
0	0.175	..
2	.046	73
4	.028	84
6	.014	92
10	.006	96
12	.008	95
Sol fraction		
0	0.216	..
2	.041	81
4	.010	95
6	.005	97
10	.006	97
12	.004	98

Effect of Molecular Weight on Sorption.—A sample of X-418 rubber obtained from the Government Pilot Plant, Akron, was fractionated by the method of Carr, Kolthoff and Carr.¹¹ Six fractions were obtained and their sorption from *n*-heptane solution was determined. The data are

shown graphically in Fig. 7. The intrinsic viscosities given¹² represent those of the polymer in benzene as the solvent; *n*-heptane gave values of 0.5 for all fractions.

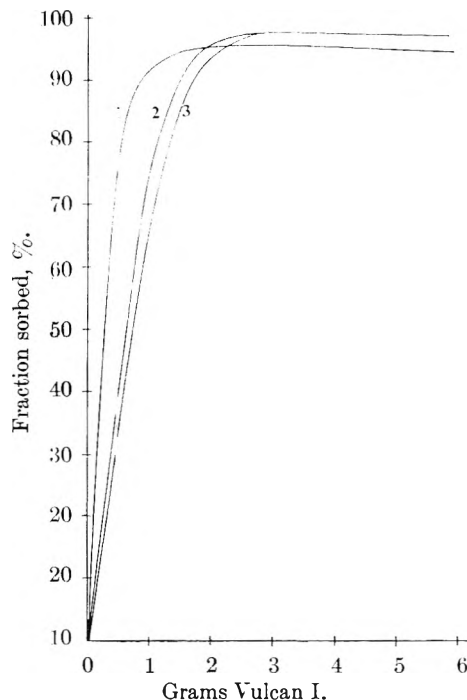


Fig. 7.—Sorption of fractions in *n*-heptane by Vulcan 1. (1) Fraction 1, $[\eta] = 3.69$, mol. wt. 596,000; (2) Fraction 2, $[\eta] = 2.98$, mol. wt. 433,000; (3) Fractions 3, 4, 5 and 6; Fraction 3, $[\eta] = 1.94$, mol. wt. 229,000; Fraction 4, $[\eta] = 1.52$, mol. wt. 159,000; Fraction 5, $[\eta] = 1.21$, mol. wt. 113,000; Fraction 6, $[\eta] = 1.00$, mol. wt. 85,000.

Although there is some spread in the curve for the different fractions, on the whole the sorption does not vary appreciably from the fraction having a molecular weight of 433,000 ($[\eta] = 2.98$) to that of a molecular weight of 85,000 ($[\eta] = 1.00$). The sorption was appreciably greater with the molecular weight fraction of 596,000 ($[\eta] = 3.69$).

Effect of Time of Shaking.—The change in the amount of non-sorbed rubber and the intrinsic viscosity of the solution with time of shaking has been considered previously. Using Graphon and benzene solutions of GR-S, it was found that there was little change in the amount of rubber sorbed after one hour. The intrinsic viscosity of the supernatant liquid increased initially and then decreased, up to 48 hours of shaking. For the sake of completeness, data are given on a time study of the sorption of GR-S in *n*-heptane by 1.5 g. of Vulcan 1 (Table IV). There is very little change in the amount of rubber sorbed after two hours of shaking, but the intrinsic viscosity of the residual rubber (determined in benzene solution) decreased continuously with time. This indicates that the low molecular weight rubber is sorbed more rapidly than the higher molecular weight polymer, but that the latter replaces the former slowly from the carbon black.

In order to test the conclusion that low molecular weight fractions of rubber are sorbed first and are gradually replaced by the higher molecular weight fractions, experiments of the following nature were made.

One hundred ml. of the high (or low) molecular weight fraction was shaken with one gram of Vulcan 1 for 40 hours at 30°. The supernatant liquid was siphoned off, and 100

(9) W. O. Baker, *Ind. Eng. Chem.*, **41**, 511 (1949).

(10) A. I. Medalia and I. M. Kolthoff, *J. Polymer Sci.*, **6**, 433 (1951).

(11) C. W. Carr, I. M. Kolthoff and Betty Carr, Report to Office of Rubber Reserve.

(12) Actually, the inherent viscosity $= \ln \eta_r / c$ was determined, where η_r is the relative viscosity and c is concentration in g./100 ml. However, at the concentrations used this is a close approximation to the intrinsic viscosity. The average molecular weights were calculated from the relation $\log M = 4.93 + 1.49 \log [\eta]$, where M is the molecular weight and $[\eta]$ the intrinsic viscosity.^{13,14}

(13) D. M. French and R. H. Ewart, *Ind. Eng. Chem., Anal. Ed.*, **19**, 165 (1947).

(14) R. L. Scott, W. C. Carter and M. Magat, *J. Am. Chem. Soc.*, **71**, 220 (1949).

TABLE IV

EFFECT OF TIME OF SHAKING ON SORPTION OF GR-S (57.5% CONVERSION) IN *n*-HEPTANE ON VULCAN 1

Time, hours	Residual rubber, g./100 ml. soln.	Rubber sorbed, g.	Intrinsic viscosity ^a
0	0.238	...	1.21
0.25	.119	0.119	1.15
1.0	.096	.142	1.16
2.0	.089	.149	0.98
4.0	.077	.161	.86
24.0	.068	.170	.64
40.0	.072	.166	.57

^a Intrinsic viscosities determined in benzene.

ml. of the low (or high) molecular weight fraction was added to the black and shaken another 40 hours. The amount of residual rubber and the intrinsic viscosity of the solutions were determined. The solvent used for the fractions was *n*-heptane; all viscosities were measured in benzene. Some typical results are given in Table V.

TABLE V

EXPERIMENTS WITH FRACTIONS OF HIGH AND LOW MOLECULAR WEIGHT

	ln η_r/c
I. Fraction A shaken with 1 g. Vulcan 1 for 40 hours	
Fraction A, initial concn. 0.192 g./100 ml.	2.98
Rubber sorbed 0.138 g.	2.24
Remove fraction A, add fraction B, shake 40 hr.	
Fraction B, initial concn. 0.235 g./100 ml.	1.00
Rubber sorbed 0.042 g.	1.14
Total amount of rubber sorbed 0.180 g.	
II. Fraction B shaken with 1 g. Vulcan 1 for 40 hours	
Fraction B, initial concn. 0.235 g./100 ml.	1.00
Rubber sorbed 0.134 g.	0.94
Remove fraction B, add fraction A, shake 40 hours	
Fraction A, initial concn. 0.192 g./100 ml.	2.98
Rubber sorbed 0.022 g.	1.60
Total amount of rubber sorbed 0.156 g.	

It appears that when a high molecular weight fraction is sorbed on the carbon and a low molecular weight fraction added, there is very little change in the intrinsic viscosity of the latter. If a low molecular fraction is sorbed on the carbon and a high molecular weight fraction added, there is a considerable decrease in the viscosity of the unadsorbed rubber, resulting chiefly from the displacement of some of the sorbed low molecular weight fraction by the more strongly sorbed high molecular weight fraction. The fact that the final values of the intrinsic viscosity reached in each member of a pair of experiments were quite different would seem to indicate incomplete reversibility of sorption. It may also be noted that somewhat greater sorption of rubber occurred in the experiments in which the high molecular weight fraction was present initially, than in those in which the low molecular weight fraction was present at the start.

Fractionation of Rubber by Sorption on a Carbon Column.

—On the basis of the foregoing and the information provided by time studies of sorption, it was thought possible to fractionate a rubber sample in solution by allowing a solution to flow through a column of carbon black and collecting and analyzing the eluate. This method of adsorption analysis was developed by Claesson¹⁵ and is known as "frontal

analysis." For a single solute in solution, the first fractions of the eluant contain chiefly pure solvent, after which the concentration of solute increases sharply until the original value is reached.

Twenty grams of Philblack A was placed in a glass column and retained there by a 2-cm. layer of glass wool in the bottom of the column. A carbon column, 15 cm. high and a diameter of 2 cm., was formed. Five-hundred ml. of a 0.25% solution of GR-S (66% conversion) in chloroform was allowed to flow through the column at a rate of ca. 3 ml./minute. No external pressure was applied. Fifty-ml. portions of the eluant were collected; the concentration of the rubber and the approximate intrinsic viscosity were determined. The results are given in Table VI. Experiments with benzene and chloroform solutions using Vulcan 1 as the adsorbent were unsuccessful, since both the rubber and solvent were so strongly sorbed that the flow rate, even under pressure, was very small. For that reason, Philblack A, which sorbs relatively little rubber, was selected.

The results show that partial fractionation was obtained; after the fifth fraction the solution passed through the column substantially unchanged (*i.e.*, 250 ml. of a 0.25% solution was the saturation volume for this column). From the viscosity figures it appears that the higher molecular weight rubber was more strongly sorbed. The low concentration in fraction 10 indicates that the sorbed rubber is tightly held on the black. Due to the low concentration, no great accuracy can be ascribed to the viscosity value for this fraction.

TABLE VI

FRACTIONATION OF A 0.25% SOLUTION OF GR-S BY A COLUMN OF PHILBLACK A

Fraction	Concn. of rubber g./100 ml. soln.	ln η_r/c
Original solution	0.247	1.34
1	.140	0.96
2	.200	0.96
3	.223	1.17
4	.230	1.13
5	.236	1.24
6	.236	1.30
7	.239	1.27
8	.240	1.27
9	.238	1.31

At this point the liquid on top was allowed to reach the level of the adsorbent, and then pure chloroform was added.

10	0.017	1.42
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A second experiment similar to the above was made in order to ascertain whether the sorbed rubber could be desorbed from the column by a "good" solvent such as xylene. To obtain practically complete sorption of the rubber, Sterling 105 was selected instead of the weakly-sorbing Philblack A. After eight portions of eluant had been collected, xylene was added to the column. It was found that of 0.469 g. of rubber sorbed, 0.296 g. or 63% was desorbed from the column by 100 ml. of xylene.

Bound Rubber Formation.—The correlation between the properties of carbon blacks and their behavior in compounded rubber stocks has been widely studied. Mixing of carbon black with rubber by cold milling under conditions which do not lead to the formation of polymer gel, insolubilizes a portion of the rubber, known as "bound rubber."¹⁶ An investigation of the conditions necessary to produce "bound rubber" was made and some results are reported below.

Table VII gives the amount of insoluble polymer present in samples of standard GR-S X-418 which had been cold-milled with equal parts of carbon black at the Government Pilot Plant in Akron. It is seen that heating of the milled polymer up to 4 hours in air at 110° or in vacuum at 80° up to 48 hours produces practically no increase in the amount of insoluble rubber. However, it was found that heating for more than 8 hours in air at 120° produces appreciable insol-

(15) S. Claesson, *Ann. N. Y. Acad. Sci.*, **49**, 183 (1948).(16) C. W. Sweitzer, W. C. Goodrich and K. A. Burgess, *Rubber Age (N. Y.)*, **66**, Sept. 1949.

bilization (gel-formation, "bound rubber," or oxygen vulcanization, or a combination of these). The data in Table VII were obtained by placing 0.5-g. samples in 100-mesh wire cages, which were suspended in 100 ml. of chloroform for 48 hours. The cages and contents were weighed before and after immersion. The per cent. of "bound rubber" was calculated on the basis of rubber hydrocarbon.

TABLE VII

BOUND RUBBER IN COLD-MILLED RUBBER-CARBON MIXES

Sample	% rubber bound by 100 parts	
	Vulcan I	Sterling 105
GR-S X-418 cold milled with 100 parts carbon black	49.0	34.2
GR-S X-418 cold milled, heated 4 hr. at 110°	48.2	34.5
GR-S X-418 cold milled, heated 48 hr. in vacuum at 80°	51.7	38.0

In another experiment a 6-g. sample of X-418 was swollen in chloroform and an equal weight of carbon black added

and mixed intimately with the rubber. The chloroform was removed under vacuum, and portions of the mixture were placed in the solvent before and after further drying *in vacuo* or after milling and drying. Solubilities were determined, using wire cages as before. Some results, given in Table VIII, were poorly reproducible, probably due to incomplete mixing of the black with the rubber on evaporation of the solvent. However, they serve to indicate that milling is not necessary to obtain "bound rubber."

TABLE VIII

EFFECT OF HEATING AND MILLING ON RUBBER BOUND BY VULCAN I

Carbon added per 100 parts rubber	Method of drying	% Insoluble (on rubber hydrocarbon)	
		Not milled	Milled 10 passes
100 parts Vulcan I	Aspirator dried only	18.9	..
	80°, vacuum, 24 hours	19.7	33.4
	room temp., vacuum, 24 hours	20.4	21.5

THE TEMPERATURE COEFFICIENT OF HETEROGENEOUS REACTIONS

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The extension of the Nernst diffusion theory to the general case of a solid-fluid system wherein the observed rate is a function both of the rate of chemical reaction at the surface and of the rate of a transport process is utilized for a simple, general treatment of the temperature coefficient of heterogeneous reactions.

Nernst postulated that the rate of chemical reaction occurring at the interface between two phases is always very much faster than the rate of one of the two transport processes (transport of reactant to the surface, and of products from the surface) such that the observed rate is always "diffusion-controlled."¹ As has been pointed out,^{2,3} many workers supported this theory whilst others have denied that the rate of a transport process plays any part in determining the observed rate; other forms of control, particularly adsorptive control (see, for example, ref. 4), have been suggested.

It is now generally accepted that for certain systems the observed rate is determined solely by the rate of a transport process, whereas for other systems the observed rate is subject to chemical (i.e., to the so-called "activation") control. Early workers, particularly Van Name and Hill,⁵ recognized the possibility of systems of intermediate type for which the observed rate is a function both of the rate of chemical reaction at the surface and of the rate of a transport process.

Under certain circumstances, the temperature coefficient is one of the most useful of the criteria for distinguishing reaction type (see references 3, 6,

7, and 8 for discussions of the available criteria). In the present communication it is shown that by making reasonable assumptions a general treatment of the dependence of the observed (i.e., over-all) velocity constant on temperature is possible, from which the respective contributions of the chemical reaction and of the transport process to the over-all process may sometimes be evaluated. The discussion will be limited to solid-fluid systems in which reaction takes place between the massive solid and a solute species. It is assumed that the chemical reaction at the interface is first-order with respect to the concentration of solute, and that the reaction products are soluble.

Extension of the Nernst Theory to the General Case

Many workers have proposed theoretical treatments for reactions of intermediate type, i.e., reactions in which the concentration of solute at the interface is neither the same as the concentration in the bulk of the solution nor equal to the equilibrium concentration (for references, see ref. 6). These treatments are essentially the same and depend upon the reasonable assumption that a steady state is rapidly established such that the velocity of the chemical process at the interface is equal to the velocity of the transport process supplying reactant to, or removing products from,

(1) W. Nernst, *Z. physik. Chem.*, **47**, 52 (1904).

(2) E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," 2nd. ed., Clarendon Press, Oxford, 1947.

(3) J. F. Zimmerman, *This Journal*, **53**, 562 (1949).

(4) M. Centnerszwer and W. Heller, *J. chim. phys.*, **34**, 217 (1937).

(5) R. G. Van Name and D. U. Hill, *Am. J. Sci.*, **43**, 301 (1916).

(6) L. L. Bircumshaw and A. C. Riddiford, *Quart. Rev.*, (in press).

(7) C. V. King, *Trans. N. Y. Acad. Sci.*, **10**, 262 (1948).

(8) T. R. E. Kressman and J. A. Kitchener, *Discussions Faraday Soc.*, No. 7, 90 (1949).

the interface. For the chemical reaction at the interface

$$-dc_i/dt = k_C(A/V)c_i \quad (1)$$

where c_i is the concentration of reactant at the interface, A is the surface area, V the volume of solution, and k_C is the chemical rate constant per unit area at unit volume. For the transport process

$$-dc/dt = k_T(A/V)(c - c_i) \quad (2)$$

where c is the concentration of reactant in the bulk of the solution and k_T is the rate constant of the transport process per unit area at unit volume. From the Nernst theory

$$k_T = D/\delta \quad (3)$$

where D is the coefficient of diffusion of the solute and δ is the thickness of the Nernst diffusion layer. Elimination of c_i between equations 1 and 2 yields the expression

$$-\frac{dc}{dt} = \frac{A}{V} \left(\frac{k_T k_C}{k_T + k_C} \right) c \quad (4)$$

i.e.

$$k = k_T k_C / (k_T + k_C) \quad (5)$$

where k is the observed velocity constant per unit area at unit volume. Under circumstances where $k_T \gg k_C$ (i.e., $k_T > 10^2 k_C$) the observed rate is solely determined by the rate of the chemical process; the corresponding condition $k_T \ll k_C$ (i.e., $10^2 k_T < k_C$) represents the other limiting case, that of transport control. A change in the experimental conditions may result in a shift of control toward one of the limiting cases, but before dealing with the effect of temperature in this connection it is desirable to consider two points regarding the simple treatment given above.

Firstly, it is assumed that the areas appearing in equations 1 and 2 are the same. In general this will be but an approximation: the over-all chemical rate constant ($k_C A$) is a function of the true surface area, whereas the over-all transport constant is a function of the apparent (i.e., geometric) surface area.⁹ For most systems the apparent surface area will change so slowly that it may be regarded as constant over reasonably short time intervals, whereas the true surface area, for reactions in which the solid phase undergoes dissolution, may increase due to progressive roughening of the surface.

Secondly, equation 4 is naturally subject to all the defects inherent in the original Nernst theory. Roller¹⁰ and King¹¹ have considered this question in some detail. In particular, the assumption that the solute concentration within the diffusion layer varies linearly with the distance from the surface is but an approximation. Nevertheless this idealized layer serves to correlate the experimental data in a simple fashion, and can be related to the physical properties of the fluid under certain circumstances.¹²

The Temperature Coefficient of Heterogeneous Reactions

If one assumes that both k_C and k_T vary exponentially with temperature, i.e.

$$k_C = Z_C e^{-E_C/RT} \quad (6)$$

$$k_T = Z_T e^{-E_T/RT} \quad (7)$$

(where the pre-exponential factors and the energies of activation are assumed to be independent of temperature over a wide range), a simple treatment is possible. From equations 5, 6 and 7

$$\frac{d(\ln k)}{dT} = \frac{1}{RT^2} \left[\left(\frac{k_C}{k_T + k_C} \right) E_T + \left(\frac{k_T}{k_T + k_C} \right) E_C \right] \quad (8)$$

Define an experimental energy of activation, E , by the relation

$$d(\ln k)/dT = E/RT^2$$

so that E may be determined at any value of T from the tangent to the curve of $\ln k$ on $1/T$; then from equation 8

$$E = \left(\frac{k_C/k_T}{1 + k_C/k_T} \right) E_T + \left(\frac{1}{1 + k_C/k_T} \right) E_C \quad (9)$$

For the special case when E_C and E_T have the same value, $E = E_C = E_T$; for this case, k varies exponentially with T . In general, however, E_C and E_T will differ, and the variation of E with T is governed by the variation of the ratio k_C/k_T . Since for all practical cases $Z_C \gg Z_T$ (see below), there are two cases to be considered: (i) $E_C > E_T$, (ii) $E_C < E_T$. Case (ii) corresponds to the condition $k_C \gg k_T$ at all temperatures, and hence $E = E_T$ at all temperatures. Case (i) is treated as follows

$$\lim_{T \rightarrow 0} k_C/k_T = 0; \text{ therefore } \lim_{T \rightarrow 0} E = E_C$$

$$\lim_{T \rightarrow \infty} k_C/k_T = Z_C/Z_T \gg 1; \text{ therefore } \lim_{T \rightarrow \infty} E = E_T$$

For this case, then, a change of slope may occur in the Arrhenius plot indicating chemical control at low temperatures, with a transition to transport control at high temperatures. Depending on the magnitudes of E_C and E_T , and upon the temperature range which can be investigated in practice (i.e., on the limitations imposed by studying the reaction in solution, etc.), so a part or the whole of the predicted Arrhenius plot will be found.

The case when $E_C = E_T$ is of importance for two reasons. Firstly, there is the possibility that it may be confused with case (ii); for these cases, the rate-determining step may not be diagnosed solely from a study of the temperature coefficient. Secondly, when E_C and E_T have almost the same value it may be difficult to distinguish between case (i) and the present case.

These conclusions are dependent upon the validity of the original assumptions, which must now be considered. Equation 6 is evidently subject to all the limitations of the corresponding expression for homogeneous reactions,² nevertheless it will represent satisfactorily the greater part of the experimental results. The use of equation 7 may be justified on experimental grounds, since it is found to apply to systems in which, by the application of other criteria, the observed rate is known to be solely determined by the rate of a transport process. The question, however, merits rather more attention. It is accepted¹³ that the variation of D with temperature for liquid systems may be expressed

$$D = Z_D e^{-E_D/RT} \quad (10)$$

$$(13) \text{ H. S. Taylor, } J. \text{ Chem. Phys., } \mathbf{6}, 331 \text{ (1938)}$$

(9) L. Bruner and St. Tolloczko, *Z. physik. Chem.*, **35**, 283 (1900).

(10) P. S. Roller, *This Journal*, **39**, 221 (1935).

(11) C. V. King, *J. Am. Chem. Soc.*, **57**, 828 (1935).

(12) V. Levich, *Acta Physicochim. U.R.S.S.*, **17**, 257 (1942).

Hence, equation 7 requires that δ must also vary exponentially with temperature or be temperature-invariant; in the past, the latter has sometimes been assumed to be the case. That in fact δ does vary exponentially with temperature is evident from the following considerations.

For systems in which the solid surface may be regarded as the only surface of discontinuity, Levich¹² has shown that δ is a function of the coefficient of diffusion of the solute D , the kinematic viscosity of the fluid ν , and of the characteristic fluid velocity U . For laminar flow the dependence for solid-liquid systems may be expressed

$$\delta = BU^{-1/2}D^{1/3}\nu^{1/6} \quad (11)$$

where B is a number which depends only upon the geometry of the system.¹⁴ For the particular case of a plane disc electrode rotating about an axis perpendicular to the plane the value of B may be calculated, giving the expression

$$\delta = 1.613\omega^{-1/2}D^{1/3}\nu^{1/6} \quad (12)$$

where ω is the angular velocity in radians per second, and D and ν are expressed in c.g.s. units. The turbulent region is characterized by a more marked dependence of δ on ν and U ; the powers on these quantities rise to limiting values of $2/3$ and -1 , respectively, as the degree of turbulence increases, so that the final dependence may be expressed

$$\delta = B'U^{-1}D^{1/3}\nu^{2/3} \quad (13)$$

For equations 11 and 13, for constant fluid velocity

$$d(\ln \delta)/dT = (2E_D - E_\nu)/6RT^2 \quad (\text{for laminar flow}) \quad (14a)$$

$$= (E_D - 2E_\nu)/3RT^2$$

$$(\text{for strongly turbulent flow}) \quad (14b)$$

where E_ν is the critical increment for kinematic viscous flow. Since E_D and E_ν are of the same order of magnitude,¹⁵ it is of interest to note that, whereas for laminar flow δ increases with increasing temperature, its temperature coefficient is negative under conditions of strongly turbulent flow. In either case, since E_D is of the order of 4 kcal./mole for aqueous systems, the variation of δ with T will be small in comparison to the variation of the other quantities. From equations 3, 10 and 14

$$E_T = (4E_D + E_\nu)/6 \quad (\text{for laminar flow}) \quad (15a)$$

$$= 2(E_D + E_\nu)/3 \quad (\text{for strongly turbulent flow}) \quad (15b)$$

so that whereas under non-turbulent conditions E_T will be somewhat less than E_D ,¹⁶ E_T may be larger than E_D for strongly turbulent flow.^{17,18}

Lastly, it was assumed that Z_C is always very much greater than Z_T . Again this appears to be justified by experimental data and, moreover, can

quite simply be shown to be the case for systems to which equation 12 applies.¹⁹ For such systems

$$Z_T = 0.62 \omega^{1/2} Z_D^{2/3} Z_\nu^{-1/6} \quad (16)$$

where Z_ν is the pre-exponential factor in the equation for kinematic viscous flow corresponding to equations 6 and 7. For aqueous systems,^{16,20} $Z_D \approx 0.2$, $Z_\nu \approx 2 \times 10^{-5}$, whence $Z_T \approx 1.3\omega^{1/2}$, i.e., of the order of 10^2 , or less. Since Z_C will be of the order of magnitude of the collision frequency per unit area for molecules colliding with a surface, the assumption is justified.

As an example of case (i) where the transition from chemical to transport control occurs, one may consider the rate of combustion of carbon spheres in a flowing gas stream, studied by Tu, Davis and Hottel.²¹ Their results²² for a sphere 25.4 mm. in diameter burning in air flowing at 3.51 cm./sec. are plotted in Fig. 1. The composite nature of the reaction is very marked. The section AB corresponds to the region of transport control (observed constant = $0.27 \times e^{-0.040/RT}$), as is evidenced by the dependence of the observed velocity on the velocity of the gas stream; the section CD corresponds to chemical control (observed constant = $1.90 \times 10^7 e^{-40,701/RT}$), where the observed constant is independent of the velocity of gas flow. Over the section BC, the reaction is of intermediate type. This transition is evident in other systems (see, for example, ref. 23 and 24).

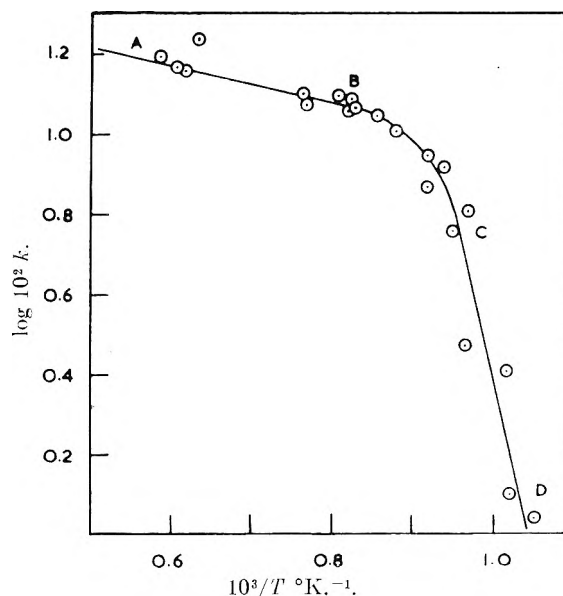


Fig. 1.—Log $10^3 k$ vs. $1/T$ for the combustion of carbon spheres in air.

Although the discussion has centered on processes for which the chemical reaction is first-order with respect to the solute concentration, there is no doubt

(19) Equation 12 applies also to a rotating paddle-type specimen (see ref. 20).

(20) A. C. Riddiford and L. L. Bircumshaw, *J. Chem. Soc.*, 698 (1952).

(21) C. M. Tu, H. Davis and H. C. Hottel, *Ind. Eng. Chem.*, **26**, 749 (1934).

(22) In Fig. 1, the values of T are the arithmetic means of the furnace temp. and the temp. at the carbon surface.

(23) M. B. Abramson and C. V. King, *J. Am. Chem. Soc.*, **61**, 2290 (1939).

(24) R. W. Clson, R. W. Schuler and J. M. Smith, *Chem. Eng. Progress*, **46**, 614 (1950).

(14) For the case of fluid flow parallel to a plane solid surface, δ is also a function of the distance measured along the surface. By the usual experimental techniques, only a mean value of δ can be determined, but in any case this dependence is of no importance in the present discussion since we are concerned only with those factors which are temperature-dependent.

(15) $(E_D - E_\nu)$ is commonly of the order of 0.5-1.0 kcal./mole for aqueous systems.

(16) L. L. Bircumshaw and A. C. Riddiford, *J. Chem. Soc.*, 598 (1951).

(17) More generally, if the power on U in equation 13 is $-a$ (where $1 \geq a \geq 0.5$); $d(\ln \delta)/dT = (E_D - (3a - 1)E_\nu)/3RT^2$; $E_T = (2E_D + (3a - 1)E_\nu)/3$. As a rough guide, $E_T \approx E_D$ when $a = 2/3$.

(18) P. Alexander, D. Gough and R. F. Hudson, *Trans. Faraday Soc.*, **45**, 1058, 1109 (1949).

that similar transitions are to be observed for reactions of higher order. Thus Marc²⁵ found the velocity of crystallization at low temperatures to be of the second order, whilst at higher temperatures the process is first-order. Peshkov²⁶ and

(25) R. Marc, *Z. physik. Chem.*, **73**, 685 (1910).

(26) B. Peshkov, *Acta Physicochim. U. R. S. S.*, **21**, 109 (1946).

Barkhuysen²⁷ are but two of the workers who have postulated a transport mechanism for the crystallization process; this, together with the work reported at the recent Faraday Society Discussion on Crystal Growth, suggests that the process is one of intermediate type.

(27) F. H. C. Barkhuysen, *Chem. Weekblad.*, **43**, 234 (1947).

THE SYNTHESIS OF ORGANO-BENTONITE ANHYDRIDES

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The acylation of bentonite clay has been achieved by treating both the acid form and various metal forms of the clay with benzoyl chloride and acetyl chloride in anhydrous media. Several types of analyses have been made in order to identify the products thus formed, and methods for the estimation of the extent of acylation have been developed. The availability of the base-exchange ion for this type of reaction has been studied and several postulates have been made to account for the variations observed.

Several successful methods have been reported by which certain organic groups have been attached to the laminar clays of high base-exchange capacity. Among these are the amine salt product¹⁻⁵ which has received by far the most attention up to the present. Methylated complexes^{6,7} have been made by introducing the methyl group with azomethane. An esterification product⁸ has been made by the action of an alkyl halide on bentonite clay. In all these studies, it is the conclusion that the attachment of the organic group to the laminar silicate structure is at the base-exchange site. The present work is concerned with the reaction between bentonite and acyl halides wherein it again appears that the reaction site is identical with the base-exchange site.

From the standpoint of chemical and structural composition, bentonite may be considered as a giant molecule of laminar structure which consists of numerous cells, each cell bearing a negative charge as the result of the isomorphous substitution of a magnesium atom for an aluminum atom in the gibbsite layer.⁹ The negative charge of this cell is balanced by a cation which is commonly termed the exchangeable ion. This cation is usually an alkali ion in natural bentonite, but it may be substituted with various other metal ions as well as hydrogen. The exact position of this cation as well as the exact location of the negative charge carried by the clay lamina are conjectural. The ionic system is undoubtedly governed by Pauling's electrostatic valence principle—neutrality on the smallest possible scale—even though the bond distance is modified by ionic size, charge and steric factors.

(1) J. E. Giesekeing, *Soil Sci.*, **47**, 1 (1939).

(2) E. A. Hauser, *Chem. Revs.*, **37**, 307 (1945).

(3) E. A. Hauser in Jerome Alexander, "Colloid Chemistry," Vol. VII, Reinhold Publishing Corp., New York, N. Y., 1950, pp. 431-432.

(4) E. A. Hauser, U. S. Patents 2,531,427 and 2,531,812.

(5) C. R. Smith, *J. Am. Chem. Soc.*, **56**, 1561 (1934).

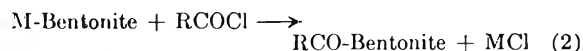
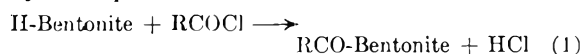
(6) G. Berger, *Chem. Weekblad.*, **38**, 42 (1941).

(7) G. Berger, *Compt. rend. conf. pedol. mediterr.*, 119 (1947).

(8) R. Bart and S. Gusman, "A Study of the Esterification of Bentonite," S. B. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1946.

(9) U. Hofmann, K. Endell and D. Wilm, *Z. Krist.*, **86**, 340 (1933).

With these ideas in mind, the reaction between bentonite and an acyl halide may be represented by the equations



In equation (2), M is any cation, assuming that proper allowance is made for its valence. Polyvalent ions will satisfy more than one base-exchange site. In view of the analogy to ordinary anhydride formation, the reaction product is termed a mixed anhydride.

Experimental

Materials.—A typical Wyoming bentonite which showed base-exchange capacities of 68 meq. per 100 g. bentonite by titration of the hydrogen-bentonite form and of 88 meq. per 100 g. bentonite by the ammonium acetate absorption method¹⁰ was used. The raw clay was converted to the hydrogen form by electro dialysis. Similar results were obtained with hydrogen-bentonite prepared by leaching the clay with 0.05 N HCl. However, it was somewhat easier to obtain uniform samples of the prepared clay by the former method. The metal forms of the clay were obtained by titrating the hydrogen form with the appropriate base to a pH of 8.5. The acetyl chloride and benzoyl chloride used in this work were of Eastman Kodak Company practical grade.

Procedure.—Two grams of the prepared bentonite, dried at 105° for 2 hours, was dispersed in 15 ml. of dioxane and refluxed with 1 ml. of the acyl halide for 1 hour. The ratio of acyl halide to bentonite was not critical, except that when larger amounts of the acyl halide were present it was necessary to reduce the time of refluxing in order to prevent carbonization. Acetyl chloride reacted more rapidly than benzoyl chloride, the products otherwise being essentially identical. This study was based for the most part upon the benzoyl chloride reaction. The product was washed with 80% ethyl alcohol on the filter and dried overnight at 105° in order to remove all traces of alcohol. The product was very similar in appearance to the original clay.

Proof of Formation of an Organo-bentonite Anhydride (1).—The alcohol washings from the separation of the product from the reaction mixture were concentrated, ignited, taken up in water and then titrated with AgNO₃ in order to determine the amount of metal chloride formed during the reaction. Barring side reaction, this result should be an indication of the amount of acyl groups which have reacted with and become attached to the clay. These data are col-

(10) Robert P. Graham and J. D. Sullivan, *J. Am. Ceram. Soc.*, **21**, 176 (1938).

lected in Table I. When bentonite was refluxed with pure dioxane, entirely negative results were obtained for all three tests listed in Table I.

(2).—The mixed anhydrides, when treated with NaOH at room temperature slowly underwent hydrolysis. At 65°, this hydrolysis reaction occurred more rapidly with about 5 minutes being sufficient for the system to equilibrate. Figure 1 shows a curve obtained by titrating benzoyl bentonite anhydride with NaOH at 65°. The plateau region of the curve at A corresponds to the hydrolysis reaction with the end-point at B. Up to 30% of the base-exchange capacity can be associated with anhydride formation.

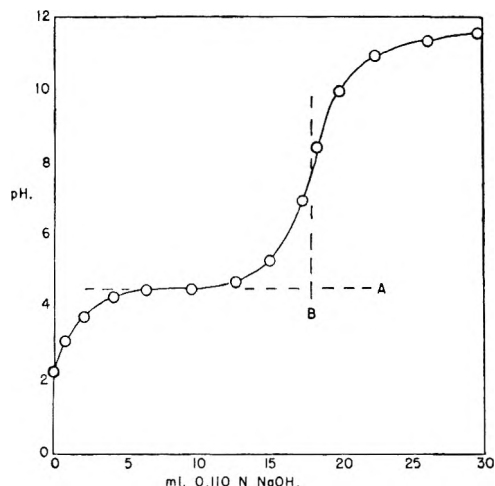


Fig. 1.—Potentiometric titration of 3 g. of benzoyl bentonite anhydride with 0.11 N NaOH at 65°, with 5-minute intervals between additions of the alkali; end-point of titration at B.

(3).—When the benzoyl bentonite anhydride was hydrolyzed with NaOH, the sodium benzoate which was formed was converted to benzoic acid and conclusively identified. This involvement apparently produced no structural changes in the benzoyl group.

(4).—A hydrolysis value for the mixed anhydride was determined by heating 1 g. of the product at 80° for 1 hour with 10 ml. of 0.1 N NaOH, then titrating the excess alkali with HCl. Figure 2 shows a typical set of potentiometric titration curves obtained in this analysis. A comparison to the curve for the untreated bentonite at a pH of 7.0 gives the amount of NaOH which evidently was required for the hydrolysis reaction. The untreated metal bentonite appar-

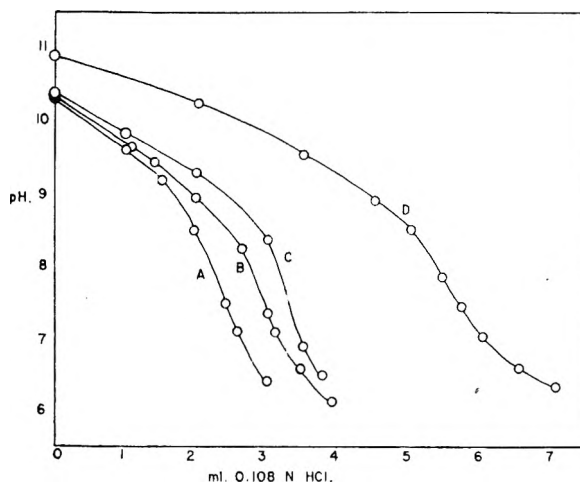


Fig. 2.—Determination of hydrolysis value by back-titration of hydrolysis mixture of 10 ml. of 0.099 N NaOH and 1 g. of benzoyl bentonite anhydride prepared from: A, Na-bentonite; B, Ca-bentonite; C, K-bentonite. D, using untreated metal bentonite, serves as control.

ently reacts with a significant amount of NaOH, hence a comparison to a blank sample was necessary. Table I contains these data.

(5).—Combustion analysis of the mixed anhydrides gave reproducible results which indicated a definite composition. This method of analysis was based primarily on the carbon content inasmuch as the hydrogen determination were seriously influenced by the cation in the base-exchange position and the condensibility of the hydroxyl groups on the clay structure, which in turn affects the amount of water formed in the combustion analysis. These data are included in Table I.

TABLE II

BASE-EXCHANGE CAPACITY OF A BEIDELLITE CLAY WITH ALKALI IONS IN THE EXCHANGE POSITION

Cation	Base-exchange capacity
Li	89.7
Na	89.4
K	76.9
Rb	54.4
Cs	43.8

Discussion of Results

It is readily noted that there are considerable differences among the three methods of analysis given in Table I. However, if the data for the alkali and alkaline earth ions are plotted, as in Figs. 3 and 4, there appears to be a good degree of correlation.

The data based upon combustion analysis are probably most dependable. Between these data and the hydrolysis values are considerable differences, although these differences are almost constant at 7.0 ± 1.0 meq., per 100 g. of bentonite for the alkali ions. The results for the other metals, particularly Be and Mg, show considerable anomalies. Evidently the organo-bentonite structure reacts with a certain amount of the NaOH above that required for the hydrolysis of the acyl groups. The surfaces of the laminar particles may react with NaOH either through surface adsorption of OH groups, neutralization of weakly acidic groups, or decomposition of the clay to give soluble silicates.¹¹

TABLE I

EXTENT OF FORMATION OF BENZOYL BENTONITE ANHYDRIDE

Exchangeable ion on bentonite lamina	Metal chloride	Meq. benzoyl per 100 g. bentonite Hydrolysis value	Carbon combustion
Li	34	12.0	4.0
Na	40	18.4	11.0
K	28	12.0	5.5
Rb	27	12.5	6.2
Cs	18	12.5	6.5
Be	14	10.5	4.0
Mg	26	15.4	4.8
Ca	29	15.4	15.2
Sr	30	17.0	15.8
Ba		17.0	15.8
Tl (ic)		11.6	19.4
NH ₄		27.2	19.2
C ₆ H ₅ NH ₂		21.2	46.0 ^a
HOC ₂ H ₅ NH ₂		22.5	16.9
H		26.3	21.1

^a Considerable carbonization is indicated by this high result.

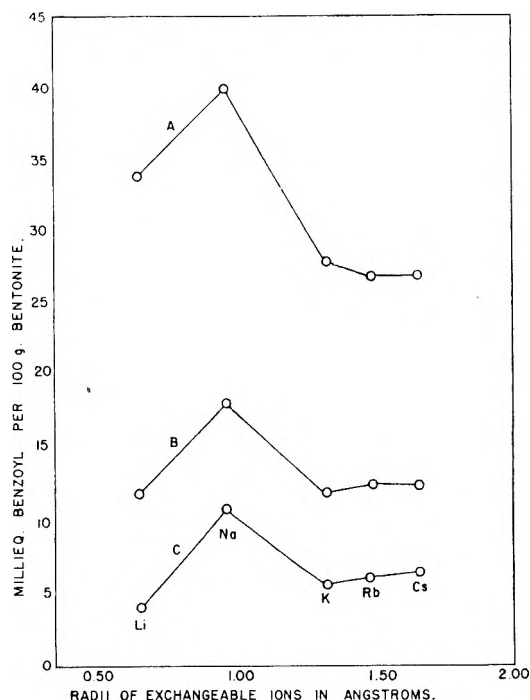


Fig. 3.—Extent of formation of benzoyl bentonite anhydride from alkali-bentonites. Analyses are based upon: A, amount of metal chloride found in reaction mixture; B, hydrolysis values; C, carbon combustion analysis.

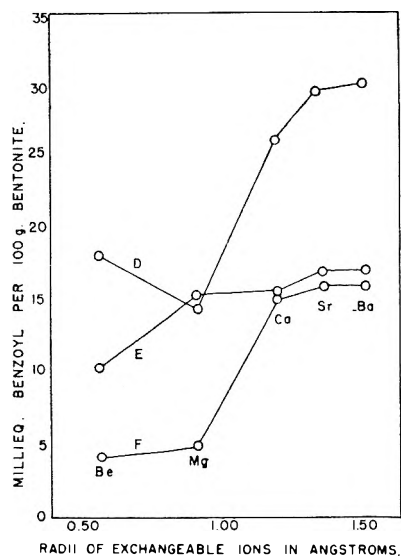


Fig. 4.—Extent of formation of benzoyl bentonite anhydride from alkaline earth bentonites. Analyses are based upon: D, amount of metal chloride found in reaction mixture; E, hydrolysis values; F, carbon combustion analysis.

It has been suggested¹² that five factors determine the extent of ion exchange, namely, diffusion, ionic size, charge, steric availability and exchange position. Since the formation of organo-bentonite anhydrides involves the base-exchange sites, these same factors would determine to a considerable extent, the amount of anhydride formed with an acyl halide. With the exception of sodium, in Fig. 3 there is a definite trend which shows that as

the cation becomes larger it is more readily replaced by the acyl group.

It is noted in Fig. 4 that the divalent ions react more readily than the univalent cations. Inasmuch as the base-exchange sites are univalent, a divalent cation will be associated with two of these sites,¹³ with the result that the latter type of cation will exhibit a greater degree of steric availability. Because of their greater availability trivalent cations which occur in thallic bentonite are more available and reactive with an acyl halide than are the divalent cations.

The differences of behavior of the alkali ions in the exchange position are influenced by the laminar silicate structure. It has been fairly well established¹⁴ that the structure of these clays consists of oxygen-populated surfaces composed of hexagonal arrangements of groups in the Si_2O_5 layer. The holes in this layer which are bounded by 6 oxygen atoms are of approximately the same radius as a potassium ion, namely, 1.33 Å. Since the clay is dried at 105° before it is treated with the acyl halide, the exchangeable ions become more or less firmly attached in this hole, depending upon their sizes. It is assumed on the basis of Grim's work¹⁵ that the negative charge of the silicate layer is situated in the vicinity of the bottom of this hole. If the lithium ion were dehydrated, it could easily drop into this hole and then form a more covalent bond than the other alkali ions. The sodium ion is small enough (0.98 Å) to slip in and out of the hole easily. The potassium ion becomes more or less sterically attached to these holes, as has been shown by previous studies.¹⁶ Rubidium and cesium ions, only slightly larger than the potassium ion, become less hindered by the fact that they cannot penetrate into the hole as far as the potassium ion. With respect to the performance of Na- and K-clays in this reaction, these results are in agreement with Page and Bayer¹⁶ but disagree with the results of Bart and Gusman.⁸ There are undoubtedly undetermined factors which influence the availability of cations for exchange, but in view of the generally recognized structure of these laminar clays, this hypothesis accounts at least partially for the results of this study.

In a recent electrochemical study¹⁷ of the bond energies in K- and Na-bentonite the activity of the potassium ion has been shown to be considerably less than that of the sodium ion. This observation substantiates the results obtained in the present acylation study.

The availability of the ammonium ion (1.43 Å. radius) should be similar to that of the potassium ion. However, the acyl halide can readily react with the hydrogen atoms of the ammonium ion with the formation of a peptide linkage. The same would be true for the clays containing aniline and ethanolamine, the latter providing an addi-

(13) W. H. Slabaugh and J. L. Culbertson, *This Journal*, **55**, 744 (1951).

(14) C. E. Marshall, "Colloid Chemistry of Silicate Minerals," Academic Press Inc., New York, N. Y., 1949, p. 52.

(15) Ralph E. Grim, *J. Geol.*, **50**, 225 (1942).

(16) J. B. Page and L. D. Bayer, *Soil Sci. Soc. Am. Proc.*, **4**, 150 (1939).

(17) S. K. Mikhherjee and C. E. Marshall, *This Journal*, **55**, 61 (1951).

(12) F. C. Nachod and W. Wood, *J. Am. Chem. Soc.*, **66**, 1380 (1944).

tional reactive point at the hydroxyl group. These complexes contain groups that are both sterically and chemically reactive toward the acylating agent. The results in Table I bear out these arguments.

The typical erratic and unpredicted behavior of hydrogen ions on clay is shown in the results obtained when acyl halide reacts with this type of clay. One concept offered in this respect is based upon the idea that in H-bentonite, some of the hydrogen ions penetrate the silicate lattice and release an equivalent amount of aluminum ions.¹⁸ Since this system is highly reactive toward the acyl halide, there are apparently fairly reactive cations on the clay which may or may not be identical with the original base-exchange sites.

In spite of efforts to maintain anhydrous reaction mixtures the presence of a small amount of moisture will produce HCl from the acyl halide to exchange with the metal ions on the clay. These released metal ions would then contribute to the

content of metal chloride found in the washings of the reaction products and thus give high results as noted in Figs. 3 and 4. The base-exchange capacity of the alkali clays themselves (Table II) is reflected in the metal chloride analyses, which show an opposite trend to the hydrolysis values and combustion analysis data. Although the larger cations are individually sterically available for reaction with an acyl halide, there is statistically a smaller tendency for these cations to be available for base-exchange reactions. Thus, the data obtained from the metal chloride analysis is largely influenced by the base-exchange capacity of the metal-bentonite.

The color of the product formed from the reaction between benzoyl chloride and the aniline bentonite complex was dark gray with a strong violet undertone. Since this color developed early in the reaction and the hydrolysis value of the product is relatively high, the color is probably not due entirely to carbonization. An investigation of the synthesis of anhydrides from organic-clay complexes is being planned.

(18) S. B. Hendricks and L. T. Alexander, *Proc. Soil Sci. Am.*, **5**, 95 (1940)

ORGANIC DERIVATIVES OF MONTMORILLONITE¹

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The nature of the OH groups on montmorillonite was studied by attempting to replace these groups by organic groups. The phenyl derivative of montmorillonite was prepared from dry montmorillonite chloride by treating it with phenylmagnesium bromide. The montmorillonite chloride was prepared by treating dry H-montmorillonite with thionyl chloride. Acetyl derivatives of montmorillonite were prepared by refluxing dry H-montmorillonite with either acetyl chloride or acetic anhydride. The montmorillonite was converted from a highly hydrophilic condition to a hydrophobic and somewhat organophilic condition by the substitution of OH groups by organic groups. When the acetyl groups were removed from acetylated montmorillonite by hydrolysis with 0.2 *N* Ba(OH)₂ the resulting material again exhibited hydrophilic properties. It was not possible to remove all of the organic radicals from phenyl montmorillonite by boiling with 35% KOH for 30 minutes. The results indicate that the phenyl radicals formed a silicone type of bond with the montmorillonite.

Introduction

The montmorillonites possess large amounts of highly reactive surfaces. Berger³ first detected the presence of OH groups in the montmorillonite surfaces by esterification with diazomethane. Two general types of organic montmorillonite derivatives have been studied in the past. These types are: (1) clay salts with organic cations on the exchange positions and (2) complexes in which the organic group is attached to the clay through a covalent bond. The organic cation clay complex has been studied more extensively and systematically than the latter type of complex. Gieseking⁴ studied the mechanism of exchange reactions in the montmorillonite-type clays and demonstrated that the organic cations tend to be attracted onto the surfaces of the mineral plates. Jordan⁵ has studied extensively the swelling properties of organic amine

clay complexes. Deuel⁶ succeeded in preparing some organic montmorillonite derivatives with a covalent ether- or ester-type linkage (C-O-Si). He found that approximately 60 meq. of OH groups per 100 g. of clay were esterified. Gieseking⁷ observed that montmorillonite, when treated with acetyl chloride, lost its hydrophilic properties. The purpose of this investigation was to prepare some covalent bonded organic derivatives of montmorillonite and to study their stability and properties in an attempt to add to the knowledge of the surface characteristics and crystal structure of montmorillonites.

Preparations

H-Montmorillonite.—Wyoming bentonite, finer than one micron, was the source of the H-montmorillonite used throughout this investigation. Sodium saturated Wyoming bentonite was washed by decantation with 0.1 *N* HCl to replace the sodium ions and excess HCl was removed by washing three times with distilled water. A Sharples supercentrifuge was used to separate the clay. The hydrogen saturated montmorillonite was dispersed in 95% ethanol in a Waring blender and washed three times with absolute

(1) Contribution from the Department of Agronomy, University of Illinois, Urbana, Illinois. Published with the approval of the Director. Presented before the Colloid Division of the Jubilee Meeting of the American Chemical Society in New York, September 3-7, 1951

(2) Atomic Energy Commission Fellow.

(3) G. Berger, *Chem. Weekblad*, **38**, 42 (1941).

(4) J. E. Gieseking, *Soil Science*, **47**, 1 (1939).

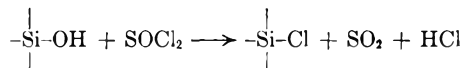
(5) J. W. Jordan, *This Journal*, **53**, 294 (1949).

(6) H. Deuel, G. Huber and R. Iberg, *Helv. Chim. Acta*, **33**, 1229 (1950).

(7) J. E. Gieseking, *Advances in Agronomy*, **1**, 159 (1949).

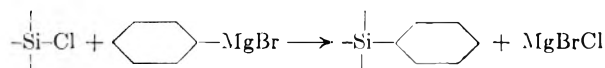
ethanol and three times with absolute ether to remove the adsorbed water.

Montmorillonite Chloride and Phenyl Montmorillonite.—To prepare montmorillonite chloride, 14.6 g. of the previously dried H-montmorillonite and 150 ml. of redistilled thionyl chloride were refluxed until SO₂ and HCl evolution ceased. The excess thionyl chloride was then removed by distilling under reduced pressure over a heated water-bath. According to Deuel⁶ the reaction is



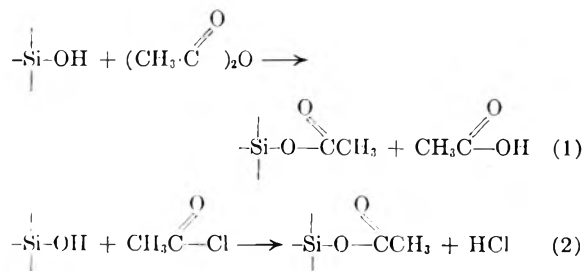
To prepare phenyl montmorillonite, the montmorillonite chloride, prepared above, was suspended in absolute ether and a reflux condenser was attached to the flask. An ethereal solution of phenylmagnesium bromide (prepared from 20 g. of bromobenzene and 3.2 g. of magnesium turnings) was added slowly to the montmorillonite chloride suspension. The mixture was refluxed for one hour after which the ether was removed by distillation. The residue was heated in an oil-bath at 160° for three hours. After cooling, the excess Grignard reagent was destroyed by adding cold water. The mixture was steam distilled for two hours to remove impurities such as phenol and diphenyl derivatives. The product was washed in a buchner funnel with water, until free of halides, twice with acetone, and finally with ether until a clear filtrate was obtained. The phenyl montmorillonite was then dried at 110°.

The method for the preparation of phenyl montmorillonite was based on the technique used by Cusa and Kipping⁸ for the preparation of tetraphenylsilanes. The reaction can probably be represented as



Acetylated Montmorillonite.—Attempts were made to acetylate montmorillonite by treating dried H-montmorillonite with acetic anhydride and with acetyl chloride. (1) The reaction with acetic anhydride was carried out by refluxing 9.4 g. of H-montmorillonite with 160 ml. of acetic anhydride for 3 hours. Then most of the excess acetic anhydride was removed from the product by decantation and the remainder was removed by washing 12 times with absolute ether. (2) The reaction with acetyl chloride was carried out by refluxing 12 g. of H-montmorillonite with 200 ml. of acetyl chloride for 3 hours. After cooling, most of the excess acetyl chloride was removed by decantation and the remainder was removed by washing 12 times with absolute ether.

The acetylation of montmorillonite by acetic anhydride and acetyl chloride can probably be represented by the two reactions



Properties of the Montmorillonite Derivatives

Montmorillonite chloride released 63.6 meq. of chlorides per 100 g. when hydrolyzed with a weak KOH solution. Samples of this derivative gave no chlorides when heated to 110° before treating with a KOH solution.

Phenyl montmorillonite was found to have a higher carbon content and a lower cation exchange capacity than H-montmorillonite. The X-ray diffraction data in Table I indicate that phenyl groups entered the crystal lattice in a regular manner between planes along the "C"-axes of the crystals and that these groups were not completely removed by boiling in a 30% KOH solution.

(8) N. W. Cusa and F. S. Kipping, *J. Chem. Soc.*, 1040 (1933).

TABLE I
BASAL REFLECTIONS (*d*00*l*) OF ORGANIC MONTMORILLONITE DERIVATIVES

Complex		None A.	Treatment	
			Hydro- lyzed with water A.	Hydro- lyzed with Ba(OH) ₂ A.
Acetic anhydride- montmorillonite	No glycerol	12.77 ^a	13.01	12.64
	Glycerol	13.01	13.01	14.2
Acetyl chloride- montmorillonite	No glycerol	13.4 ^a	15.3	12.65
	Glycerol	15.1	17.6	17.8
Phenyl montmorillonite	No glycerol	14.84 ^a	...	...
	Glycerol	17.5	...	...
H-Montmorillonite	No glycerol	12.36	...	...
Phenyl montmoril- lonite 35% KOH (boiled 30 minutes)	No glycerol	14.2	...	...
H-Montmorillonite 35% KOH	No glycerol	11.7	...	...

^a Dried from ether.

Phenyl montmorillonite was subjected to wettability tests as described by Bancroft,⁹ Hofmann¹⁰ and Reinders.¹¹ The results in Table II show that H-montmorillonite was changed from a hydrophilic substance to a hydrophobic substance by phenylation.

TABLE II
DISTRIBUTION OF THE FINELY GROUND DERIVATIVES BETWEEN TWO IMMISCIBLE LIQUIDS

w, the solid goes nearly completely into the water phase; i, the solid collects nearly quantitatively in the interface; iw, the solid goes partly into the interface and somewhat less into the water phase; i(w), most of the solid goes into the interface with a small portion in the bracketed phase.

Complex	Water and isoamyl alcohol	Water and chloro- form	Water and ben- zene
Acetic anhydride-montmorillonite	i(o)	i	i
Acetic anhydride-montmorillonite hydrolyzed with water	i(o)	i	i
Acetic anhydride-montmorillonite hydrolyzed with Ba(OH) ₂	iw	wi	iw
Acetyl chloride-montmorillonite	i	i(w)	i
Acetyl chloride-montmorillonite hydrolyzed with water	iw	wi	wi
Acetyl chloride-montmorillonite hydrolyzed with Ba(OH) ₂	iw	wi	wi
Phenyl montmorillonite	i	i(w)	i
H-Montmorillonite	wi	wi	wi
Montmorillonite chloride hydro- lyzed with Ba(OH) ₂	iw	wi	wi

Acetylated montmorillonite gave acetate ions when hydrolyzed with a dilute solution of Ba(OH)₂. The derivative, formed by the action of acetyl chloride on H-montmorillonite, gave no chlorides upon hydrolysis. This shows that acetyl chloride does not chlorinate montmorillonite.

Acetic anhydride acetylates montmorillonite to a much greater extent than acetyl chloride. This is probably due to the higher reflux temperature attainable with acetic anhydride.

Acetylated montmorillonite is hydrophobic in contrast to the hydrophilic H-montmorillonite from which it was prepared. When acetylated montmorillonite is hydrolyzed, a product is obtained which has the hydrophilic properties of the original H-montmorillonite.

(9) W. D. Bancroft, *This Journal*, **19**, 275 (1915).

(10) F. B. Hofmann, *Z. physik. Chem.*, **83**, 385 (1913).

(11) W. Reinders, *Kolloid Z.*, **13**, 235 (1913).

Wettability tests showed that acetylated montmorillonite adsorbs organic liquids to a greater extent than H-montmorillonite. Hydrolysis of acetylated montmorillonite gives a product with wettability similar to the original H-montmorillonite.

Acetylation of montmorillonite reduces its cation exchange capacity. Hydrolysis of acetylated montmorillonite restores the cation exchange capacity.

Montmorillonite acetylated with acetic anhydride gave a product containing 9.6% carbon compared to a trace of carbon in the original H-montmorillonite. The carbon content of this product was reduced to 1.5% by hydrolysis with $\text{Ba}(\text{OH})_2$.

The Nature of the OH Groups in Montmorillonite

Martin and Kipping¹² found that the silicols were chlorinated by acetyl chloride but did not react with acetic anhydride. The acetylation of montmorillonite by both acetyl chloride and acetic anhydride indicates that the involved OH groups are more acidic than the OH groups of the silicols.

The presence of OH groups in the montmorillonite structure can be explained by either the Edelman¹³ structure or by the substitution of OH for O

in the tetrahedral layer adjacent to the site of substitution of Al for Si as postulated by McConnell¹⁴ in his modification of the Hofmann¹⁵ structure. This proximity of OH groups to the Al ions in the crystal lattices could well explain the acidic character of the OH groups in montmorillonite as a result of the strong electrostatic attraction between the Al ions and the O ions of the OH groups.

Water hydrolysis of montmorillonite, acetylated with acetic anhydride, released approximately 20% of the total acetyl groups and increased the cation exchange capacity of the derivative an equivalent amount. Since Hendricks¹⁶ found that 20% of the cation exchange capacity of montmorillonite resides on the edges of the plate-like crystals, it would seem that the acetylated edges of the montmorillonite crystals are less stable toward water hydrolysis than the acetylated flat surfaces of the crystals.

(14) D. McConnell, *Am. Mineral.*, **35**, 166 (1950).

(15) U. Hofmann, K. Endell and D. Wilm, *Z. Krist.*, **86A**, 340 (1933).

(16) S. B. Hendricks, R. A. Nelson and L. T. Alexander, *J. Am. Chem. Soc.*, **62**, 1437 (1940).

(12) G. Martin and F. S. Kipping, *J. Chem. Soc.*, **95**, 302 (1909).

(13) C. H. Edelman and J. C. L. Favejee, *Z. Krist.*, **102**, 417 (1940).

SURFACE COMPLEXES ON CARBON BLACKS. I. HIGH TEMPERATURE EVACUATION STUDIES

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Surface complexes on four commercial carbon blacks have been studied by heating the blacks during evacuation at temperatures as high as 1200° and collecting and analyzing the evolved gases. Much of the water vapor and carbon dioxide is given off at or below 600°. The carbon monoxide and hydrogen are evolved primarily in the 600–900 and 900–1200° regions, respectively. Surface area measurements show that the gas evolution from Spheron 6, Black Pearls 1, and Mogul could be accounted for by postulating the existence of a monomolecular layer of surface complexes. On the other hand, the gas from Lampblack T is several fold too great to be attributed to a single layer of surface complex and presumably arises from a layer several molecules thick.

It has been known for many years that oxygen complexes are formed on all types of carbon.^{2–6} These complexes can be removed at considerably higher temperatures as oxides of carbon. Johnson⁷ showed that the oxygen complex on several commercial carbon blacks decomposed at an appreciable rate at temperatures above 400°, and at 955° was fairly completely removed in 30 minutes. To obtain more precise data on the oxygen complex of carbon blacks, several commercial blacks were evacuated at high temperature and the gases collected and analyzed. The results of these experiments together with calculations utilizing surface area measurements on the samples are reported in the present paper.

Experimental

The samples studied included three carbon blacks, Spheron 6, Black Pearls 1, and Mogul. A sample of lampblack, Samue Cabot's T black, was also included. These samples were furnished by Godfrey L. Cabot, Inc., and have been described in detail recently by Emmett and Cines.⁸

The apparatus for high temperature evacuation has been described previously,² and will be discussed only briefly here. The sample was placed in a platinum crucible within a quartz tube. The crucible was heated to temperatures of 900° with a resistance furnace and to 1200° with an induction furnace. The quartz tube was connected by a graded seal to the Pyrex tubing of the pumping system which included a Stimson mercury pump backed by an automatic Toepler pump. The evolved gases were fractionated into three parts, volatile, respectively, in liquid nitrogen, Dry Ice and warm water. Each fraction was analyzed by the semi-micro method of Taylor and Saunders.⁹ Actually, CO , CO_2 , CH_4 , H_2 , H_2O and free N_2 were determined. However, the volumes of methane were so small (0 to 0.3 cc.) that they were considered negligible. The evolved nitrogen was not listed in the table but is discussed below.

The following procedure was used in the degassing experiments: The sample, which had been dried for a week or more over P_2O_5 , was pumped at room temperature to a vacuum of 10^{-6} mm. Then, a collection of the evolved gases was started while the sample was being heated rapidly to 300°.

(1) (a) Central Experiment Station, Bureau of Mines, Pittsburgh 13, Pennsylvania. (b) Mellon Institute, Pittsburgh 13, Pennsylvania.

(2) R. B. Anderson and P. H. Emmett, *THIS JOURNAL*, **51**, 1308 (1947).

(3) R. M. Barrer, *J. Chem. Soc.*, 1261 (1936).

(4) I. Langmuir, *J. Am. Chem. Soc.*, **37**, 1139 (1915).

(5) H. H. Lowry and G. A. Hulet, *ibid.*, **42**, 1408 (1920).

(6) T. F. E. Rhead and R. V. Wheeler, *J. Chem. Soc.*, **103**, 461, 1210 (1915); *Proc. Chem. Soc. (London)*, **29**, 51, 193 (1913).

(7) C. R. Johnson, *Ind. Eng. Chem.*, **20**, 904 (1928); **21**, 1288 (1929).

(8) P. H. Emmett and M. L. Cines, *THIS JOURNAL*, **51**, 1329 (1947).

(9) H. A. Taylor and K. W. Saunders, *J. Chem. Phys.*, **9**, 616 (1941).

When, after about an hour at 300°, a vacuum of 10^{-5} mm. was reached, the collected gas was measured and transferred to an evacuated bulb for analysis. The temperature was then increased to 600, 900 and 1200° in succession, and the evolved gases were collected and analyzed as for the heating at 300°.

Results and Discussion

In Tables I and II are given the data of the high temperature evacuation experiments. Table I presents the volumes of evolved gases in cc. (S.T.P.) per gram over successively higher temperature ranges. In Table II the evolved gases are expressed in weight per cent., and the total loss in weight is compared with the results of the standard volatile test (ASTM Proc. D271-48). The loss in weight of the various blacks due to the removal of hydrogen, water, carbon monoxide and carbon dioxide, the surface area of the blacks, the volume of free and combined hydrogen and combined oxygen removed per square meter of surface, and the ratios of combined oxygen (calculated as cc. of O₂) and free and combined hydrogen, respectively, to the volume of nitrogen required to form

TABLE I
GASES EVOLVED IN HIGH TEMPERATURE EVACUATION OF CARBON BLACKS, CC. (S.T.P.) PER GRAM OF ORIGINAL BLACK

Temp., °C.	H ₂	CO	CO ₂	H ₂ O (vapor)
A. Spheron 6				
25-300	0.04	0.13	0.62	2.16
300-600	0.16	7.71	2.98	2.48
600-900	17.60	19.35	1.58	2.87
900-1200	35.42	2.62	0.12	0.06
Total	53.22	29.81	5.30	7.57
B. Spheron 6, degassed over different temperature ranges than in A.				
25-800	19.20	26.76	5.28	7.81
800-1000	24.05	1.26	0.00	0.02
Totals to 1000°	43.25	28.02	5.28	7.83
C. Black Pearls 1				
25-300	0.00	(0.21) ^a	1.32	2.30
300-600	0.32	25.85	4.88	3.35
600-900	5.42	78.40	3.60	0.15
900-1200	30.60	1.95	0.05	0.05
Total	36.34	106.41	9.85	5.85
D. Lampblack T				
25-300	0.03	0.28	3.09	9.91
300-600	0.11	5.08	3.19	1.77
600-900	15.40	16.95	1.27	1.42
900-1200	48.00	3.25	0.24	0.04
Total	63.54	25.56	7.79	13.14
E. Mogul				
25-300	0.00	(0.20) ^a	0.78	2.88
300-600	0.23	25.25	4.89	3.16
600-900	6.92	59.63	2.77	0.24
900-1200	31.18	2.68	0.54	0.19
Total	38.33	87.94	8.98	6.47

^a These small volumes were assumed to be CO without analysis; they might have been N₂.

a physically adsorbed monolayer are also included in Table II.

TABLE II
WEIGHT PER CENT. OF VARIOUS GASES EVOLVED FROM CARBON BLACKS IN HIGH TEMPERATURE EVACUATION, AND RELATED DATA

	Spheron 6	Black Pearls 1	Lamp-black T	Mogul
Weight % removed as:				
CO	3.73	13.29	3.19	10.98
CO ₂	1.04	1.93	1.53	1.76
H ₂	0.48	0.32	0.57	0.34
H ₂ O	0.61	0.47	1.06	0.52
Total weight loss, %	5.86	16.01	6.35	13.60
Weight loss to 900°C., %	5.21	15.50	5.51	12.99
% volatile by conventional method	5.5	16.7	5.5	11.5
Hydrogen in black by ultimate analysis, wt. %				
Hydrogen evolved, wt. %	0.55	0.38	0.69	0.40
Oxygen evolved, wt. %	3.43	9.41	3.87	8.02
Surface area, ^a m. ² /g.	131.8	998.0	28.8	522.0
Combined oxygen evolved (expressed as cc. of O ₂ /m. ²)				
H ₂ evolved, cc./m. ²	0.182	0.066	0.943	0.108
Ratio of combined oxygen evolved (expressed as cc. of O ₂) to V _m for N ₂ ^a	0.798	.289	4.13	.471
Ratio of hydrogen evolved (cc.) to V _m for N ₂ ^a				
	2.02	.185	11.75	.376

^a These areas were computed from nitrogen isotherms at -195° by a modified form of the BET equation [Anderson, *J. Am. Chem. Soc.*, **68**, 686 (1946); **70**, 1727 (1948)], and are about 10% greater than those from the simple BET equation. Areas were computed by the modified BET equation because the simple BET equation does not fit the nitrogen isotherm for Mogul over a very large range. V_{mN₂} is the volume of nitrogen required to form a monolayer of physically adsorbed nitrogen over the surface of a sample of carbon black.

Free oxygen was not found in the gases evolved from any of the blacks in any of the temperature ranges. However, with Spheron 6 and Lampblack T, 0.33 and 0.68 cc. (S.T.P.) of free nitrogen, respectively, were found per gram of sample in the gases evolved in the 25-300° range. With Black Pearls 1 and Mogul the total non-condensable gas evolved in this temperature range was about 0.20 cc. per gram and was assumed to be carbon monoxide. It appears doubtful that the free nitrogen obtained from the former samples was chemisorbed on the carbon, since the nitrogen complex formed by the action of ammonia on charcoal did not decompose appreciably below 900°. It seems more likely that the nitrogen was occluded within the particles during the formation of the black. Nitrogen was not found in the gases evolved at higher temperatures.

In the four degassing experiments the largest amounts of hydrogen were evolved in the 900-1200° range, whereas the largest amounts of carbon monoxide and carbon dioxide were evolved in the 600-900° and 300-600° ranges, respectively. Most of the water was given off below 600°. In general, the evolved gases were not in amounts corresponding to the water gas equilibrium or the equilibrium between carbon dioxide, carbon monoxide and carbon, except in the 600-900° range, where the distribution of products roughly corresponded to the water gas equilibrium. This may indicate that the complex exists in at least qualitatively

different forms and that the composition of the evolved gas is a function of the type of complex decomposing in each temperature range.

It is interesting to consider the extent of the surface covered by oxygen complex for each of the carbon blacks. Biscoe and Warren¹⁰ reported a structure for carbon blacks which is similar to that of graphite but more disordered. The *a* and *c* distances (the width of the graphite-like ring of carbon atoms and twice the interplanar spacing of the layers, respectively) were 2.45 and 7.0 Å. Thus, each surface carbon atom in the hexagonal planes (termed *a-a* planes hereafter) occupies 2.6 Å.², and in the faces perpendicular to these (called *a-c* planes) the area per carbon atom is 4.95 Å.².

In Table III are given the volumes of gases evolved on degassing to 1200° computed as molec-

material, but that the amount of oxygen per unit surface area was decreased by the air treatment.

The evolved hydrogen, computed as atoms, appears to exceed a monolayer (of one hydrogen atom per surface carbon) slightly for Spheron 6 and five- to tenfold for Lampblack. For Mogul and Black Pearls 1 the ratios of the hydrogen atoms to surface carbons were much lower than unity. The data indicate that Lampblack T requires several layers of complex to account for either evolved hydrogen or evolved oxides of carbon. Spheron 6 appears capable of holding all of its oxygen and most of its hydrogen in a single layer, and Black Pearls 1 and Mogul can hold all or both their oxygen and hydrogen as surface complex.

Of the blacks studied, Spheron 6 and Lampblack T had not been treated after formation, whereas Black Pearls 1 and Mogul were prepared from a finely divided channel black and a relatively coarser black, respectively, by subsequent treatment with air. The total amount of hydrogen removable from these treated samples as well as the amount of hydrogen per unit surface was less than for the untreated Spheron 6. Thus, it appears that the air treatment removes some of the hydrogen of the black either by thermal decomposition or by oxidation.

In a previous paper on charcoal,² the accuracy of the high temperature evacuation and gas analysis used here was shown to be satisfactory by comparing the loss in weight of the sample during degassing with the weights of the evolved gases. In the present work with carbon black, no such direct comparison was made. However, as shown in Table II, the total weight of gas evolved to 900° compares well with the "per cent. volatile"¹¹ for these blacks as measured by the Godfrey L. Cabot Co. by the usual procedure of heating the samples in a covered platinum crucible in a muffle furnace.

A detailed comparison shows that the amount of hydrogen removed as free hydrogen or as water vapor during the degassing is somewhat smaller in all samples than the hydrogen content given by ultimate analysis. Therefore, it appears that some of the hydrogen in the blacks is dispersed throughout the particles in some form that is not readily removed at or below 1200°.

Acknowledgment.—The authors would like to express their appreciation to Godfrey L. Cabot, Inc., for furnishing the carbon black samples and for defraying the cost of the work covered by both Papers I and II of this series.

(11) It is realized, of course, that no exact agreement is to be expected between weight losses of the samples during high temperature evacuation in the present experiments and weight losses during the conventional determination of the per cent. of volatile material. This follows because the exact ratio of CO:CO₂:H₂O in the volatilized material will probably be different for these two divergent devolatilization procedures.

TABLE III

FRACTION OF SURFACE COVERED BY OXYGEN AND HYDROGEN

Carbon black	Total combined oxygen removed, cc. O ₂ /g.	Total H ₂ removed, cc. H ₂ /g.	% Surface covered by ^a			
			Oxygen <i>a-c</i> planes	Oxygen <i>a-a</i> planes	Hydrogen <i>a-a</i> planes	Hydrogen <i>a-c</i> planes
Spheron 6	24.00	60.79	25.6	48.7	64.8	123.4
Black Pearls 1	65.98	42.19	9.3	17.7	8.2	15.7
Lampblack T	27.14	76.68	132.5	252	374	712
Mogul	56.18	44.80	15.1	28.8	12.1	23.0

^a Assuming one oxygen or one hydrogen atom adsorbed per one surface carbon atom in *a-a* or *a-c* planes.

ular oxygen and hydrogen and the calculated percentage of the carbon atoms covered by oxygen and hydrogen atoms if the surface is composed entirely of *a-a* or *a-c* planes, respectively, and if each surface carbon is assumed to hold one oxygen atom and one hydrogen atom. Only with Lampblack T is the oxygen more than enough to cover the surface of the sample. Adsorption studies, presented in the next paper, give further evidence that the oxygen complex on this sample is several layers in depth. Actually, for three of the blacks there is sufficient surface to accommodate all of the oxygen if it is assumed that each oxygen atom is held by two surface carbon atoms. Only for Lampblack T must one conclude that the evolved oxygen comes from several layers rather than a single layer of complex. It is interesting to note that the percentage of oxygen in Mogul, which was formed by air treatment at 800°F. of a material similar to Spheron 6, was greater than that of its parent

(10) J. Biscoe and B. E. Warren, *J. Applied Phys.*, **13**, 364 (1942).

SURFACE COMPLEXES ON CARBON BLACKS. II. THE ADSORPTION OF NH_3 , C_2H_2 , C_4H_{10} , CH_3NH_2 AND WATER VAPOR

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For Spheron 6, Black Pearls 1, Mogul, and Lampblack T surface areas as calculated from nitrogen adsorption isotherms by the BET method, are in satisfactory agreement with those calculated by the BET method as modified by Anderson and Hall or by the method proposed by Harkins and Jura, both for the original blacks and for the samples from which the complex had been removed by degassing at 1200°. The adsorption of acetylene at -78° and of butane at 0° appeared to be purely physical in nature and yielded areas in satisfactory agreement with those obtained from the nitrogen isotherms at -195°. For Lampblack T, ammonia and methylamine isotherms gave apparent areas several fold greater than those obtained from nitrogen. The result presumably indicates the solution of ammonia and of methylamine in the large amount of oxygen complex known to be present in a layer several molecules thick on Lampblack T. For after-treated Lampblack and for a lampblack sample degassed at 1200° the area obtained from the ammonia adsorption isotherms at -46° were in satisfactory agreement with those obtained from nitrogen adsorption at -195°. In confirmation of previous observations the water adsorption isotherms on the various carbon blacks were shifted in the direction of higher relative pressures for a given water sorption as the complex was removed from the surface by high temperature degassing.

In 1941 some experiments were undertaken in an attempt to find an adsorbate that would be preferentially adsorbed either by the portion of the surface of carbon black that was covered with oxygen complex, or by the portion that was free of complex. Such an adsorbate would help materially in determining rapidly the fraction of the surface of a carbon black free of surface complex. Although the war terminated the research before such an adsorbate was found, a number of interesting experimental data were obtained that are here being reported. Specifically, adsorption isotherms for nitrogen, ammonia, acetylene and water vapor were determined on a series of carbon blacks both before and after the blacks were evacuated at high temperature to remove surface complexes; a few measurements were also made of the adsorption of methylamine and *n*-butane.

Experimental

Adsorption data for all of the gases and vapors except water were obtained on a standard volumetric adsorption apparatus.^{2,3} A few of the water vapor isotherms were determined by this method, but the majority were determined by a gravimetric method.⁴ The usual types of cold baths were employed: liquid nitrogen for -195°, Dry Ice-acetone for -78°, well-stirred chlorobenzene cooled by Dry Ice for -46°, and wet ice for 0°.

The source and purification of the adsorbates were as follows: prepurified nitrogen (Air Reduction) was condensed in a liquid nitrogen trap, and the middle portion distilled into a storage bulb. The remainder of the adsorbates were solids at liquid nitrogen temperatures, and after condensation at -195° were freed from volatile gases by repeatedly melting, freezing, and evacuating them or by repeated distillation from one trap to another in vacuum. The *n*-butane was a C.P. grade from the Ohio Chemical Co., and the ammonia was taken from a cylinder of anhydrous ammonia. Distilled water freed from air as described above was stored as liquid in a Pyrex bulb. Methylamine was prepared by treating recrystallized methylamine hydrochloride with sodium hydroxide solution, and drying the resulting methylamine. Commercial welding acetylene was purified by passing it through two scrubbers containing saturated sodium bisulfite solution and through a soda lime tower.

Most of the carbon black samples were the same as those that have already been described by Emmett and Cines.⁵ Three additional blacks used for some of the measurements were as follows: Spheron 4, a pelletized rubber grade channel black; a steam-activated black prepared by treating Spheron 4 with steam for two hours at 481°; and a sample of Shawinigan acetylene black. All samples were furnished by the Godfrey L. Cabot Co. Samples referred to as having been "degassed" were those that had been evacuated in an induction furnace at temperatures up to 1200°. They were believed to be fairly free of oxygen complexes after this treatment. By a suitable technique described in the previous paper,⁶ it was possible to transfer the degassed samples to the adsorption apparatus without exposing them to air.

Surface areas were calculated from adsorption isotherms by three methods: by the BET theory for multilayer adsorption⁷ (equation 1), by the modification of this theory proposed by Anderson and Hall^{8,9} (equation 2), and by the equation of Harkins and Jura¹⁰ (equations 3 and 4).

$$\frac{x}{V(1-x)} = \frac{1}{V_m C} + \frac{(C-1)x}{V_m C} \quad (1)$$

$$\frac{x}{V(1-kx)} = \frac{1}{V_m Ck} + \frac{(C-1)x}{V_m C} \quad (2)$$

$$\log x = B - A/V^2 \quad (3)$$

$$\text{surface area} = k'(A)^{1/2} \quad (4)$$

In all of these equations, V represents the volume of gas (S.T.P.) adsorbed; x , the relative pressure; C , a constant defined by the equation $C = \frac{a_1 b_2}{a_2 b_1} e^{(E_1 - E_L)/RT}$, where a_1 , a_2 , b_1 and b_2 are constants, E_1 is the "average heat of adsorption" in the first layer, and E_L is the heat of liquefaction of the adsorbate; V_m , the volume of gas required to form a monolayer on the surface of the adsorbent; A , the slope of the plot of $\log x$ against $1/V^2$ according to equation 3; and k' is a proportionality constant. Constant k is experimentally determined for each isotherm. Its significance has been discussed in previous publications.^{8,9}

Experimental Results

The experimental data are presented in Figs. 1 to 8 and in Tables I to III.

Discussion

For the determination of surface areas by equations 1 and 2, the cross-sectional molecular areas

(1) Central Experiment Station, Bureau of Mines, Pittsburgh 13, Pennsylvania. (b) Mellon Institute, Pittsburgh 13, Pennsylvania.

(2) P. H. Emmett, American Society for Testing Materials, Symposium on New Methods for Particle Size Determination in the Sub-sieve Range, 1941, p. 95.

(3) P. H. Emmett, *Advances in Colloid Sci.*, **1**, 1 (1942).

(4) P. H. Emmett and R. B. Anderson, *J. Am. Chem. Soc.*, **67**, 1492 (1945).

(5) P. H. Emmett and M. Cines, *This Journal*, **51**, 1329 (1947).

(6) R. B. Anderson and P. H. Emmett, *ibid.*, **51**, 1308 (1947).

(7) S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

(8) R. B. Anderson, *ibid.*, **68**, 686 (1946).

(9) R. B. Anderson and W. K. Hall, *ibid.*, **70**, 1727 (1948).

(10) W. D. Harkins and G. Jura, *ibid.*, **66**, 1366 (1944).

TABLE I
 SURFACE AREAS OF CARBON BLACKS

	Adsorbate	Temp., °C.	BET (eq. 1)	Modified BET (eq. 2)	<i>k</i>	Harkins and Jura (eq. 3)	Linear range
			Surface area, m. ² /g.	Surface area, m. ² /g.		Surface area m. ² /g.	
Spheron 6 original	N ₂	-195	116.4	131.8	0.67	127.4 ^a	0.01-0.55
	C ₂ H ₂	-78	110.0	130.9	.65	112.3 ^b	.22- .90
	NH ₃	-46	115.5	118.2	.90	96.6 ^c	.03- .75
Spheron 6 degassed	N ₂	-195	106.6	128.4	.67	110.8 ^a	.20- .75
	C ₂ H ₂	-78	99.1	118.0	.65	98.7 ^b	.20- .95
	NH ₃	-46	60.0	60.0	1.00		
Black Pearls 1 original	N ₂	-195	942.0	998.0	0.51	1080 ^a	.15- .60
	NH ₃	-46	858.0	1015.0	.70	958 ^c	.16- .90
Black Pearls 1 degassed	N ₂	-195	767.0	860.0	.60	940 ^a	.10- .60
	NH ₃	-46	617.0	789.0	.65	590 ^c	.25- .80
Mogul original	N ₂	-195	•	522.0	.40	929 ^a	.1- .3
	NH ₃	-46	•	448.0	.45	556 ^c	.08- .60
Mogul degassed	N ₂	-195	166.5	184.0	.70	176.6 ^a	.1- .8
	NH ₃	-46	124.6	154.5	.80	96.2 ^c	.13- .40
Lampblack T original	N ₂	-195	25.5	28.8	.65	25.8 ^a	.10- .90
	C ₄ H ₁₀	0	27.6	31.5	.65	36.2 ^d	.15- .60
	NH ₃	-46	71.8	106.5	.40	85.9 ^c	.18- .7
Lampblack T degassed	N ₂	-195	20.6	23.5	.80	20.9 ^a	.17- .95
	NH ₃	-46	25.8	25.8	1.00	•	
Lampblack T after-treated	N ₂	-195	•	228.0	0.30	350 ^a	.17- .65
	NH ₃	-46	•	277.0	.30	377 ^c	.14- .80
Spheron 4	N ₂	-195	128.5	148.2	.70	143.9 ^a	.16- .70
	NH ₃	-46	134.7	155.6	.73	143.3 ^c	.15- .70
Spheron 4 steam-activated	N ₂	-195	•	510.0	.40	598 ^a	.18- .65
	NH ₃	-46	•	379.0	.53	428 ^c	.15- .75

• The value of H. and J. *k'* taken as 4.06. ^b The value of H. and J. *k'* taken as 5.04, the av. exptl. values compared with N₂. ^c The value of H. and J. *k'* taken as 4.13, the av. exptl. values compared with N₂. ^d The value of H. and J. *k'* taken as 13.6. • Equation does not fit over an appreciable range.

TABLE II

ADSORPTION OF WATER VAPOR AND AMMONIA AS A FUNCTION OF FRACTION OF SURFACE COVERED BY OXYGEN COMPLEX

Black	Volatiles content, % ^a	% Volatile, × 100 surface area ^b	% Surface covered at relative pressure of 0.4 ^c H ₂ O	NH ₃
Lampblack T	5.5	19.1	352	365
Lampblack T, after treated	11.0	4.8	90	133
Spheron 6	5.5	4.2	67	135
Spheron 4	4.0	2.7	62	133
Mogul	11.5	2.2	49	155
Black Pearls 1	16.7	1.7	36	125
Spheron 6, degassed	1.2	0.9	4.8	73
Spheron 4, steam activated	<1.0	<.7	5.2	86
Mogul, degassed	0.0	0	0.7	104
Black Pearls 1, degassed	0	0	2.8	101
Lampblack T, degassed	0	0	...	71

^a Obtained from standard volatility test.²¹ These values were obtained from published data and from unpublished results of Godfrey L. Cabot, Inc. ^b In these calculations the surface areas from nitrogen isotherms computed with equation 2 were assumed to represent the area of the black. Equation 2 was used since it satisfactorily fits all the nitrogen isotherms including those of the porous blacks. ^c The molecular cross-sectional area of water and ammonia were taken as 10.5 and 12.8 Å², respectively, in these calculations.

TABLE III

VALUES OF *C* FROM EQUATIONS 1 AND 2

Black	Treat- ment ^a	N ₂ (-195°) modified	NH ₃ (-46°) modified	C ₂ H ₂ (-78°) modified	
		BET (eq. 1)	BET (eq. 2)	BET (eq. 1)	BET (eq. 2)
Spheron Grade 6	O	161	87	38	31
	D'	83	67	8	8
Black Pearls 1	O	246	324	32	25
	D	176	214	23	19
Mogul	O	...	382	...	132
	D	361	132	13	9
Lampblack T	O	113	82	23	...
	D	369	97	4	...
	AT	...	556	...	...
Spheron Grade 4	O	258	200	31	26
	SA	...	262	...	37

^a O, original sample; D', degassed to 950-1000°; D, degassed to 1200°; AT, air treated at 417°; SA, steam activated at 481°.

for N₂, H₂O, C₄H₁₀, CH₃NH₂ and C₂H₂ were calculated from the liquid densities in the usual manner,¹¹ and were, respectively, 16.2, 10.5, 32.1, 19.1, and 18.5 Å². The following values of *k'* of equation 4 were employed: 4.06 for N₂ at -195°, 13.6 for C₄H₁₀ at 0°, 5.04 for C₂H₂ at -78°.

(11) S. Brunauer and P. H. Finmet, *J. Am. Chem. Soc.*, **59**, 2682 (1937).

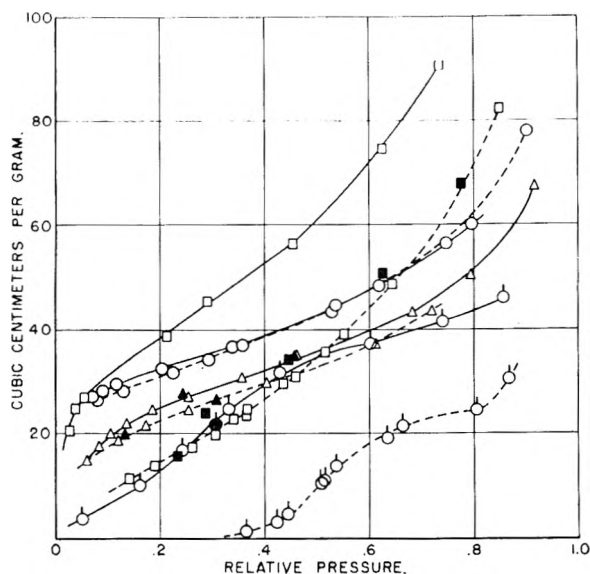


Fig. 1.—Adsorption on Spheron 6 before (solid lines) and after (broken lines) degassing to 950–1000°, where (○) represents N_2 at -195° ; (□), NH_3 at -46° ; (◇), H_2O at 25° ; and (Δ), C_2H_2 at -78° . Desorption points are solid.

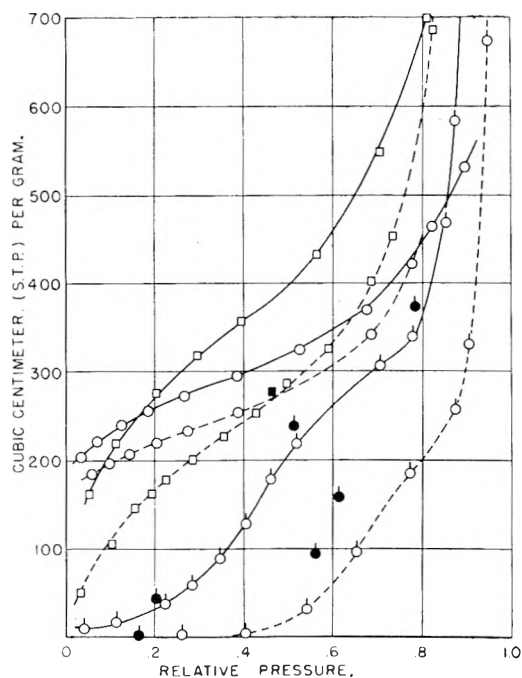


Fig. 2.—Adsorption on Black Pearls 1 before (solid line) and after (broken line) degassing to 1200° where (○) represents N_2 at -195° ; (□), NH_3 at -46° ; and (◇), H_2O at 25° . Desorption points are solid.

and 4.13 for NH_3 at -46° . The first two values have been suggested by Harkins and Jura.¹⁰ The latter two values were chosen to give the best agreement between areas predicted by equation 1 using nitrogen as adsorbate and those calculated for the isotherms of C_2H_2 and NH_3 , respectively. Ammonia isotherms for porous blacks or those showing an enhanced adsorption of ammonia were not used in this calculation.

Surface areas calculated from nitrogen isotherms of non-porous blacks by equations 1, 2 and 3 are in good agreement. In most cases, equation 1 fitted

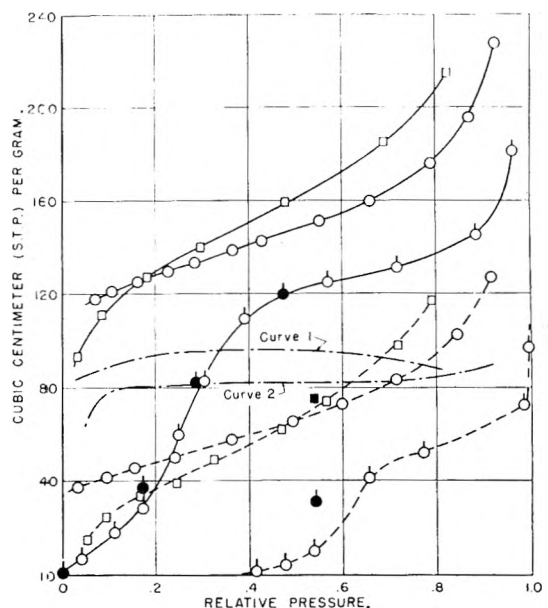


Fig. 3.—Adsorption on Mogul carbon black before (solid line) and after (broken line) degassing to 1200°, where (○) represents N_2 at -195° ; (□), NH_3 at -46° ; and (◇), H_2O at 25° . Desorption points are solid. Curves 1 and 2 represent the decrease in volume of adsorbed ammonia and nitrogen, respectively, resulting from high temperature evacuation.

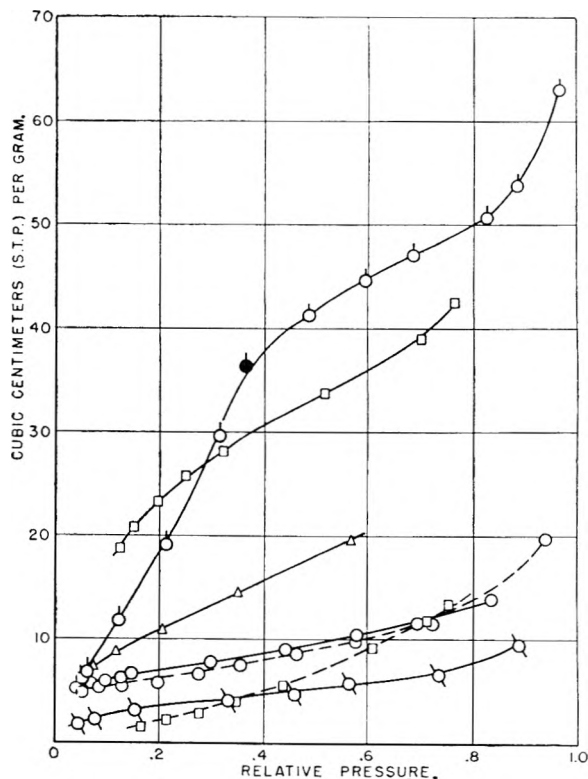


Fig. 4.—Adsorption on Lampblack T (solid lines) and Lampblack T after high temperature evacuation (broken lines), where (○) represents N_2 at -195° ; (□), NH_3 at -46° ; (◇), H_2O at 25° ; (▽), $n-C_4H_{10}$ at 0° ; and (Δ), CH_3NH_2 at 0° . Desorption points are solid.

the experimental data in the range of $x = 0.05$ to 0.35 ; and equation 2, from $x = 0.05$ to 0.70 . The values of k varied from 0.6 to 0.7. The fit of equation 3 was over the relative pressure range 0.15

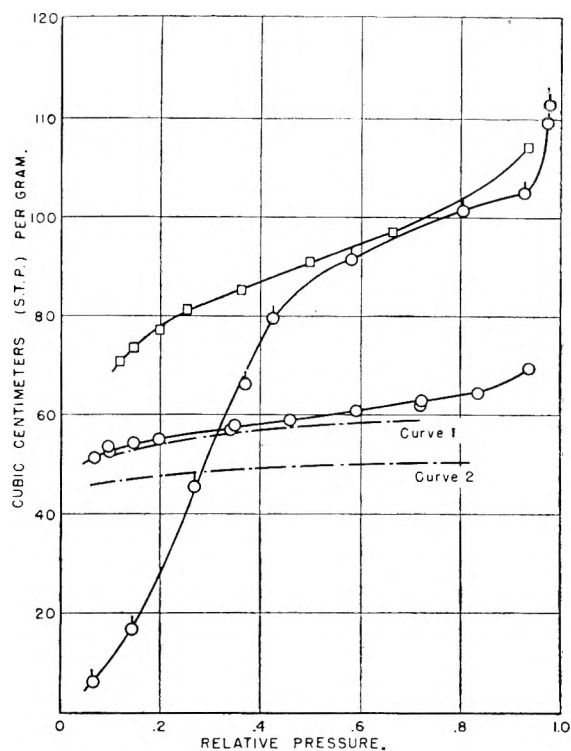


Fig. 5.—Adsorption on Lampblack T after treating with air at 427° where $\circ$ represents N_2 at -195° ; $\square$, NH_3 at -46° ; and $\diamond$, H_2O at 25° . Curves 1 and 2 represent, respectively, the increase in ammonia and nitrogen adsorption resulting from air treatment of Lampblack T.

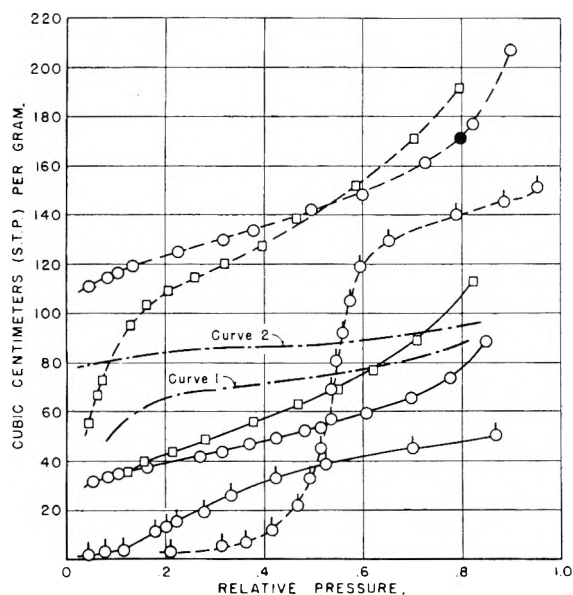


Fig. 6.—Adsorption on Spheron 4 before (solid lines) and after (broken lines) activation by steam at 900° , where $\circ$ represents N_2 at -195° ; $\square$, NH_3 at -46° ; and $\diamond$, H_2O at 25° . Curves 1 and 2 represent the increase in volume of adsorbed ammonia and nitrogen, respectively, resulting from steam activation. Descriptive point is solid.

to 0.80. Usually, the areas predicted by equation 2 were about ten per cent. greater than those from equation 1. The areas from equation 3 differed from those from equations 1 and 2 in a more or less random manner, but in many cases the areas from equation 3 were between those from equations 1

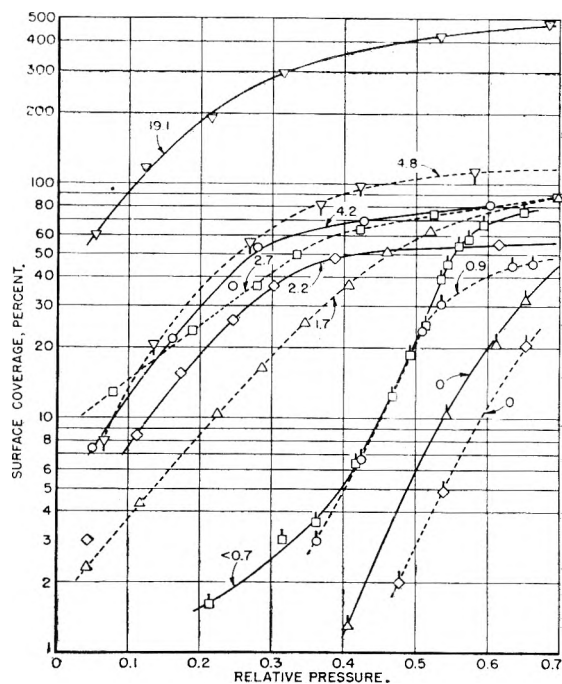


Fig. 7.—The variation of water adsorption at 25° with oxygen content. The percentage of the surface (based on nitrogen surface area) covered by water as a function of relative pressure. The numbers indicate the oxygen content of the blacks per unit surface area expressed as $100 \times$ per cent. volatile/surface area per gram. $\circ$, Spheron 6; δ , Spheron 6, degassed; $\triangle$, Black Pearls 1; δ , Black Pearls 1, degassed; $\diamond$, Mogul; δ , Mogul, degassed; $\square$, Spheron 4; δ , Spheron 4, steam activated; ∇ , Lampblack T; δ , Lampblack T, after treated.

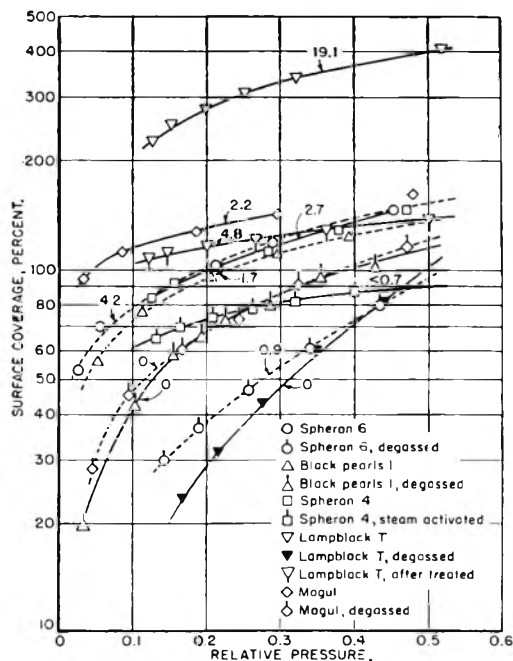


Fig. 8.—The variation of ammonia adsorption at -46° with oxygen content. The percentage of the surface (based on nitrogen surface area) covered by ammonia as a function of relative pressure. The numbers indicate the oxygen content of the blacks per unit surface area expressed as $100 \times$ per cent. volatile/surface area per gram.

and 2. For most of the blacks, the areas obtained from the nitrogen isotherms also agreed with those

calculated from acetylene, butane or ammonia isotherms. Only for Lampblack T did the ammonia and methylamine isotherms give areas distinctly larger than those obtained from nitrogen isotherms. This result will be discussed below. The water vapor isotherms have unique and characteristic shapes, which are not adequately described by equations 1, 2 or 3 or any of the equations that have been proposed for multilayer adsorption.

The shapes of the isotherms for Mogul, after-treated Lampblack T and steam-activated Spheron 4 indicate that the blacks are porous. For these blacks the simple BET equation 1 is not applicable; however, the modified BET equation 2 apparently yields reasonable values for the surface areas. The values of k of equation 2 for isotherms on these porous blacks are considerably lower than those for isotherms on presumably non-porous blacks. It is understandable that these three blacks are porous since each of them during manufacture had been given an air or steam treatment that would naturally lead to the development of pores. Evidence for this porosity can be obtained from the isotherms in Figs. 3, 4 and 6 by subtracting in each figure the isotherms for nitrogen or ammonia on the non-porous adsorbent from the corresponding isotherm on the porous sample. Curves 1 and 2 of Fig. 3 which represent such difference plots for the isotherms of nitrogen and ammonia, respectively, clearly indicate that the degassed Mogul has lost most of its porosity. Similarly, curves 1 and 2 of Figs. 5 and 6 represent, respectively, such difference curves for Lampblack T before and after air treatment and for Spheron 4 before and after steam activation. The difference curves 1 and 2 of Figs. 5 and 6 are all of the type obtained for charcoals. Therefore, there can be no doubt that the activation processes developed considerable porosity.

It has been pointed out in numerous previous publications that removal of the oxygen complex from the surface of a carbon black or charcoal tends to decrease the water adsorption at a given relative pressure and to shift to much higher values the relative humidity required to produce a given adsorption. This is amply confirmed by the water isotherms for the original and the degassed samples of Mogul, Spheron 6 and Black Pearls 1 as shown in Fig. 7. Even the steam activation of Spheron 4 apparently removes most of the complex and thus decreases and shifts to higher relative pressures the adsorption of water vapor. This would be expected since the temperature of the steam activation (1650°F.) is sufficiently high to remove most of the oxygen complex and since treatment with steam does not form appreciable amounts of complex on carbon black or charcoal.⁵

Oxygen complex on the surface of charcoal is known to increase the adsorption of alkali from solution, and also to increase the adsorption of ammonia from the gas phase. The present results in general confirm this effect for the adsorption of ammonia by carbon black. Figure 8 shows the ammonia adsorption in per cent. of the surface (as determined by nitrogen) covered by ammonia and indicates that the removal of complex from a

given carbon black always decreases the ammonia adsorption. This effect is also evident in the data of Table II.

It will be noted, however, that the adsorption of ammonia at a given relative pressure does not increase uniformly with the % volatile content if the data for all the blacks are compared. Specifically, the porous blacks, such as Mogul, steam-activated Spheron 4 and after-treated Lampblack all have larger fractions of the surface covered with ammonia at a given relative pressure and per cent. volatile than do the non-porous blacks. This, presumably, can be explained by the fact that adsorption at low relative pressure in charcoals or carbons which, like charcoal, have very small pores, is much greater per unit area than on non-porous carbon blacks regardless of the adsorbate used. Furthermore, it will be noticed in Fig. 8 that very finely divided blacks (Black Pearls 1, for example) have larger ammonia adsorption per unit area at a given relative pressure than do coarser blacks (Lampblack T, for example). This is in accord with the general observation that adsorption on the blacks of smallest particle size is more exothermic than on coarser carbon particles. These two effects seem to account for any irregularities in the variation of the extent of ammonia adsorption with % volatile for the blacks as shown in Fig. 8.

It was hoped that the adsorption of acetylene might be quite different on carbon blacks before and after degassing. However, a set of measurements on Spheron 6 before and after removal of the surface complex was almost identical; apparently acetylene is merely physically adsorbed. The areas obtained from equations 1 and 2 for this gas are in good agreement with those obtained from nitrogen isotherms. Presumably, acetylene resembles other unsaturated hydrocarbons and also saturated hydrocarbons which have been found by Beebe¹² and co-workers to have heats of adsorption on degassed blacks that are substantially the same as on the original blacks.

The isotherms on the samples of Lampblack (Figs. 4 and 5) merit special comment. The isotherms for ammonia and methylamine on Lampblack T constitute the first examples in which the adsorption of any vapor except water at a given relative pressure greatly exceeds the adsorption of nitrogen. In Table I the area calculated in the usual way is three times as great when based on the ammonia isotherm as when based on the nitrogen isotherm and, similarly, the area calculated from the methylamine isotherm is twice as great as that calculated from the adsorption of nitrogen. However, the enhanced adsorption of water vapor by the lampblacks as shown in Table II is not without precedent. Numerous organic materials such as proteins,^{13,14} starch¹⁵ and most types of coal¹⁶ have been shown capable of absorbing many times more moles of water vapor at room temperature

(12) R. A. Beebe, M. H. Polley, W. R. Smith and C. B. Wendell, *J. Am. Chem. Soc.*, **69**, 2294 (1947).

(13) S. W. Benson and D. A. Ellis, *ibid.*, **70**, 3563 (1948); S. W. Benson, D. A. Ellis and R. W. Zwanzig, *ibid.*, **72**, 2102 (1950).

(14) H. J. Frey and W. J. Moore, *ibid.*, **70**, 3644 (1948).

(15) N. N. Hellman and E. H. Melvin, *ibid.*, **72**, 5186 (1950).

(16) J. A. Lecky, W. K. Hall and R. B. Anderson, *Nature*, **168**, 124 (1951).

than of nitrogen at -195° . Similarly, methyl alcohol¹¹ and probably some of the higher alcohols are absorbed much more extensively by coal than would be expected on the basis of surface area measurements with nitrogen. In contrast to these results, the butane isotherm for Lampblack T yields a surface area that is in approximate agreement with that for the nitrogen isotherm.

The excessive adsorption of water vapor and ammonia might be attributed to penetration in capillaries that are too small for nitrogen molecules. However, this could not account for the excessive absorption of methylamine since its molecular diameter is as large as that of nitrogen. The only reasonable explanation is that ammonia, water and methylamine dissolve in the thick layer of oxygen complex that is known¹⁷ to be present on this black, whereas the nitrogen and the butane adsorption covers merely the outer surface of the black. Possibly this solubility is connected with the polarity of these molecules and especially with their ability to form hydrogen bonds with the constituents of the oxygen complex. When the complex is removed from this black by degassing at 1200° , the adsorption of ammonia becomes normal and yields a surface area for the degassed black that is in good agreement with that obtained from the nitrogen isotherm (Table II). An alternate interpretation to the solution theory is the hypothesis that these three gases—water, ammonia and methylamine—actually react with the thick layer of oxygen complex. However, this is not very plausible because the isotherms for these gases increase gradually from zero adsorption at zero pressure. If the adsorbates reacted with the layer of complex, their isotherms would be expected to rise sharply at very low pressures.

Table III lists the C values calculated from the adsorption isotherms according to equations 1 and 2. The removal of the surface complex by de-

gassing the samples to 1200° invariably results in ammonia isotherms yielding smaller values of C than for the original samples. Since the constant C can be taken as at least a qualitative measure of the heat of adsorption, the heat of adsorption of ammonia is much less on the degassed samples than on the original samples. For nitrogen isotherms the values of C are relatively high both before and after degassing; however, activation processes that increased the porosity of the sample produced a marked increase in the value of C as determined by equation 2.

In conclusion it may be well to call attention to the fact that the water adsorption isotherms shown in Fig. 7 are all of types III or IV of the classification suggested by Brunauer, Deming, Deming and Teller.¹⁸ If the water isotherms are interpreted on the basis of their theory, it would follow that the water isotherms for the degassed samples have heats of adsorption less than the heats of liquefaction. However, as recently pointed out by Smith and Pierce,¹⁹ these negative heats cannot be accepted as real until independent evidence for them has been obtained. For example, their data show that type III isotherms for ammonia on graphite have positive heats of adsorption if judged by the Clausius-Clapeyron calculations from the ammonia isotherms. However, Hill²⁰ has questioned the correctness of the usual procedure for calculating the heats of adsorption by this method. He believes that calculations should be made at constant surface potential rather than at constant number of molecules adsorbed. Until the correctness of a method for calculating these heats is established or until experimental calorimetric data are obtained, the value for the heat of adsorption for type III isotherms must remain in doubt.

(18) S. Brunauer, L. S. Deming, W. E. Deming and E. Teller, *J. Am. Chem. Soc.*, **62**, 1723 (1940).

(19) R. N. Smith and C. Pierce, *THIS JOURNAL*, **52**, 1115 (1948).

(20) T. Hill, *J. Chem. Phys.*, **17**, 520 (1949).

(21) W. R. Smith, F. S. Thornhill and R. I. Bray, *Ind. Eng. Chem.*, **33**, 1303 (1941).

(17) R. B. Anderson and P. H. Emmett, *THIS JOURNAL*, **56**, 753 (1952).

FACTORS GOVERNING HARDNESS AND TRANSPARENCY OF ALUMINA GELS

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This paper describes the preparation of a number of samples of alumina gel. Some of these, like some samples of silica gel, are hard and transparent, obtainable in large grains, and do not crumble in contact with water. It was found that the ageing of the precipitated alumina at room temperature, particularly in the presence of large quantities of soluble salts, leads to soft, chalky gels. Hard, fairly transparent gels can be prepared by precipitation from boiling solutions and immediate washing. The deterioration of the precipitated hydroxide can be prevented by addition of small quantities of acetic acid.

Introduction

It is comparatively easy to prepare samples of silica gel which are good in respect of transparency, hardness and adsorptive capacity, and are therefore commercially acceptable. This is not true about gels of aluminium, chromium and iron oxides. These materials have found considerable use as catalysts in a number of laboratory and technical preparations. Besides, aluminum oxide gels have been used as general adsorbents like silica gel. This paper deals with the preparation of satisfactory samples of adsorbent alumina.

Munro and Johnson¹ prepared an adsorbent alumina gel by precipitating the hydroxide from a hot solution of aluminium nitrate, 300 g. in 2 liters, with ammonium hydroxide, diluting to 6 liters and boiling off all free ammonia. The ammonium nitrate was then washed out by decantation and the raw jelly dried first at 100° for 24 hours, then at 300° for one hour. Pearce and Alvarado² adopted an essentially similar method. Perry³ started with a solution of aluminum sulfate instead of aluminum nitrate and performed the precipitation at room temperature. After thorough washing the gel was dried, first at 60°, when a hard, glass-like material was obtained, and finally at 200°. Brückner and Hirth⁴ studied the preparation thoroughly and found that the concentration of aluminium ion when precipitation starts should not be greater than 2%, and an excess of 25% ammonium hydroxide must be used to obtain a strong, hard gel. They also recommend that the washing and drying must be performed rapidly to avoid ageing and possible crystallization of the amorphous material. On the other hand, Alekseevskii and Belotzerkovskii⁵ do not find any changes in the structure of the gel due to variations in the concentrations of ammonium hydroxide (2 to 20%) or aluminum sulfate (0.14 to 0.16 *M*). They further recommend precipitation of the hydroxide at 50–60° and an initial drying for ten to 25 days at room temperature followed by slow drying at 50–60° till the moisture content is reduced to 50–80%. Reference may also be made to the work of I. I. Krasikov and I. I. Ivanov⁶ who started with aluminum nitrate and sodium carbon-

ate in rather concentrated solutions, mixed them at 25–30° and filtered, whereupon the filtrate was reported to gel.

Preparations

A comparison of the different methods shows that contradictions are not lacking. It is quite likely that these workers obtained different products in the final stage. Under these circumstances, it was considered worthwhile to find out by experiment a suitable method for preparing hard, granular and transparent alumina which might be useful as an adsorbent or a catalyst. A number of samples were prepared under the conditions and with the results described below. The chemicals were all of ordinary quality.

Sample 1.—Ten grams of aluminum sulfate dissolved in 100 ml. of water was added to 100 ml. of strong ammonia solution with brisk stirring at room temperature (22°). The precipitate was washed at room temperature practically free from aluminum sulfate and ammonium hydroxide. The resulting gel was dried slowly at room temperature. It had a chalky appearance and shrank appreciably on heating to dull red, but did not crumble. On cooling and wetting with water a good deal of heat was evolved but the grains did not break.

Sample 2.—The aluminum hydroxide was precipitated as above, washed well at room temperature, then boiled with water for 15 minutes. After filtration, the mass set to a chalky gel. It appeared still chalky after drying for about six hours at 40° and immediately fell to a powder on coming in contact with water. The resulting coarse powder was glassy rather than chalky.

Sample 3.—The aluminum hydroxide was precipitated at room temperature as above, filtered and dried for 2 days at room temperature without washing. The soft gel was then broken up and the drying continued at about 70°. The final product was similar to 3 but the grains were smaller, probably due to rapid drying. This gel had the tendency to crumble in contact with water.

Sample 5.—Twenty grams of aluminum sulfate in 100 ml. of water was mixed with 100 ml. of strong ammonium hydroxide under vigorous shaking. The mixture was kept over the water-bath for several hours with occasional shaking, then filtered and the precipitate dried for ten hours below 50°. The material was then transferred to a phosphorus pentoxide desiccator. Next day it was twice washed to remove most of the soluble salts and put back in the desiccator. The product was a soft gel quite similar to 2.

Sample 6.—The aluminum hydroxide was precipitated from a boiling solution of aluminum sulfate (10 g. in 100 ml. of water) by addition of strong ammonium hydroxide (50 ml. of NH_4OH , density 0.88 + 50 ml. of water). After separation the hydroxide was peptized by the addition of just sufficient quantity of 10% acetic acid, then heated to about 100° for a few minutes. A fine transparent jelly was obtained which was colored slightly brown. It was then dried slowly in an air-bath at 70°, washed with boiling water, and further dried in the air-bath. The final sample was like 4 in appearance but did not crumble in contact with water.

Sample 7.—Twenty ml. of 10% acetic acid was added to 10 g. of aluminum sulfate in 100 ml. of water. The hydroxide was precipitated from boiling solution by adding 50 ml. of strong ammonium hydroxide solution and the mixture was left on a water-bath for half an hour. The

(1) L. A. Munro and F. M. G. Johnson, *THIS JOURNAL*, **30**, 172 (1926).

(2) J. N. Pearce and A. M. Alvarado, *ibid.*, **29**, 256 (1925).

(3) J. H. Perry, *ibid.*, **29**, 1462 (1925).

(4) L. Hirth and H. Brückner, *Angew. Chem.*, **49**, 360 (1936).

(5) E. V. Alekseevskii and G. M. Belotzerkovskii, *J. Gen. Chem. (U.S.S.R.)*, **6**, 370, 382 (1936).

(6) I. I. Krasikov and I. I. Ivanov, *Chem. Zentr.*, **111**, II, 1261 (1940).

precipitate was then separated and dried at about 70° in an air-bath. When it had shrunk considerably it was washed free from salts and further dried in the air oven (about 100°). The product was a hard gel in large grains though considerably opalescent.

Sample 8.—Ten grams of aluminum sulfate in 100 ml. of water and 18 g. of ammonium acetate in saturated solution were boiled separately and mixed. A white precipitate appeared immediately. On centrifuging, this white precipitate with poor gelling qualities settled down and an opalescent solution remained above which gave the usual gelatinous precipitate on adding ammonium hydroxide. The precipitate was slightly dried (when a raw gel was obtained), washed thoroughly and dried again in an air oven. The product was a fine, clear and hard gel.

Sample 9.—Ten grams of aluminum sulfate in 100 ml. of water was mixed with 50 ml. of strong ammonium hydroxide while boiling. The precipitate was washed rapidly with boiling water on a sintered glass filter, and the precipitate dried, first at 70°, then at about 150°. The product was a hard, somewhat opalescent gel in the form of large grains.

Sample 10.—Ten grams of aluminum sulfate in 100 ml. of water was boiled and mixed with 50 ml. of strong ammonium hydroxide; the precipitate was washed free from soluble salts, then mixed with 20 ml. of 10% acetic acid and put on the water-bath. A beautiful, transparent raw gel appeared after five minutes. It was then transferred in an air oven and dried at about 70°. Hard grains were obtained which were transparent though small in size. They did not crumble in contact with water. Probably by slower drying it might have been possible to obtain larger grains.

Sample 11.—The aluminum hydroxide was obtained from the solutions used in 10 in the cold and the washing was also done in the cold. The precipitate was peptized with 10 ml. of 10% acetic acid and put on the water-bath. When it had set to a gel, it was dried at room temperature for five days, then transferred to an air oven at 70°. The resulting product was a fine, transparent gel as in 10. None of the samples 7 to 11 crumbled in contact with water.

Discussion

From these limited experiments one cannot say anything very definite about the correlations between conditions under which the hydroxide is precipitated, its subsequent treatment, and the properties of its final product, but certain tendencies can be noted. Thus, for example, if the hydroxide is precipitated at room temperature and allowed to age at similar temperatures, it develops a chalky character whether it is washed after precipitation (prior to gelling) or not (samples 1 and 4). The sooner the hydroxide is heated after precipitation, the better the hardness and transparency (samples 2 and 4). It also appears that the sooner the extraneous salts are removed from the precipitated

hydroxides the better the gel in respect of hardness, transparency and grain size.

These observations thus require that in order to obtain a good gel with the qualities just mentioned, the precipitation of the hydroxide should be carried out from boiling solutions and the soluble salts and excess ammonia removed by washing with hot water on a rapid filter. These expectations were fully satisfied in the preparation of sample 9.

If small quantities of acetic acid are added to the suspension after precipitation (sample 6) or to the aluminum sulfate solution before precipitation, the acid appears to improve the transparency of the gel. Excess of ammonium acetate, however, has a harmful effect (sample 8), leading to precipitation of a large part of the hydroxide as a white precipitate with poor gelling qualities. Nevertheless, a satisfactory gel can be obtained from the opalescent solution left after the white precipitate settles down. Particularly transparent gels are obtained by washing the freshly precipitated aluminum hydroxide (obtained and washed either in the hot or in the cold), then adding enough 10% acetic acid to nearly peptize the precipitate, and then gelling the mixture on the water-bath (samples 10 and 11). It is to be noted that the hydroxide peptized by acetic acid does not undergo the same deterioration as the unpeptized gel at room temperature so far as its gelling qualities are concerned.

To understand the difference between the different samples of alumina prepared, it is necessary to measure, among other things, the adsorptive properties of these gels. The author has previously observed extensive changes in the adsorptive properties of silica gels prepared by him, due to ageing, and duration and temperatures of heating.⁷ It is more than probable that alumina gels undergo similar changes. It is no easy matter to be able to study the adsorptive properties of all the samples prepared under exactly similar conditions. However, using sample 10 it has been found that the isotherms of water vapor are similar to those usually found with silica gel. Adsorption is good and hysteresis exists. The heats of adsorption and desorption are each higher than the heat of condensation of water vapor at the same temperature. A complete account of these measurements will be published later.

(7) B. P. Gyani, *J. Indian Chem. Soc.*, **27**, 577 (1950).

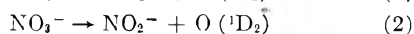
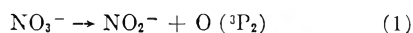
THE PHOTOLYSIS OF CRYSTALLINE NITRATES

By PAUL DOIGAN¹ AND T. W. DAVIS*Chemistry Department, New York University, University Heights**Received October 8, 1961*

The photochemical decomposition of solid nitrates under the influence of light from a high pressure mercury arc produces nitrite and oxygen. Approximate quantum yields vary from 0.002 for lithium nitrate to 0.19 for cesium nitrate in the order: LiNO_3 , $\text{Sr}(\text{NO}_3)_2$, NH_4NO_3 , AgNO_3 , $\text{Pb}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3$, $\text{Ba}(\text{NO}_3)_2$, KNO_3 , $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and CsNO_3 . The rate of photolysis is little affected by initial temperature in the range 30° to 250° . Water of hydration increases sensitivity to radiation. The rate of decomposition of the anhydrous nitrates varies in the same manner as the polarization properties of the cations.

Narayanswamy² observed that solid nitrates, when irradiated by light of wave length 2200 to 2500 Å., decompose but the decomposition is restricted to surface layers only. He considered this localization of the reaction to be the result of back-reaction between entrapped oxygen and nitrite. Only in the surface zone could the oxygen escape and nitrite be formed. Allen and Ghormley, however, found that at low percentages of decomposition, the recombination of oxygen and nitrite within the body of the crystals is unimportant.³ They found that barium nitrate, exposed to 1.2 mv. cathode rays, decomposed extensively. Most of the liberated oxygen remained within the crystals until the crystals were dissolved in water. Allen and Ghormley, therefore, ascribed Narayanswamy's observation to low penetration by the actinic light. We have confirmed this conclusion. We have, furthermore, determined the effect of different cations on the quantum yield and the effects of water of hydration and of temperature in the photolysis of solid nitrates.

Nitrates show two absorption bands in the range 2000–3500 Å., one starting at 3300 Å. with a peak at 3000 Å. and the other, much sharper and more intense, starting at 2630 Å. and proceeding through a maximum around 2000 Å. The processes occurring in the two regions are presumed⁴ to be



The two bands occur in essentially the same positions for solutions, for molten potassium nitrate and for crystalline potassium nitrate.^{5,6} These bands are attributable to the nitrate ion and are presumably the same for all inorganic nitrates.

Experimental

A General Electric type A-H6 high-pressure mercury arc was used as light source. The lamp operates on 840 v. and at a power level of about 1 kw. The radiation below 3000 Å. amounts to about 9% of the power input. Since the useful life of the lamps in the low wave length region was short, at most about 12 hours, it was necessary to check each lamp frequently by making standard exposures of barium nitrate. It was not enough to observe that the arc was struck, for a lamp apparently operating normally might emit no light at

all effective in causing nitrate decomposition. Ellis⁷ and Gillam and Morton⁸ have also noted that the deterioration of mercury lamps begins in the low wave length region. Because of the short life of the arcs, individual exposure periods were kept below two hours. Longer exposures would have made it impossible to complete certain series of experiments with a single lamp.

The reaction vessel was a cylindrical fused-silica tube, 15 cm. long and 2.5 cm. in diameter. A silica-to-Pyrex graded seal was interposed between the reaction vessel and a standard-taper ground glass joint that served to attach the reaction vessel to a vacuum system. The reaction vessel was surrounded by a specially constructed furnace with two polished silica windows through which radiation was admitted. The mercury arc was permanently installed at a distance of 8 cm. from the reaction vessel. A mask made from aluminum foil with a slit 0.9×7.7 cm. was placed over the uppermost silica plate in order to define the incident beam.

Solutions of nitrates were used to establish the light fluxes. To keep the solutions from boiling during irradiation, it was necessary to maintain a rapid circulation of water around the reaction vessel. Warburg⁹ has reported the quantum efficiency to be 0.25 at 2070 Å. and 0.17 at 2540 Å. with a sharp drop at longer wave lengths. We observed that 0.07 to 0.08 *N* solutions of KNO_3 , NaNO_3 , $\text{Sr}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ undergo equal amounts of decomposition for equal irradiation. This observation lends support to the idea that light-absorption and the subsequent decomposition in solution, at least, involve principally the nitrate ion.

The salts used in this investigation were of the highest purity available. After being ground to a fine powder in a mortar, they were dried at 105° to constant weight and were stored over anhydrous calcium sulfate. Those nitrates which were obtained initially as hydrates were heated in a vacuum oven at 40° for two to four hours prior to drying at 105° . An appropriate sample was weighed into the reaction vessel and the vessel was attached to the vacuum system. The pressure was ordinarily reduced to 10^{-5} mm. and the temperature of the furnace was, if necessary, brought to the desired point before the arc was turned on.

After illumination of the salt, the gaseous product was removed by a Toepler pump and its amount was determined. The residue left in the reaction vessel was dissolved in water and the content of nitrite determined by modification of the method of Shinn.¹⁰ Since we found the absorption curve of the coupling product formed between diazotized *p*-aminobenzene sulfonamide and *N*-(1-naphthyl)-ethylene diamine dihydrochloride to have a maximum at 5400 Å., we determined the extinctions at this wave length.

Barium nitrate was more extensively studied than the other salts. The amount decomposed increased linearly with time up to about 1% decomposition (the upper limit reached for this salt in our studies). Fine powder (100–200 mesh) decomposed about 30% faster than large crystals (retained by a 16 mesh screen). This difference is ascribed to more complete absorption of light by the smaller crystals.

Under similar circumstances, cesium nitrate decomposes more rapidly than barium nitrate and there is a pronounced falling off of the rate of nitrite formation after about 3% of

(1) General Electric Co., Pittsfield, Mass.

(2) L. K. Narayanswamy, *Trans. Faraday Soc.*, **31**, 1411 (1935).

(3) A. O. Allen and J. A. Ghormley, *J. Chem. Phys.*, **15**, 208 (1947).

(4) K. S. Krishnan and A. C. Guha, *Current Sci. (India)*, **2**, 476 (1934).

(5) I. Maslakowicz, *Z. Physik*, **51**, 703 (1928); H. Ley and F. Volbert, *Z. Physik. Chem.*, **130**, 308 (1927).

(6) K. Schaeffer, *Z. anorg. Chem.*, **97**, 285 (1916).

(7) C. Ellis and A. A. Wells, "The Chemical Action of Ultraviolet Rays," Reinhold Publishing Corp., New York, N. Y., 1941.

(8) A. E. Gillam and R. A. Morton, *J. Soc. Chem. Ind.*, **46**, 415 (1927).

(9) E. Warburg, *Sitz. ber. preuss. Akad. Wiss. Physik. math. Klasse*, **1228** (1918).

(10) M. B. Shinn, *Ind. Eng. Chem., Anal. Ed.*, **13**, 33 (1941).

the salt has decomposed. A rather unreliable extrapolation indicates that at about 20 to 30% decomposition the rate would become zero. Had the decomposition of the barium salt been carried as far as that of the cesium nitrate, its rate might have shown a decrease also. Such a finding would be consistent with the estimate⁸ of a steady state at 40% decomposition when barium nitrate is subjected to a beam of 1.2 mv. electrons.

When the temperature of the irradiation vessel was brought initially to a value between 30° and 250°, the rate of decomposition of barium nitrate was changed less than 20%. The decomposition, therefore, is photal rather than thermal.

Narayanswamy found that different nitrates were decomposed at different rates when exposed to the same light source. We sought to confirm these effects. Our results appear in Table I. The figures represent averages of two or more determinations for each substance. The results¹¹ secured with different lamps were combined by comparing the decomposition of the standard substances, potassium nitrate, sodium nitrate and barium nitrate. These comparisons provide a way of correcting for the differing radiant efficiencies of the lamps. The hydrated lanthanum nitrate, it may be noted, was used as received without preliminary drying. The starting pressure of residual gas in the reaction vessel, when this salt was used, was higher than for the other substances.

TABLE I

RELATIVE RATES OF DECOMPOSITION OF SEVERAL NITRATES UNDER COMPARABLE LIGHT CONDITIONS

Salt	Relative rate of nitrite formation	Approximate quantum yield
CsNO ₃	14.0 ^a	0.19
La(NO ₃) ₃ ·6H ₂ O	9.0	.12
KNO ₃	7.5	.098
Ba(NO ₃) ₂	3.6	.048
La(NO ₃) ₃	3.1	.041
Pb(NO ₃) ₂	2.8	.037
AgNO ₃	2.7	.036
NH ₄ NO ₃	2.2	.030
Sr(NO ₃) ₂	1.0	.013
NaNO ₃	0.8	.011
LiNO ₃	0.16	.002

^a Initial rate.

The quantum yields given in Table I are based on 0.20 as quantum yield of nitrite from nitrate solutions, and on the assumption that the absorption in the solid salts is the same as in the solution. Since no allowance has been made for scattering losses, the listed quantum yields are not of high accuracy.

It will be observed that hydrated lanthanum nitrate decomposes more rapidly than the anhydrous salt. The same effect of water of hydration in promoting photodecomposition was noted with calcium nitrate. Calcium nitrate is dispensed as the tetrahydrate. When samples of that hydrate were placed in the reaction vessel and pumped for varying lengths of time before illumination, the following amounts of nitrite were obtained: with no pumping, 5.0 mg.; after 12 hours, 1.7 mg.; after 17 to 71 hours, 1.3 mg.

Narayanswamy listed the nitrates in order of increasing sensitivity to light as follows: NH₄NO₃, Pb(NO₃)₂, Al(NO₃)₃, Cd(NO₃)₂, Ba(NO₃)₂, Sr(NO₃)₂, NaNO₃, KNO₃.

We found the order: LiNO₃, NaNO₃, Sr(NO₃)₂, NH₄NO₃, AgNO₃, Pb(NO₃)₂, La(NO₃)₃, Ba(NO₃)₂, KNO₃, La(NO₃)₃·6H₂O, CsNO₃.

It is possible that some of the disagreement between the two lists arises from differences in degree of desiccation of the salts. Narayanswamy does not report whether or how he dried his materials, and even if they were initially dry he presumably exposed them in open vessels with an accompanying possibility that some absorbed moisture from the air before and during illumination. Our procedure avoided such uncertainty.

Discussion

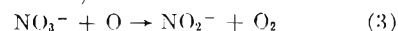
The rates of decomposition of the alkali nitrates as given in Table I increase from lithium to cesium, that is, they increase with increasing size or with decreasing field strengths of the cations. Ammonium nitrate is observed to be more stable than potassium nitrate, although these two salts have nearly equal molar volumes. However, as other properties show¹² the polynuclear ammonium ion does not exhibit the same field strength as an alkali ion of comparable size. Also of interest is the result that silver nitrate decomposes faster than sodium nitrate, although their molar volumes do not differ much. The polarization properties of silver ion, however, which has an 18-electron outer shell, are very different from those of sodium ion, which is of the noble gas type.¹³

Similar interrelations can be found for the nitrates of doubly charged cations. Strontium nitrate decomposes more slowly than barium nitrate because the field of barium ion is weaker than that of strontium ion. On the other hand, although strontium and lead nitrates have nearly equal molar volumes, their decomposition rates are different because lead does not have a noble gas type structure.

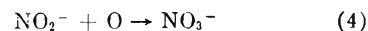
The positions in Table I of the nitrates of strontium and barium as compared with those of sodium and potassium are in accord with the relative tightening, derived from refractivity data on silicates,¹⁴ exerted on anions by the doubly and singly charged cations.

While the above facts clearly indicate that the decomposition of the nitrate ion is dependent on the field strength of the cation, to which it is bound in the anhydrous crystal, it would be premature to draw further conclusions concerning the nature of the interionic interaction involved. It suffices to add that the greater decomposition rate of the nitrate ion in aqueous solution as well as in hydrated nitrates, as compared to the anhydrous nitrates, might be related to the fact that the field of the water dipoles, separating the nitrate ions from the cations, is weaker than that of the latter.

Narayanswamy has suggested that the effect of the absorbed light is to detach oxygen atoms from nitrate ions.² Once released the oxygen atoms seem to have two principal courses open to them. They can either combine with each other or they can react with other nitrate ions,



A possible reversal of the initial dissociation would be



The absence of any considerable temperature effect in the photolysis suggests that reactions (3) and (4) either do not occur or occur with equal energies of activation.

The oxygen atoms, in any event, seem to end up as oxygen gas. Only part of the gas appears during illumination; the rest can be pumped off in the course of two hours following the cessation of illumination provided the salt is kept at 100°. At the

(12) K. Fajans and O. Johnson, *J. Am. Chem. Soc.*, **64**, 668 (1942).

(13) K. Fajans, *Ceram. Age*, **54**, 288 (1949).

(14) K. Fajans and N. J. Kreidel, *J. Am. Ceram. Soc.*, **31**, 105 (1948).

(11) More complete tables are listed in the Ph.D. thesis of P. Doigan, New York University, 1950.

end of two hours of pumping, the recovered gas closely matches the amount of oxygen expected on the basis of the nitrite analysis. Villars found only oxygen in the gases from photolyzed nitrate solutions.¹⁵ We were unable to identify any other component in the gas coming from the crystals.

(15) D. S. Villars, *J. Am. Chem. Soc.*, **49**, 328 (1927).

Essentially all the gas recovered was soluble in alkaline pyrogallol and essentially all of it was absorbed by hot copper.

Acknowledgment.—The authors gratefully acknowledge the assistance of Dr. Seymour Lewin and of Dr. Kasimir Fajans in the preparation of this report.

AN EXPLANATION OF "TACKYPYKNOSIS"

By R. N. THOMPSON

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Received October 15, 1951

It has been shown that the equilibrium torque measured by a rotational type viscometer on a thixotropic system is a function of the rate of shear and the amount of thixotropy in the system at that rate of shear. There will be a definite equilibrium torque for each shearing rate and these torques will only approach one another as the difference between the rates of shear approaches zero. The phenomenon which Van Wazer chose to call "tackypyknosis" is really not a distinct phenomenon. It is thixotropy and should be recognized as such.

Van Wazer and Besmertnik¹ in their paper on the "Action of Phosphates on Kaolin Suspensions" reported an anomalous flow phenomenon of deflocculated kaolin suspensions which they chose to call "tackypyknosis." They observed that when a deflocculated kaolin suspension "is contained in a viscosimeter in which the shearing rate is adjustable and the resulting shearing force is measured, it is found that upon the application of a fast rate of shear to the material, the resulting torque rises sharply and then slowly decreases from a high value to a constant value. If the shearing rate is suddenly lowered, the shearing force quickly falls away and then slowly increases again to practically the same constant value. When the speed remains constant, the shearing forces reach a given value which appears to be practically independent of shearing rate."

This phenomenon has been investigated by means of both a MacMicheal viscometer and a Hagan viscometer which is capable of producing much higher rates of shear than the MacMicheal instrument. In this investigation the Green² system of rheological analysis was used. The MacMicheal viscometer had instrumental constants $S = 0.011$ and $C = 0.027$ and could produce a maximum rate of shear of about 10 reciprocal seconds. The Hagan viscometer is a rotation type of viscometer wherein the bob is driven and the shearing force is measured on the cup. The instrumental constants for the cup and bob used were $S = 0.0036$ and $C = 0.0180$ and under these conditions produced a maximum shearing rate of about 533 reciprocal seconds.

Procedure

Paper coating grade kaolins were used in this investigation. They were deflocculated with sufficient glassy sodium metaphosphate so that the resulting suspensions were very fluid at 68% total solids. Rheograms were obtained for the suspensions on both the MacMicheal and Hagan viscometers,

thus obtaining the flow characteristics at both low and high rates of shear.

Three rheograms were obtained by first running the up curve to some predetermined rate of shear, allowing the shearing force to reach equilibrium at that rate of shear, and then running the down curve. Secondly, after allowing the kaolin suspension to return to its original condition, the above procedure was repeated only running the up curve to a higher predetermined rate of shear. Thirdly, after allowing the kaolin suspension to return again to its original condition, an up curve was run to the second or higher rate of shear; the rate of shear was held constant until the shearing force had reached equilibrium and then the rate of shear was decreased to the first or lower shearing rate which was again held constant until the shearing force had reached an equilibrium value.

Results

Figure 1 shows the rheograms obtained on the MacMicheal viscometer with a 68% total solids kaolin suspension. The angular velocity in radians per second may be converted into rate of shear in reciprocal seconds by multiplying by the constant 2.3. By plotting the time to go from T' to T_E' and the time to go from T_E to T_E' , Fig. 2 is obtained which corresponds to Van Wazer's example of "tackypyknosis." Figure 3 shows the rheograms obtained on the Hagan viscometer for the same kaolin suspension as reported in Fig. 1. The angular velocity in radians per second may be converted into rate of shear in reciprocal seconds by multiplying by the constant 4.8. It will be noted that T_E and T_E' no longer approach one another in value as they did at low rates of shear. The point T_E in Figs. 1 and 3 can be reached by several paths.

Discussion of Results

Green² has derived the equation for the equilibrium torque at a given rate of shear to be

$$T_E = T - \frac{B}{S} \omega \ln \left(\frac{t_E}{t} \right) \quad (1)$$

where T_E = equilibrium torque, T = maximum torque on up curve, B = coefficient of thixotropic breakdown with time, ω = angular velocity of cup or bob, t = time required to produce up curve, t_E = time required to reach equilibrium torque at a

(1) J. R. Van Wazer and E. Besmertnik, *This Journal*, **54**, 89 (1950).

(2) Henry Green, "Industrial Rheology and Rheological Structure," New York, N. Y., 1949.

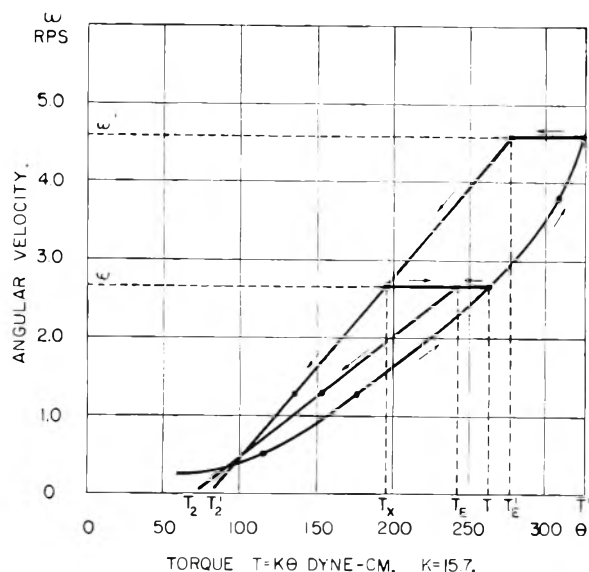


Fig. 1.

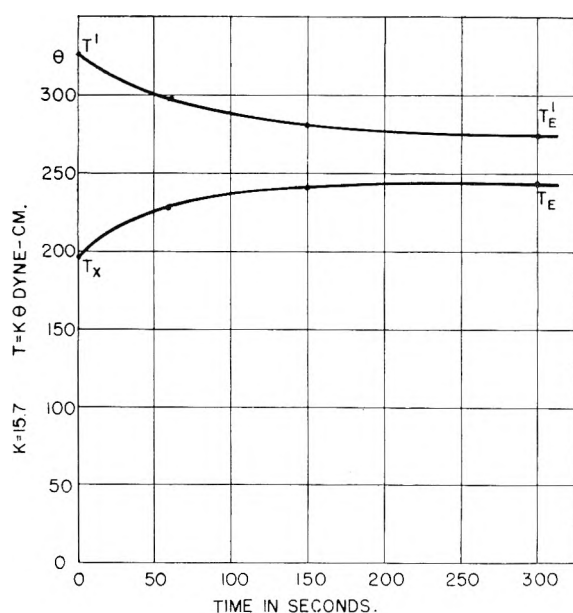


Fig. 2.

given angular velocity and S = an instrumental constant whose value is

$$\left(\frac{1}{R_b^2} - \frac{1}{R_c^2} \right) / 4\pi h$$

The plastic viscosity, U , of the system will equal

$$U = ((T - T_2)S) / \omega \quad (2)$$

where T_2 = intercept of the torque down curve with the torque axis. The yield value, f , of the system will equal

$$f = CT_2 \quad (3)$$

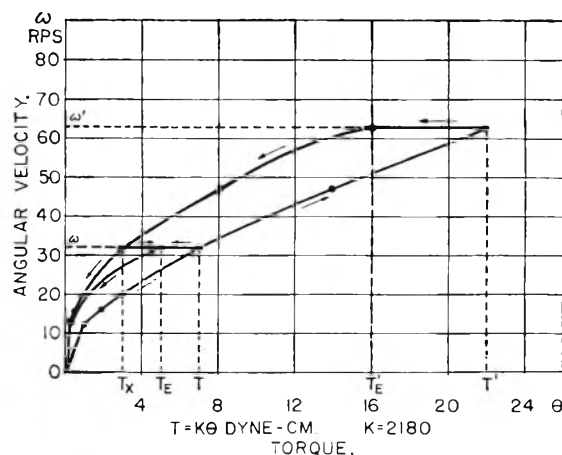


Fig. 3.

where C is an instrumental constant whose value is

$$\frac{S}{\ln(R_c/R_b)}$$

Rearranging equations (2) and (3) to solve for T and T_2 and substituting in equation (1) gives

$$T_E = \frac{f}{C} + \left[\frac{U}{S} \omega - \frac{B}{S} \omega \ln \left(\frac{t_E}{t} \right) \right] \quad (4)$$

Now the rate of shear, dv/dr , can be approximated when $R_c - R_b$ is small by

$$dv/dr = \omega k \quad (5)$$

where k is an instrumental constant

$$k = 1 / \left(2 \frac{(R_c R_b)^2}{2} h S \right) \quad (6)$$

where R_c = the cup radius, R_b = bob radius and h = bob height. Rearranging equation (5) to solve for ω and substituting in equation (4) gives

$$T_E = \frac{f}{C} + \frac{(dv/dr)}{k} \left[\frac{U}{S} - \frac{B}{S} \ln \left(\frac{t_E}{t} \right) \right] \quad (7)$$

Equation (7) gives a direct mathematical derivation of the equation for the equilibrium torque, T_E , in terms of yield value, rate of shear, plastic viscosity and coefficient of thixotropic breakdown with time. This shows that the equilibrium torque is not independent of the rate of shear as suggested by Van Wazer. This is confirmed by the results reported in Figs. 1 and 3. It can be seen from inspection of equation (7) that when the plastic viscosities are small and the difference between the two rates of shear approaches zero, the equilibrium torques at the two different shearing rates will approach each other. It can be seen from Figs. 1 and 2 that Van Wazer's "tackypyknosis" is merely a plot of part of the hysteresis loops caused by the thixotropic breakdown of the system being studied at different rates of shear.

ELECTRON MICROSCOPIC AND OTHER STUDIES ON A COPPER-CYSTINE COMPLEX

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Received October 20, 1951

Cystine added to formvar coated copper screens produces clumps of fine fibers. Similar fibers were obtained when cupric salts were added to a cystine solution and placed on formvar coated nickel screens. The fibers form upon drying and do not exist as such in solution. Their diameter is 85 Å. Various other amino acids were tried with copper, and various metal salts were mixed with cystine, but none gave a similar fiber formation. Two H⁺ ions are released for each copper-cystine complex formed, the ratio of copper to cystine in the complex being unity. The fibers were seen when the solutions varied in pH from 3 to 8.8. The complex in solution consists of small units which aggregate on vigorous blending into large fibers. The use of copper screens in the electron microscopic study of biological material which may contain cystine gives rise to the possibility of fibrous artifacts.

The fibrous state is of wide occurrence in biology, a few familiar examples being denatured proteins, collagen, cellulose, fibrinogen-thrombin clots and nucleic acid. The present report is concerned with fibers obtained from a complex of cystine and copper. There appears to be no reference to such fibers in the literature. In addition, this study deals with the stoichiometric and other properties of the copper complex in solution.

Copper-cystine (CuC₆H₁₀N₂O₄S₂) in the form of needles was prepared and analyzed for copper content about 50 years ago.^{2,3,4} Ray and Sen⁵ made determinations of magnetic moment on 3:3 copper complexes including a copper-cystine, (CuC₆H₁₀N₂O₄S₂·2H₂O). Numerous studies of complex formation between copper and other amino acids, notably glycine,⁶⁻¹³ have emphasized the change in type of complex formation with change in pH.

Materials.—An aqueous solution of cystine (Nutritional Biochemicals Corporation) was made up 0.000425 molar, which is slightly less than saturated, as a stock solution. The copper screens (Lektro-mesh) as used in the following electron microscopic experiments appeared to be coated with a light superficial film of copper salts but no attempt at analysis was made. The nickel screens (C. O. Jelliff Mfg. Corp.) were spectrographically analyzed (Mineral Technology Division, P. M. Ambrose, Chief, U. S. Bureau Mines). This disclosed the presence of 1% copper and less than 0.05% chromium.

Experimental.—Drops of the cystine solution were put on copper screens coated with formvar and after being dried were found by use of the electron microscope (type EMU) to give rise to the characteristic hexagonal plates of cystine and a large number of fine fibers of high density, usually occurring in clumps. (Similar results were obtained when the cystine was recrystallized four times from water, and from a specially purified preparation kindly donated by Dr. J. P. Greenstein.) When drops of the same cystine solution were dried on nickel screens no fibers were observed. Fibers were also obtained by immersing a copper wire in a

cystine solution. Since the use of copper in the reduced state (metal) with cystine probably involves a set of oxidation-reduction reactions,¹¹ the use of cupric salts with cystine would be a chemically simpler system, free from oxidation complications.

Solutions of cupric chloride, nitrate, sulfate or acetate when added to the cystine solution and dried on formvar coated nickel screens gave rise to fiber production (Fig. 1a) if the molar ratio of copper to cystine was in the neighborhood of unity. If the ratio deviated from unity by a factor of ten in either direction, the fibers became very scarce. These tests indicated that the cystine diffused through the formvar film and reacted with copper ions to form a copper-cystine compound.

Measurements of Size.—The lengths of the fibers seem to be a function of the method of preparation and treatment, very dilute solutions giving fibers of shorter lengths. The diameter of the fibers was determined by methods previously described for tobacco mosaic measurement.¹⁴ For measurement of fiber width the most accurate results were obtained by measuring across a group of contiguous fibers and dividing by the number of fibers, while for the determination of height shadow methods were used. However, while tobacco mosaic particles are quite rigid, the rod shaped particles lining up in close juxtaposition, the copper-cystine fibers have a greater tendency to coil and there are relatively few situations where good measurements can be made on particles lined up side by side. On prolonged searching several groups of fibers in close juxtaposition were found for which a width measurement of 85 ± 10 Å. was made. The heights were determined by the double shadow method,¹¹ 20 fibers giving a height of 85 ± 5 Å., the height and width measurements being equal.

Other Materials.—Copper chloride was mixed with a series of other amino acids: alanine, arginine, cysteine, glycine, glutamic acid, histidine, lysine, methionine, phenylalanine, serine, tyrosine and valine. None of these mixtures gave the fine fibrous structure of copper-cystine.¹⁵

Cystine was mixed with a series of metallic salts, cobaltous chloride, ferric chloride, mercuric chloride, nickel chloride, platinous chloride, potassium platinous chloride, silver nitrate, stannous chloride, uranyl nitrate and zinc chloride. These gave no evidence of fine fiber formation.

Cupric chloride alone acidified with HCl to pH 4 gave no indication of fibers.

The outstanding characteristic of the copper-cystine complex as compared to other metallic complexes, for example nickel-cystine, is its tendency to polymerize linearly on concentration and drying.

Electrometric Titrations.—Graphs of a series of titrations of cupric chloride plus acidified cystine against NaOH are shown in Fig. 2. Successive curves correspond to increasing proportions of CuCl₂ added to a constant large volume of acidified

(1) Public Health Service, National Institutes of Health, Federal Security Agency.

(2) G. Eubden, *Z. physiol. Chem.*, **32**, 94 (1901).

(3) J. Mauthner, *Z. Biol.*, **42**, 176 (1901).

(4) C. Neuberg and P. Mayer, *Z. physiol. Chem.*, **44**, 502 (1905).

(5) P. Ray and D. N. Sen, *J. Indian Chem. Soc.*, **25**, 473 (1948).

(6) A. Albert, *Biochem. J.*, **47**, 531 (1950).

(7) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," Copenhagen, 1941.

(8) H. Borsook and K. V. Thimann, *J. Biol. Chem.*, **98**, 671 (1932).

(9) H. Flood and V. Loras, *Tidsskr. Kjem. Berg. og Metallurgi*, **5**, 85 (1945).

(10) R. Keeler, *J. Am. Chem. Soc.*, **68**, 2329 (1946).

(11) C. C. Lucas and J. M. R. Beveridge, *Biochem. J.*, **34**, 1356 (1940).

(12) L. E. Maley and D. P. Mellor, *Nature*, **165**, 453 (1950).

(13) H. L. Riley and V. Gallafent, *J. Chem. Soc.*, 2029 (1931).

(14) H. Kahler and B. J. Lloyd, Jr., *J. Appl. Phys.*, **21**, 699 (1950).

(15) Dr. W. Moos working in this laboratory with extracts of *Bacterium Pseudomonas aeruginosa*, has found large amounts of filamentous material attributable to a reaction between the extract and copper screens. A report of this work was published in the *Journal of Bacteriology* **52**, 767 (1951).

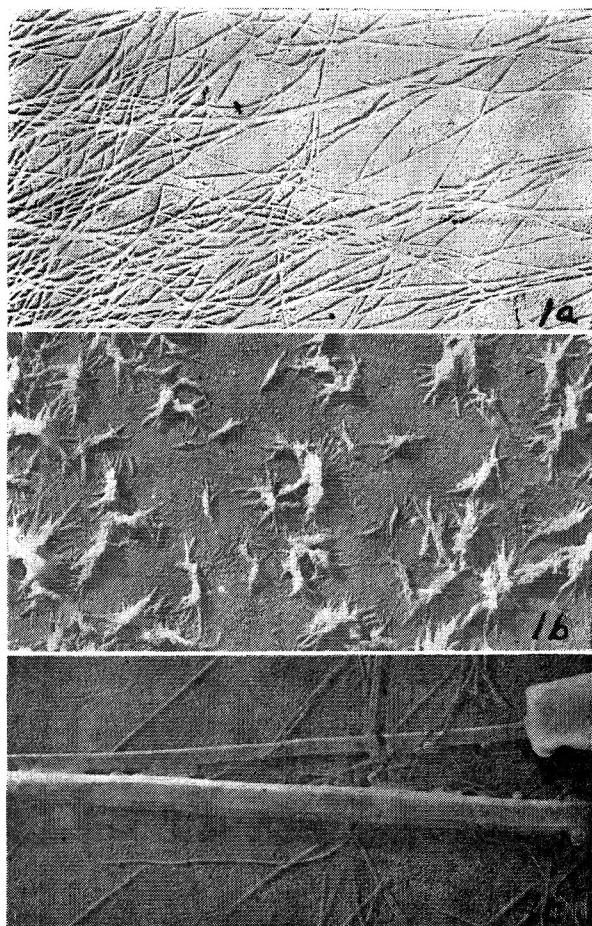
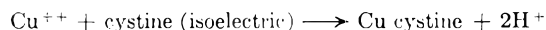


Fig. 1.—(a) Equal mixtures of 0.000425 *M* CuCl_2 and cystine on formvar coated nickel screens. Cr. shadowed. (b) Same as above except solution sprayed on screen in fine droplets. (c) Equal volumes of solutions of copper chloride and cystine (0.000425 *M*) stirred in motor-driven blender for 15 minutes. Large fibers near middle of photo. Cr. shadowed.

cystine. When the copper to cystine ratio attains a value unity, curve III, the titratable H^+ ions have reached their maximum value, two per complex. Curves IV and V indicate the formation of basic copper chlorides above pH 6.5 in the presence of an excess of copper. The formation of the complex appears to be complete at pH 6 dropping to a few per cent. at pH values near 3 as judged from a comparison of curves I and III.¹⁶ These considerations suggest as the over-all equations



copper and cystine chelating in a 1:1 ratio, 2 moles of H^+ ions being released for each mole of complex formed.

A graph of the acidimetric titration of cupric chloride against cystine is shown in Fig. 3. The drop in pH with formation of copper-cystine is symmetrical for the two halves of the curve. This is explicable, in view of the above, on the assumption that both the hydrogen ions liberated and the buffering of the solution are determined by the number of complexes formed, which will be the same at

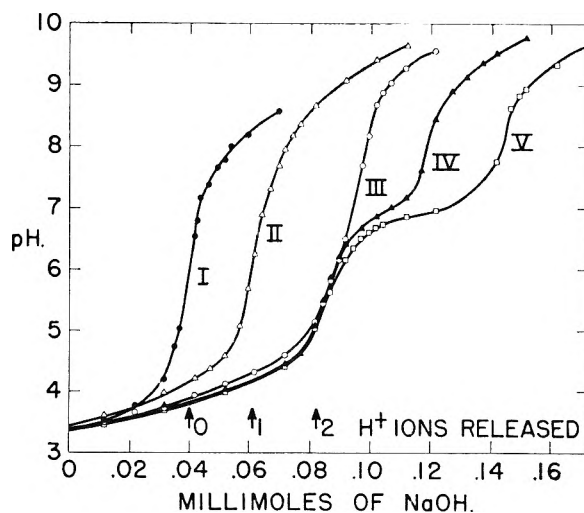


Fig. 2.—To 50-ml. aliquots containing 0.02125 millimole acidified cystine were added the following number of millimoles of CuCl_2 (in concentrated solution): curve I, 0.0; curve II, 0.0106; curve III, 0.02125; curve IV, 0.0318; curve V, 0.0425.

corresponding mole fractions at either end of the curve. This leads again to a 1:1 copper-cystine ratio.

Conductance.—Cupric chloride and cystine solutions 0.000425 *M* were mixed in a series of volume ratios and the conductance measured at 23° with a Jones Bridge (Fig. 3). Asymptotes drawn at the ends of the curve intersect near the mole fraction 0.5 which is consistent with a 1:1 ratio for copper and cystine in the reaction.

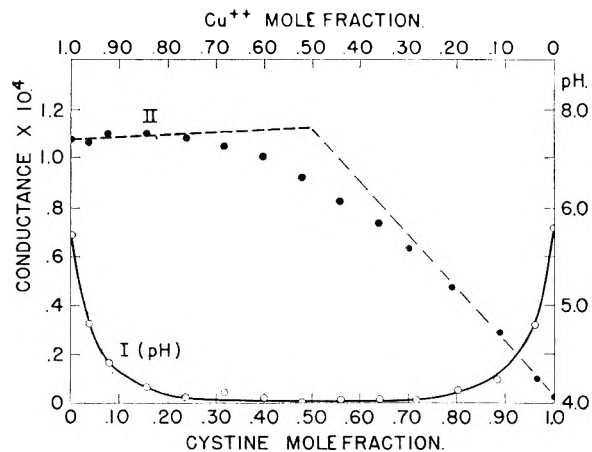


Fig. 3.—Curve I: pH titration of mixtures of 0.000425 *M* cupric chloride and cystine showing rapid drop in pH (release of hydrogen ions) with complex formation. Symmetry of curve indicates 1:1 ratio of copper and cystine in complex. Curve II: conductance of same solutions. Dashed lines intersect at mole fraction 0.5 or 1:1 ratio.

None of these considerations prove that (1) is the only reaction at pH 4 (the pH of a 1:1 mixture), the question of intermediate reactions being left open.

Similar results were obtained with copper sulfate and cystine.

Formation of Fibers.—Experiments were performed to see if the fibers visible under the electron microscope could be identified in solution or whether they were built up in the drying process on the screens. (1) Aqueous solutions 0.00021 *M* in CuCl_2 and cystine, pH 4, showed no significant

(16) J. Z. Hearon, D. Burk and A. L. Schade, *J. Nat. Cancer Inst.*, **9**, 337 (1949).

light scattering; (2) it was not possible to produce any sedimentation of fibers in the ultracentrifuge at 200,000 G for two hours; (3) finally the solution was sprayed on to the screens in the form of droplets a few microns in diameter, the fine drops drying in a matter of seconds.¹⁷⁻¹⁹ Electron micrographs (Fig. 1b) show many short fibers in contrast to the long fibers (Fig. 1a) resulting when large drops of the solution slowly dry on the former coated screens. These three tests indicate that the long fibers form upon drying or concentration and that they do not pre-exist in dilute solutions.

On the other hand, such a clear solution if stirred in a motor operated blender for 15 minutes becomes turbid and the electron micrographs show many broad filaments (Fig. 1c) which form a bulky precipitate on standing for an hour.

A similar treatment in the blender of nickel chloride and cystine failed to produce any noticeable turbidity.

The pH of 1:1 mixtures of cystine and cupric chloride was varied from 2 (with HCl) to 8.8 (with borate buffer). Below pH 3 no fibers were present, a few appearing at 3 and large numbers were present from 4 to 8.8. This indicates that the formation of fibers parallels the formation of the complex (Fig. 2, curve III). The formation of fibers at pH 8.8 took place irrespective of the order in which the three solutions of cupric chloride, sodium borate and cystine were mixed together.

Solutions standing for three days in the presence of air showed no change in pH from the original value 4.0.

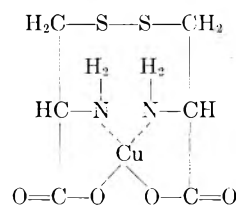
To follow the changes in pH and fiber formation which took place upon drying the following experiment was performed. One-half liter each of 0.000425 M CuCl_2 and cystine solutions were mixed in a flat dish 25 cm. in diameter which was placed so that a stream of filtered dry air from an air conditioning duct was incident upon the surface of the solution. As the solution dried to a smaller volume the pH was measured at suitable time intervals and the solution examined under the electron microscope for the presence of fibers. Starting with an initial pH value of 4 and a volume of 1000 ml., the pH dropped in a linear fashion with a decrease in volume down to about pH 3.3, volume 160 ml. Below this point the pH dropped more rapidly until at a volume of 20 ml. the pH was 2.64. Fibers were still present when drops of the solution pH 3.18 were examined but none were visible at pH 2.91 and below. The solution itself was always clear, but a steady accumulation of bluish material collected on the bottom of the dish. At the end of the experiment the solution was poured off, the dish washed four times with distilled water to remove CuCl_2 , the dish dried

and a replica made of the flat bottom of the dish. This replica under the electron microscope showed the typical Cu-cystine fibers. The clear solution pH 2.64 which showed no fibers, was brought up to pH 5 with sodium acetate, large numbers of fibers now being visible.

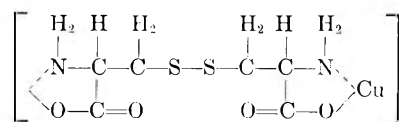
From this experiment we may conclude the following: As the solution evaporates, the pH drops steadily with the concentration of HCl. Fibers are precipitated during the concentration of the solution in the pH range above 3. In the final stage of evaporation the pH is too low for fiber formation which agrees with the titration data on complex formation. The reaction below pH 3 being incomplete, free CuCl_2 and cystine are present which will react to form fibers if the pH is raised to 5.

Discussion

Based on the foregoing evidence it is assumed that complex formation without polymerization occurs in dilute solutions. The structure of this complex may be written as



the copper chelating intramolecularly in two 5-membered rings. The formation of a polymer, on drying, suggests that the structure unfolds, each copper now chelating 2 rings intermolecularly giving a chain of indefinite length



The width of the fibers, 85 Å., indicates that some folding or side linkage takes place.

Work has been started on the structure of the copper-cystine fibers using X-ray and electron diffraction. The results of this will be reported at a later date.

(17) G. Riedel and H. Ruska, *Kolloid-Z.*, **96**, 86 (1941).

(18) A. M. Cravath, A. E. Smith, J. R. Vinograd and J. N. Wilson, *J. Appl. Phys.*, **17**, 309 (1946).

(19) R. C. Backus and R. C. Williams, *ibid.*, **21**, 11 (1950).

SORPTION OF GASES ON METAL POWDERS AND SUBSEQUENT CHANGE IN METAL REACTIVITY AT ROOM TEMPERATURE¹

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Received October 22, 1951

The amounts of Cl_2 , NO_2 , O_2 and CO taken up by powders of stainless steel, nickel and molybdenum were measured at room temperature. Only CO was truly adsorbed on stainless steel and nickel powders forming a chemisorbed monolayer. All other gases appeared to have first adsorbed, then diffused inward, and finally reacted with the metals as suggested by the pressure dependence and irreversibility of the multilayer uptakes. Reactivities of metal powders in terms of hydrogen evolution in dilute acid solutions in the absence of air were determined for reduced stainless steel, nickel and chromium powders when they were bare, with CO adsorbed, or when covered with sorbed oxygen. The chemisorbed CO or the sorbed oxygen, both in limited quantity, altered only the induction period but did not change the ultimate rate of dissolution. Sorbed oxygen retarded the dissolution of stainless steel and nickel but had the opposite effect on chromium. Chemisorbed CO increased the induction period for stainless steel slightly, and that for chromium appreciably. In the case of nickel, the chemisorbed CO retarded the dissolution at first but increased it afterwards.

Introduction

The electrochemical behavior of an iron electrode was reported to alter markedly as a result of sorption of oxygen.² Contact potentials of freshly evaporated metal films have recently been found to be affected by surface sorption of gases.^{3,4} The chemical behavior of metal surfaces may also be expected to be different before and after sorption of gases. This paper reports the sorption of oxygen, carbon monoxide, nitrogen dioxide and chlorine on stainless steel, molybdenum and nickel powders. It also describes the subsequent effect of sorption of oxygen and carbon monoxide on the reactivity of stainless steel, nickel and chromium powders in terms of relative rate of hydrogen evolution in dilute acid solutions in an air-free system at room temperature.

Experimental

Apparatus and Procedure.—Sorption measurements were made on both unreduced and reduced metal powders in an apparatus using a McBain-Bakr type quartz-spiral spring as described in an earlier paper.⁵ Reactivity measurements were made only on the reduced samples; freshly reduced and degassed samples were designated as "blank." After a known amount of gas was sorbed on a given sample, the sorption bulb was transferred without exposure to the atmosphere to another evacuated system. Here the metal powder was allowed to react with either air-free dilute sulfuric or hydrochloric acid. The hydrogen thus evolved was measured with a mercury manometer. The concentration of the acid was so adjusted as to give a convenient rate of hydrogen evolution to be measured and compared. Reactivities of blank samples were determined at frequent intervals during the course of this study.

Molybdenum powder was found to react with either dilute sulfuric acid or dilute hydrochloric acid too slowly to make any reliable measurement. The reactivity of chromium powder with or without gas sorbed was also compared although no sorption isotherm was made. The surface areas of the metal powders were measured by adsorption of krypton at liquid air temperature.

Materials.—The stainless steel powder and all the gases used except krypton were the same as described previously.⁵ The krypton was purchased from the General Electric Company, Lamp Department, Cleveland, Ohio. It was free of

active gases and contained less than 0.1% neon. The nickel powder was obtained from the International Nickel Company, Inc., New York. It was made by reduction of nickel carbonyl at high temperatures, had an average diameter of 7 μ , and was of very high purity. The molybdenum powder, supplied by the Westinghouse Electric Corporation, Lamp Division, Bloomfield, New Jersey, was hydrogen reduced, had an average diameter of 2 μ , and a purity claimed to be greater than 99.9%. Chromium powder was prepared in this Laboratory from spectroscopically pure chromium electroplate.⁶

All metal powders were degassed three times with hot benzene and then dried in air at room temperature. The pretreatment for unreduced stainless steel powder included degassing in a vacuum better than 10^{-5} mm. and then baking at 450° under vacuum for 6 to 8 hours. Unreduced nickel and molybdenum powders were degassed and baked under high vacuum for 4 to 6 hours at about 200° because it was found that those powders would sinter by prolonged heating above this temperature. Samples obtained by heating with tank hydrogen at baking temperature for two hours and then degassing thoroughly are designated as "reduced," although this reduction process may not have been completely effective as will be seen later in the paper.

The surface areas of the reduced metal powders are shown in Table I, the B.E.T. plots, in Fig. 1. The cross-sectional

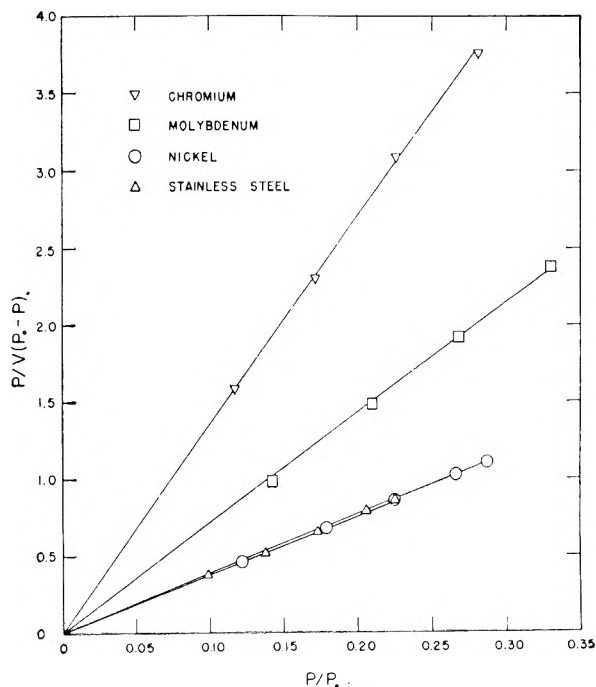


Fig. 1.—B.E.T. plot of adsorption of krypton on metal powders at liquid air temperature.

(1) This paper is based in part on a dissertation by H. L. Wang presented to the faculty of the Graduate School of the University of Texas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) R. Burshtein, N. Shumilova and K. Golbert, *Acta Physicochim. U.S.S.R.*, **11**, 785 (1946).

(3) N. Hackerman and L. L. Antes, *Science*, **112**, 471 (1950).

(4) J. C. P. Mignolet, *Faraday Society Discussion*, **8**, 105 (1950).

(5) A. L. McClellan and N. Hackerman, *This Journal*, **55**, 374 (1951).

area for krypton molecule was taken to be $20.8 \text{ \AA}^2$ as recommended by Davis, DeWitt and Emmett.⁶

Results and Discussion

Sorption.—The results of the sorption measurements on unreduced and reduced metal powders are shown in Figs. 2 to 7. A single metal sample

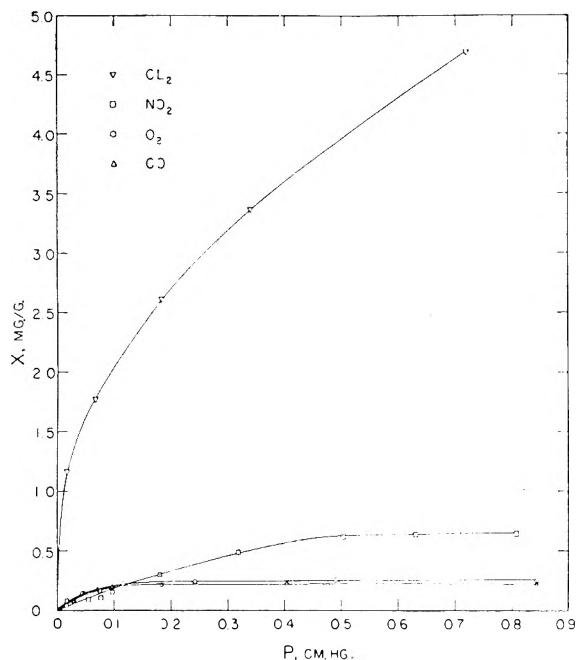


Fig. 2.—Sorption of gases on unreduced stainless steel powder at 32° .

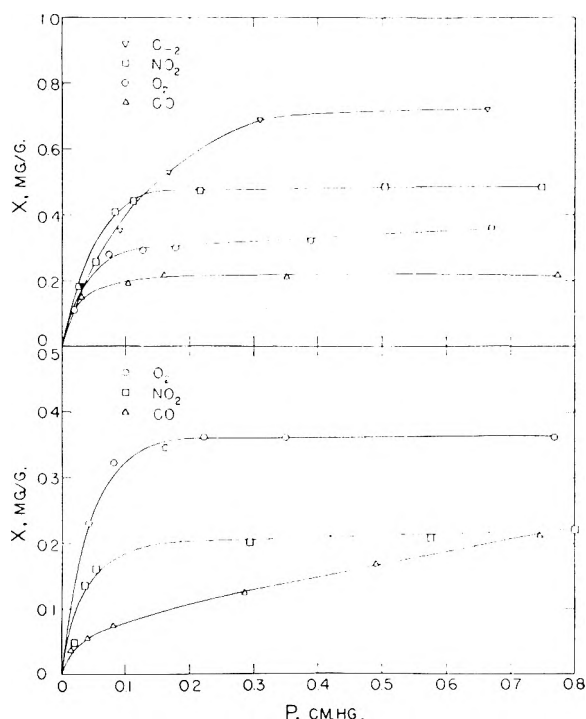


Fig. 3 (upper).—Sorption of gases on unreduced nickel powder at 33° .

Fig. 4. (lower).—Sorption of gases on unreduced molybdenum powder at 34° .

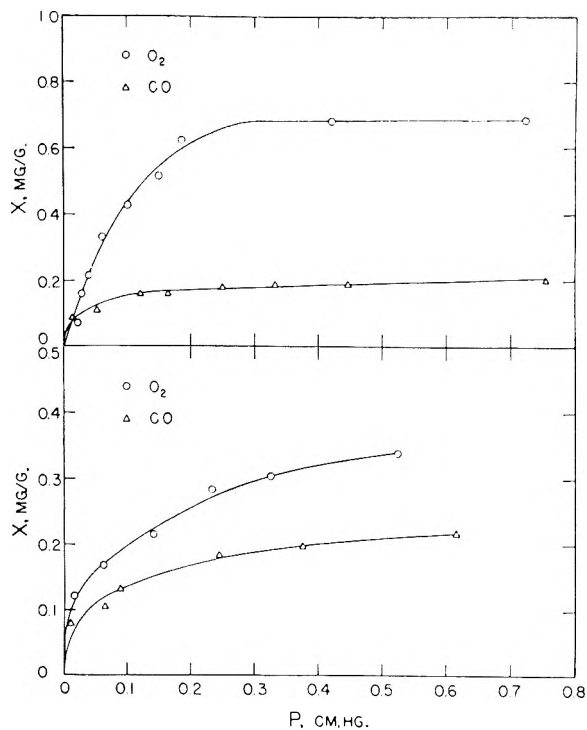


Fig. 5 (upper).—Sorption of gases on reduced stainless steel powder at 27° .

Fig. 6 (lower).—Sorption of gases on reduced nickel powder at 25° .

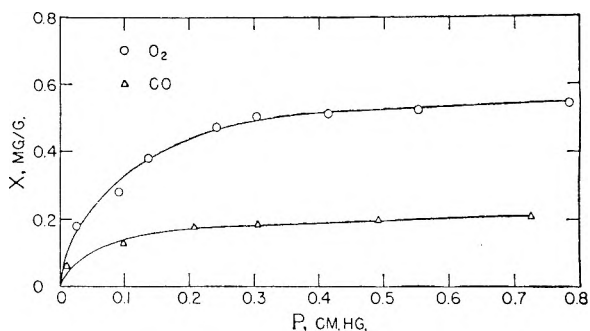


Fig. 7.—Sorption of gases on reduced molybdenum powder at 25° .

was used for most of the isotherms, in one or two cases more than one metal sample was used with no noticeable effect. The quantities of gases sorbed on unreduced stainless steel and nickel powders can be arranged in the order: $\text{Cl}_2 > \text{NO}_2 > \text{O}_2 > \text{CO}$ for both. However, the amount of chlorine taken up on nickel was much less than that on stainless steel. For the unreduced molybdenum powder the order was: $\text{O}_2 > \text{NO}_2 > \text{CO}$; the data for chlorine were very erratic and not amenable to interpretation. Only oxygen and carbon monoxide were used with reduced metal powders. The uptake of oxygen on those powders was greater in all cases than with carbon monoxide. With the exception of chlorine on stainless steel, all sorption isotherms leveled off at higher pressures, many of them at less than 0.2 cm. The pick-up of chlorine took place rather slowly, twelve or more hours were sometimes required to reach the limiting sorption value, while this state was reached quite rapidly with oxygen, carbon monoxide and nitro-

(6) R. T. Davis, T. W. DeWitt and P. H. Emmett, *THIS JOURNAL*, **51**, 1232(1947).

gen dioxide, often within two hours. A good portion of the take-up occurred virtually instantaneously. Without exception, the uptake of gas in all sorption runs was irreversible in that the sorbate could not be removed by evacuating at room temperature *in situ* once it was taken up.

TABLE I

B.E.T. SURFACE AREAS OF THE METAL POWDERS

Metal powder	Surface area, m. ² /g.
Stainless steel	0.76
Nickel	.72
Molybdenum	.39
Chromium	.21

In order to illustrate the different nature of the gas sorptions studied, the amount sorbed at highest pressure used (0.8 cm.), where most of the sorption isotherms had leveled off, was calculated as number of layers of gas molecules taken up by the metal powders. The area occupied by a single molecule was calculated on the basis of hexagonal close packing, using liquid densities for all of the materials. The values used, in Å.²/molecule, were: oxygen, 14.1; chlorine, 21.1; carbon monoxide, 16.2; nitrogen dioxide, 15.0. The coverage data are shown in Table II. B.E.T. surface area determinations were made only on reduced metal powders, and in calculating the number of layers, it was assumed that the unreduced samples had very closely the same surface areas as the reduced ones.

TABLE II

COVERAGE OF GAS MOLECULES ON THE METAL POWDERS

Metal powder	Surface area, m. ² /g.	Calculated number of layers			
		CO	O ₂	NO ₂	Cl ₂
Unreduced stainless steel	..	1.0	0.9	1.7	11.1
Reduced stainless steel	0.76	0.9	2.4	...	..
Unreduced nickel	..	1.0	1.3	1.3	1.8
Reduced nickel	0.72	1.0	1.6	...	..
Unreduced molybdenum	..	1.9	2.5	1.1	..
Reduced molybdenum	0.39	1.8	3.7	...	..

It is seen from Table II that the sorption of carbon monoxide on stainless steel and nickel powders was different from the other gases on these metals and for all gases on molybdenum in two ways. In the first place, the amounts picked up on the reduced surfaces of those metals were nearly the same as those on the unreduced surfaces. In the second place, the sorbed carbon monoxide formed a monolayer on these two metal surfaces. From these observations and the fact that none of the sorption was reversible, the following points become clear: (1) the assumption that the surface areas of these metal powders were not appreciably altered by the reduction process employed was valid; (2) carbon monoxide was truly adsorbed on stainless steel and nickel powders, both reduced and unreduced, at room temperature forming a chemisorbed monolayer; and (3) the amount of carbon monoxide chemisorbed at room temperature can therefore be used to estimate the surface areas of these two metal powders.

The total areas covered by the carbon monoxide molecules on molybdenum powder, reduced and unreduced, were almost twice that calculable from the

B.E.T. value. The amounts sorbed on reduced and unreduced samples were again very nearly the same, however. The reason for this discrepancy is not clear, although it is possible that there was some reaction between the molybdenum powder and CO.

For sorbates other than carbon monoxide the situation was entirely different. With the exception of the sorption of oxygen on the unreduced stainless steel, the amounts of sorbate picked up were all more than a monolayer thick on their true surfaces as shown by Table II. This virtually eliminated chemisorption alone since this does not involve more than one molecular layer. The irreversibility of the sorption process observed on both unreduced and reduced samples suggested that neither simple condensation nor physical adsorption was involved, because such multilayers of this type could be pumped off. Since condensation and physical adsorption were apparently not factors, the only other alternative which could account for this irreversible uptake in excess of one molecular layer appeared to be diffusion of the sorbed gas into the metal (or *vice versa*) and subsequent formation of a reaction product.

Reactivity.—The reactivity measurements of the metal powders in terms of relative rates of hydrogen evolution in dilute acid solutions are shown in Figs. 8 to 10. Blank runs were made on freshly hydrogen-reduced and thoroughly degassed metal powders. Gas-sorbed runs were made on metal powders exposed to the particular gas at the highest pressure used, 0.8 cm., until equilibrium was reached. Although no sorption isotherm was available for chromium powder, the amounts of gases sorbed were determined at 0.8 cm. and found to be 2.0 layers for oxygen and 1.0 layers for carbon monoxide. All of the rate curves, including those for the blanks, ranging from 5 minutes for nickel in 0.5 N H₂SO₄ to 20 minutes for stainless steel in 2 N HCl, before a steady state of hydrogen evolution was attained. This was taken to mean the time required for displacement or reduction of the adsorbed gas molecules, removal of the oxide films, and the slow process responsible for hydrogen overvoltage. The pressure readings were reproducible to 1 mm. in the initial stages of each run and to less than 2% in the final stages.

From Figs. 8 and 9 it is seen that sorption of oxygen on stainless steel and nickel powders increased the induction periods and the hydrogen evolution was thus retarded. This is to be expected since the sorbed oxygen and the oxide films formed acted as a shield to the metal atoms and some time was required for their removal. Once the induction periods were over, metal powders with or without pre-exposure to oxygen dissolved at practically the same rate, suggesting that bare metal surfaces were then in direct contact with the acid solution.

The role played by the sorbed carbon monoxide on stainless steel and chromium is believed to be similar to that described above. The chemisorbed carbon monoxide on the metal surfaces had to be displaced first before the metal atoms were exposed to acid solution. The very appreciable increase

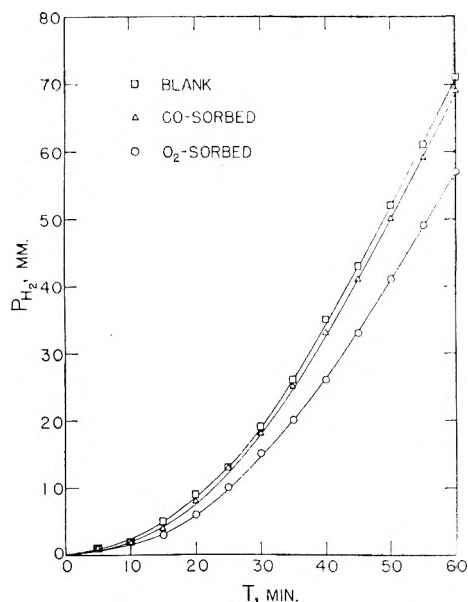


Fig. 8.—Reactivity curves for stainless steel powder in 2 *N* HCl at 33°.

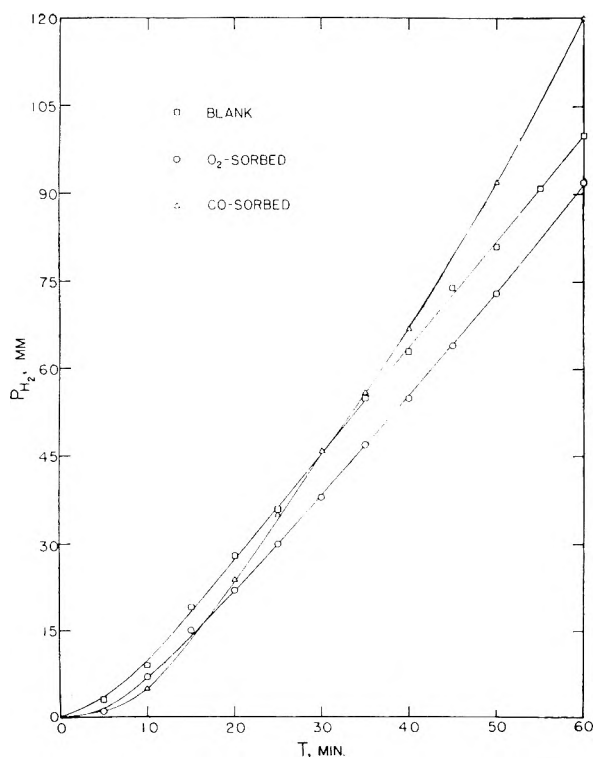


Fig. 9.—Reactivity curves for nickel powder in 0.5 *N* H₂SO₄ at 32°.

of the induction period for chromium suggests that the carbon monoxide molecules which were chemisorbed in the form of a monolayer adhered very strongly to the chromium surface. The CO monolayer on the stainless steel powder was less firmly held as indicated by the only slight increase in the induction period. The rates of hydrogen evolution after the induction period were again the

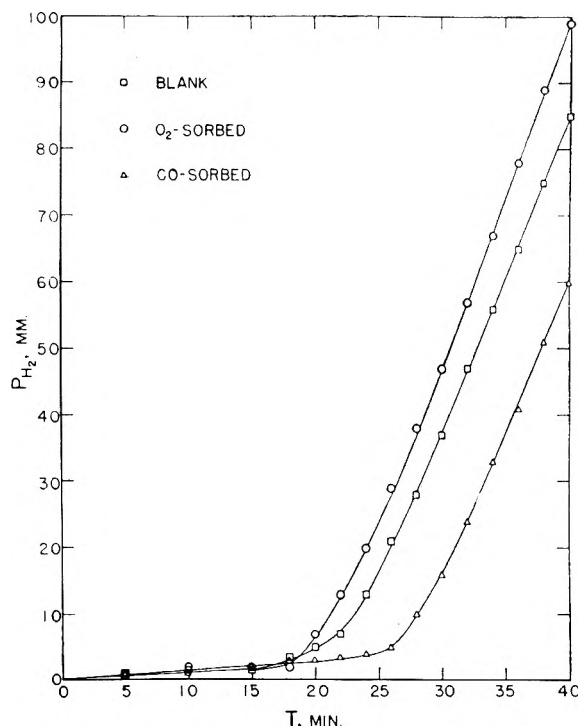


Fig. 10.—Reactivity curves for chromium powder in 1 *N* H₂SO₄ at 28°.

same as for the blank. Thus CO acted as an inhibitor for both stainless steel, as reported by Uhlig,⁷ and chromium, being much more effective in the case of chromium.

The CO chemisorbed on nickel reduced the rate of hydrogen evolution at first as expected but increased it afterwards unexpectedly. The latter effect was probably due to the presence of traces of impurities which were originally present or were redeposited from solution on the nickel surface. This would have reduced the hydrogen overvoltage and thus stimulated the hydrogen evolution. The oxygen film on chromium powder presented another unexpected result. The induction period was decreased instead of increased, but the rate of hydrogen evolution was unchanged after the induction period. The exact cause for this phenomenon is not clear. However, reduction of the Cr₂O₃ on the metal powder by hydrogen at 450° may have been ineffective as proposed by Pascal.⁸ Furthermore, Garner⁹ observed that hydrogen sorbed on Cr₂O₃ could not be completely removed even at 450°. Thus the effect may have been due not only to the fact that Cr₂O₃ was not removed but also to the fact that hydrogen was very strongly sorbed on the surface. This sorbed hydrogen could thus form an additional barrier for the metal powder and rendered the acid attack more difficult.

Acknowledgment.—The authors gratefully acknowledge the financial support of the Office of Naval Research under contract N5ori-136 T.O. II in carrying on this work.

(7) H. H. Uhlig, *Ind. Eng. Chem.*, **32**, 1490 (1940).

(8) P. Pascal, *Bull. soc. chim.*, **12**, 627 (1945).

(9) W. H. Garner, *J. Chem. Soc.*, 1239 (1947).

THE PHENOMENOLOGY OF ELECTRO-OSMOSIS AND STREAMING POTENTIAL¹

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All electrokinetic processes in a porous solid can be compactly described by two equations, with the four variables current, flow, pressure and voltage. Only three parameters are necessary: electrical conductance, permeability and the newly-defined *electropermeability*. Electropermeability can be expressed in terms of the " ζ -potential" but this is of doubtful value in electrokinetics. The three parameters are not completely independent, but are subject to the restriction that a certain quotient must be less than 1. The same quotient is an explicit expression for the electroviscous effect, and an analogous *electro-osmotic conductance effect*. Electrical conductance and permeability vary somewhat, and surface conductance can have very different values, depending on the conditions of measurement.

In connection with a study of the influence of surface forces on the flow of liquids through porous media, an investigation was undertaken of electrokinetic effects which influence this flow. It was found that previous work in this field could be more readily analyzed by developing a new formulation of electrokinetic relations. This has also been useful in predicting and interpreting new results. Electroviscosity and surface conductance, as well as the standard relations for electro-osmosis and streaming potential, are treated in the same unified development. The usual approximations that result from our incomplete knowledge of the electric double layer are avoided by basing the entire treatment on established experimental laws.

Basic Equations

The laws to start with are as follows.² When an electric field is applied to a liquid in capillaries, the rate of flow is proportional to the electric current or to the applied potential (Wiedemann's first law). If instead this flow is prevented, the electro-osmotic pressure is likewise proportional to the current or potential (Wiedemann's second law). On the other hand, when a liquid is forced through capillaries, the streaming potential or streaming current, depending on which is measured, is proportional to the pressure difference applied (Quincke's law). In recent times most of these classical laws have been confirmed quantitatively for a variety of solids and liquids, and for porous plugs as well as single circular capillaries.³⁻¹¹ Non-linear relations have been reported from time to time^{6,12-17} but

some have been found to be in error,^{5,9,11} and others have been attributed to dimensional changes in the capillaries^{12,18} or high-voltage effects similar to the Wien effect in electrolytic conduction.⁶ The present discussion applies only to those systems which do obey the classical laws, together with Ohm's law and Darcy's law.¹⁹

We postulate that when transport of liquid and transport of electric charge take place by simultaneous electrical and hydrodynamic processes, they combine by simple addition, as

$$I = C_{11}E + C_{12}P \quad (1a)$$

$$V = C_{21}E + C_{22}P \quad (1b)$$

where I = electric current through capillary system (taken as positive when it passes from side 1 to side 2); V = volume rate of fluid flow through system (in same sense); E = electric potential difference across system (taken as positive when side 1 is positive); P = pressure difference across system (taken as positive when it is high on side 1); and the C 's are experimental coefficients. Using different coefficients we might write instead

$$I = C_I E + C_V V \quad (2a)$$

$$V = C_I' I + C_P' P \quad (2b)$$

If hydrodynamic and electrical processes did not combine additively, there should be additional terms in the equations. However, the type of combination proposed explicitly in equations 1 and 2 has been implicit in many discussions in the literature of electrokinetics. There is experimental evidence against additional terms in the work of Manegold and Solf,²⁰ who reported that electro-osmotic pressure in the presence of an applied pressure difference is essentially identical with that obtained with a potential alone.

Evaluation of Coefficients

The coefficients in equations 1 and 2 are related as

$$C_V = C_{12}/C_{22} \quad (3a)$$

$$C_I = C_{21}/C_{11} \quad (3b)$$

$$C_1 = C_{11}(1 - C_{12}C_{21}/C_{11}C_{22}) \quad (3c)$$

$$C_2 = C_{22}(1 - C_{12}C_{21}/C_{11}C_{22}) \quad (3d)$$

(16) W. McK. Martin and R. A. Gortner, *J. Phys. Chem.*, **34**, 1509 (1930).

(17) N. Schönfeldt, *Wiss. Veröffent. Siemens-Konzern*, **12**, 39 (1933).

(18) Cf. N. A. Krylov, *C. A.*, **32**, 4039 (1938).

(19) M. Muskat, "The Flow of Homogeneous Fluids through Porous Media," McGraw-Hill Book Co., Inc., New York, N. Y., 1937, p. 71.

(20) E. Manegold and K. Solf, *Kolloid-Z.*, **55**, 273 (1931).

(1) Presented at the Boston Meeting of the American Chemical Society, April 4, 1951.

(2) M. v. Smoluchowski in Graetz "Handbuch der Elektrizität und des Magnetismus," Vol. 2, p. 366, Barth, Leipzig, 1921.

(3) A. S. Buchanan and E. Heymann, *Proc. Roy. Soc. (London)*, **A195**, 150 (1948).

(4) A. S. Buchanan and E. Heymann, *J. Colloid Sci.*, **4**, 157 (1949).

(5) H. B. Bull, *Kolloid-Z.*, **66**, 20 (1934).

(6) H. P. Dakin, F. Fairbrother and A. E. Stubbs, *J. Chem. Soc.*, 1229 (1935).

(7) K. Kanamaru and T. Takada, *Kolloid-Z.*, **86**, 86 (1939).

(8) K. Kanamaru, T. Takada and K. Aikawa, *ibid.*, **83**, 288, 294 (1938).

(9) M. A. Lauffer and R. A. Gortner, *THIS JOURNAL*, **42**, 641 (1938).

(10) H. Reichardt, *Z. physik. Chem.*, **A154**, 337 (1931).

(11) J. Velíšek and A. Vašicek, *ibid.*, **A171**, 281 (1935).

(12) H. B. Bull and R. A. Gortner, *THIS JOURNAL*, **36**, 111 (1932).

(13) G. Ettisch and A. Zwanzig, *Z. physik. Chem.*, **A147**, 151 (1930).

(14) F. Fairbrother and M. Balkin, *J. Chem. Soc.*, 389 (1931).

(15) G. Köhler, *Z. physik. Chem.*, **A157**, 113 (1931).

Let us define

$$Q \equiv C_{12}C_{21}/C_{11}C_{22} \quad (4)$$

Since C_1 and C_{11} (or C_2 and C_{22}) must both have the same sign, it is immediately obvious that Q cannot exceed unity. This restriction on the relative values of the coefficients should be borne in mind in assigning theoretical values to them.

To relate the coefficients of equations 1 to experiment, we remember that the standard electrokinetic formulas are relations between two of the experimental quantities I , V , E and P . Since there are four variables and only two equations, we need a third independent equation before we can arrive at a definite relation between two of the variables. This third equation generally specifies that one of the variables is held equal to zero. For example, the relation between current and voltage has a definite meaning only under some specified condition, such as $P = 0$. We see that C_{11} is the conductance, or reciprocal resistance, when there is no pressure difference. Similarly, C_{22} is the gross permeability when there is no potential difference. However, other conditions than those mentioned may be specified. For example, we may also define C_{11} by specifying any constant pressure difference

$$C_{11} = (\partial I / \partial E)_P \quad (5)$$

It is clear that the conductance, dI/dE , can have any number of values in addition to C_{11} and C_1 , and the permeability, dV/dP , any number of values in addition to C_{22} and C_2 , depending on experimental conditions.

In what follows, the subscript will be used to indicate a variable being held equal to zero. Streaming potential is measured when there is no net electric current, and electro-osmotic flow when there is no pressure gradient. Under these conditions we get

$$(E/P)_I = -C_{12}/C_{11} \quad (6)$$

$$(V/I)_P = C_{21}/C_{11} \quad (7)$$

The minus sign occurs in equation 6 because the potential and pressure gradients act in opposite directions, something which is not ordinarily considered.

We are now in a position to introduce an additional experimental law of electrokinetics. This law, established by Saxén (*cf.* ref. 2), and recently checked with accuracy,^{21,22} can be written

$$-(E/P)_I = (V/I)_P \quad (8)$$

Comparing equations 6, 7 and 8, we see that

$$C_{12} = C_{21} = C_0 \quad (9)$$

This relation, in a slightly different form, has been demonstrated theoretically by Onsager^{23,24} as a general consequence of the principle of microscopic reversibility for systems where there is coupling of two different transport processes. It should be valid even if the regions of mechanical and electrical transport do not completely overlap,²⁵ which would merely contribute extra terms to C_{11} or C_{22} .

(21) A. J. Rutgers and M. de Smet, *Trans. Faraday Soc.*, **43**, 102 (1947).

(22) P. W. O. Wijga, Thesis, Utrecht, 1946.

(23) L. Onsager, *Phys. Rev.*, **37**, 405 (1931).

(24) L. Onsager, *ibid.*, **38**, 2265 (1931).

(25) J. J. Bikerman, *This Journal*, **46**, 724 (1942).

The quantity C_e defined in equation 9 may be called the "electro-permeability." Together with electrical conductance and hydrodynamic permeability it is a characteristic parameter of electrokinetic formulas.

Comparison with Usual Formulas

If we compare the above formulas with those ordinarily given in textbooks,^{19,26} the values of the coefficients are: (a) For a circular capillary, radius r , length L

$$C_{11} = \pi r^2 \kappa / L; C_{22} = \pi r^4 / 8 \eta L; C_e = -\zeta \epsilon r^2 / 4 \eta L \quad (10)$$

(b) For a porous plug, area A , length L , specific permeability k , conductivity cell constant K

$$C_{11} = \kappa / K; C_{22} = k A / \eta L; C_e = -\zeta \epsilon / 4 \pi \eta K \quad (11)$$

In these formulas η , κ and ϵ are, respectively, the viscosity, specific conductivity and dielectric constant of the liquid in the capillaries, and ζ is the electrokinetic potential.

It has been stressed²⁷⁻²⁹ that ϵ is unknown near the interface and only the product $\zeta \epsilon$ has any real significance. This product has been related to the electric moment of the double layer. However, even the electric moment lacks significance since the viscosity near the interface is also unknown. Only the combination of variables $\zeta \epsilon / \eta \equiv \omega = 4 \pi C_e K_0$ is capable of evaluation by purely electrokinetic measurements. This quantity has the dimensions of electric charge multiplied by time and divided by mass, which has no such straightforward interpretation as electric moment. It would be well to refer to ω simply by the non-committal term "electrokinetic coefficient." For a given liquid it is proportional to ζ and has the same functional dependence on electrolyte concentration. There is less advantage than might first appear in replacing the convenient parameter C_e by a more detailed expression. The relation of C_e to the actual potential at the solid surface is of great interest in other fields besides electrokinetics but even the more-refined formulas give this relation only approximately.

This is further brought out by evaluating Q (equation 4) with the aid of equations 10 and 11 in turn

$$(a) \text{ for circular capillaries } Q = \zeta^2 \epsilon^2 / 2 \pi^2 r^2 \eta \kappa \quad (12)$$

$$(b) \text{ for porous plugs } Q = (\zeta^2 \epsilon^2 / 16 \pi^2 k \eta \kappa) \times L / A K \quad (13)$$

We have seen that Q is necessarily smaller than 1, but it is not obvious from these expressions. A dependence of apparent ζ on κ has been known,³⁰ but this new requirement places a definite restriction on the relative values of conductivity and the electrokinetic potential that has not previously been recognized.

Electrokinetic Formulas

Since there are four quantities to be taken two at a time, while a third is held equal to zero, there are 24 possible permutations. However, half of these are reciprocals, so we can expect twelve

(26) S. Glasstone, "Textbook of Physical Chemistry," D. van Nostrand Co., Inc., New York, N. Y., 1940, pp. 878, 1198, 1199.

(27) H. B. Bull and R. A. Gortner, *Physics*, **2**, 21 (1932).

(28) E. A. Guggenheim, *Trans. Faraday Soc.*, **36**, 139 (1940).

(29) L. A. Wood, *J. Am. Chem. Soc.*, **68**, 432 (1946).

(30) A. J. Rutgers, *Trans. Faraday Soc.*, **36**, 69 (1940).

separate electrokinetic relations. Six of these are readily derived from equations 1, making use of equation 9, the other six are correspondingly derived from equations 2, making use of equations 3, 4 and 9:

	From equations 1	From equations 2
Conductance	$\frac{i}{i} (I/E)_P = C_{11}$ (14)	$(I/E)_V = C_1 = C_{11}(1 - Q)$ (15)
Permeability	$\frac{i}{i} (V/P)_E = C_{22}$ (16)	$(V/P)_I = C_2 = C_{22}(1 - Q)$ (17)
Streaming current	$\frac{i}{i} (I/P)_E = C_e$ (18)	$(I/V)_E = C_V = C_e/C_{22}$ (19)
Electro-osmotic flow	$\frac{i}{i} (V/E)_P = C_e$ (20)	$(V/I)_P = C_1 = C_e/C_{11}$ (21)
Streaming potential	$\frac{i}{i} (E/P)_I = -C_e/C_{11}$ (22)	$(E/V)_I = -C_V/C_1$ (23)
		$= -C_e/(C_{22}C_{11}(1 - Q))$
		$= -C_e/(C_{22}C_{11} - C_e^2)$ (23)
Electro-osmotic pressure	$\frac{i}{i} (P/E)_V = -C_e/C_{22}$ (24)	$(P/I)_V = -C_1/C_2$ (25)
		$= -C_e/C_{11}C_{22}(1 - Q)$
		$= -C_e/(C_{11}C_{22} - C_e^2)$

Especially attention is directed to formula 25. An equation for $(P/I)_V$ has always been derived from equation 24, or *vice versa*,^{2,20,31} by use of the incorrect relation $(P/I)_V = (P/E)_V(E/I)_P$, and the term C_e^2 fails to appear in the denominator.

On examination, it appears that there are three other cross relations like Saxén's law (equation 8) between streaming and electro-osmotic effects

$$(I/P)_E = (V/E)_P \quad (26)$$

$$(I/V)_E = -(P/E)_V \quad (27)$$

$$(E/V)_I = (P/I)_V \quad (28)$$

The original Saxén's law could not be tested accurately in concentrated electrolyte solution, where the value of C_{11} in the denominator would become increasingly larger. However, the cross relations of equations 26 and 27 would not be subject to this disadvantage.³²

In a recent paper by Mazur and Overbeek^{33,34} the eight formulas for streaming and electro-osmotic effects (equations 18 through 25) are given in terms of resistance coefficients, R , rather than conductance coefficients, C , following the usage of Onsager. Let $R_{12} = R_{21} \equiv R_e$; then $R_e^2/R_{11}R_{22} = Q$, and the two notations are related as

$$R_{11}C_{11} = R_{22}C_{22} = 1/(1 - Q)$$

$$R_eC_e = -Q/(1 - Q)$$

Electroviscous Effect

We have seen that the value of the permeability depends on the conditions under which it is measured.

(31) D. Maturo, *Rev. facultad quim. ind. agr. (Univ. nacl. litoral, Santa Fe Argentina)*, **6**, 42 (1937).

(32) Equations 8, 26, 27 and 28, which are reminiscent of the familiar "Maxwell relations" of thermodynamics, were given in the equivalent differential form by Maturo,³¹ based on an "equilibrium state" where electro-osmosis supposedly occurs without thermodynamically irreversible effects. Using equation 8 and Wiedemann's first law, he derived equations equivalent to 1a and 2b.

(33) P. Mazur and J. Th. G. Overbeek, *Rec. trav. chim.*, **70**, 83 (1951).

(34) Mazur and Overbeek's paper came to the author's attention after the completion of the present paper.

ured. The usual condition of measurement is zero current, equation 17. It has long been recognized that, in this case, streaming potential has a retarding effect on the flow. This is called *electrokinetic blocking*³⁵ or *electroviscosity*.³⁶ In comparison with equation 16, the fractional decrease in permeability when a streaming potential develops is Q , which is therefore an exact expression for the relative electroviscous effect.

Four formal interpretations of the electroviscous effect have been suggested, each of which can be expressed in the present notation. The first is that the permeability of the capillaries decreases, either through rigidification of surface layers by electrical forces³⁷ or increased viscosity of the liquid in the capillaries.³⁶ If we denote the decrease in permeability by C'_{22} , $V = (C_{22} - C'_{22})P$, and $C'_{22} = QC_{22}$.

The second is that of Abramson,³⁸ who calculated a correction to Poiseuille's law, assuming a partial backward flow of liquid by electro-osmosis. If V' represents this backflow, $V = C_{22}P - V'$, and $V' = [Q/(1 - Q)]V$.

Third, Bull³⁹ suggested making the same calculation with an electro-osmotic back-pressure. If P' represents this back-pressure, $V = C_{22}(P - P')$, and $P' = QP$.

Fourth, Bull and Moyer⁴⁰ pointed out that the reduction of flow is given by the proportion of mechanical energy expended in driving the streaming current against the streaming potential. If we write i for this streaming current (which is carried along the wall, and compensated by a current back-conducted over the whole area), $V[1 - (-E_I/PV)_I] = C_{22}(1 - Q)P$. According to equations 4, 19 and 22, $Q = -(E/P)_I(I/V)_E$. It follows that $(i/V)_I$ is equal to the ordinary streaming current $(I/V)_E$.

Not all the previous treatments gave correct results. In a table of calculated values in Abramson's paper³⁸ there is one entry that would require a negative rate of flow in very small capillaries, because he used expressions that permit Q to be greater than 1. Elton's detailed calculations^{36,41} introduce an incorrect factor of 2/3. These examples are cited to illustrate the value of a simple phenomenological approach.

Electro-osmotic Conductance Effect and Surface Conductance

Neither of the two electrokinetic conductances given by equations 14 and 15 is equal to the ordinary conductance, C_0 , measured in the absence of all electrokinetic effects. The difference $(C_{11} - C_0)$ is the so-called *surface conductance*. The difference $(C_{11} - C_1)$ is an *electro-osmotic conductance effect* analogous to the electroviscous effect. It has not been specifically recognized, but could be observed by comparing conductance during flow under constant pressure (cf. equation 5) with conductance

(35) G. H. Bishop, F. Urban and H. L. White, *THIS JOURNAL*, **35**, 137 (1931).

(36) G. A. H. Elton, *Proc. Roy. Soc. (London)*, **A194**, 259 (1948).

(37) H. L. White, B. Monaghan and F. Urban, *J. Gen. Physiol.*, **18**, 515 (1935).

(38) H. A. Abramson, *ibid.*, **15**, 279 (1932).

(39) H. B. Bull, *Kolloid-Z.*, **60**, 130 (1932).

(40) H. B. Bull and L. S. Moyer, *THIS JOURNAL*, **40**, 9 (1936).

(41) G. A. H. Elton, *Proc. Roy. Soc. (London)*, **A198**, 581 (1949).

when net flow is prevented. We have for the fractional difference

$$(C_{11} - C_1)/C_{11} = Q \quad (29)$$

Surface conductance is considered to arise from the increase of electrolyte concentration and altered ionic mobility near the wall, and an electro-osmotic term, due to the motion of the liquid carrying a surplus of charges of one sign. To evaluate surface conductance theoretically, it is necessary to make a detailed analysis of the electric double layer. This has been done for single capillaries by Bikerman,⁴² Reichardt^{10,43} and Kaneko.⁴⁴ All three authors obtained fundamentally the same expression for the electro-osmotic term,⁴⁵ which reduces to the Smoluchowski expression⁴⁶ when a number of more or less customary assumptions are made

$$(C_{11} - C_0)/C_0 = \zeta^2 \epsilon^2 / 16 \pi^2 \delta r \eta \kappa_0 \quad (30)$$

where δ is the average thickness of the double layer, and κ_0 is the ordinary specific conductivity of the liquid. The similarity to equation 12 will be noted. If we define $Q_0 \equiv C_e^2 / C_0 C_{22}$, equation 30 becomes

$$(C_{11} - C_0)/C_0 = Q_0(r/8\delta) \quad (31)$$

Comparison of equations 29 and 31 shows that the electro-osmotic term of surface conductance differs from the electro-osmotic conductance effect by a

(42) J. J. Bikerman, *Z. physik. Chem.*, **A163**, 378 (1932)

(43) H. Reichardt, *ibid.*, **A166**, 433 (1933).

(44) S. Kaneko, *J. Chem. Soc. Japan*, **56**, 600 (1935).

(45) Numerical errors must be corrected in Reichardt's formula 15a⁴³ and Kaneko's formula 35. Bikerman's formula 37 omits the electro-osmotic term from conductance in the expression for streaming potential, but its presence is clearly required by formula 22 of the present paper.

(46) Reference 37, formula 43.

factor which depends on the structure of the double layer.

In general, $C_{11} = C_0(1 + Q_0F + X) = C_0(1 + X)/(1 - QF)$ where Q_0F is the electro-osmotic term and X represents the other two. F is an integral depending on the viscosity and potential distribution assumed in the double layer. It can be evaluated explicitly from the formulas of the authors mentioned.

The relative surface conductance takes the form

$$(C_{11} - C_0)/C_0 = Q_0F + X \quad (32)$$

It must be measured with a constant pressure difference. If it were measured with zero flow, it would be

$$(C_1 - C_0)/C_0 = Q_0(F - 1) + X \quad (33)$$

This quantity would have a very different value and might even be negative. Still other values of surface conductance could be measured, corresponding with the variety of possible conductances previously discussed. Perhaps if these possibilities had been realized, there might be fewer discrepancies between surface conductance values measured at different laboratories.

The relation between Q and Q_0 is

$$Q_0 = Q(1 + X)/(1 - QF)$$

It follows that $Q_0 < (1 + X)/(1 - QF) < (1 + X)/(1 - F)$, which amounts to an explicit restriction on relative values of ζ , surface conductance, and capillary radius.

The author is grateful to Dr. A. S. Coolidge, of Harvard University, for reading the original manuscript and pointing out the relation of Onsager's work to this paper.

A STUDY OF THE REACTIONS OF CARBON MONOXIDE WITH COKE¹

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The reaction between carbon monoxide and a degassed high temperature coke has been investigated in the temperature range from 700 to 1000° and in the pressure range from 1 to 63 cm. The equations $\text{CO} \rightleftharpoons (\text{CO})$ and $\text{CO} + (\text{CO}) \rightarrow \text{CO}_2 + \text{C}(1)$ where (CO) represents a molecule chemically bonded to the carbon surface are proposed for the initial reactions observed under these conditions. Rate constants and temperature coefficients that described these equations have been evaluated. The data indicate that the tendency for carbon dioxide formed during this reaction to revert to carbon monoxide increases as the carbon dioxide-carbon monoxide equilibrium composition is approached.

Introduction

The trend in use of liquid or gaseous fuels in preference to solid fuels has given impetus to research directed toward gasification of solid fuels.^{3,4} The gasification of carbonaceous fuels by oxygen, carbon dioxide or steam has long been known to be retarded by carbon monoxide and hydrogen, products

of the gasification reactions. However, lack of agreement exists between various authorities as to the mechanism of the retardation reactions.

This mechanism is usually studied by flowing carbon dioxide-carbon monoxide mixtures, or steam-hydrogen mixtures, through a bed of heated carbonaceous fuel under controlled conditions. Another approach is to study the direct interaction of carbon monoxide or o_2 hydrogen with such materials. While the reaction between hydrogen and low-ash carbons has been carefully investigated by Barrer and Rideal,^{5,6} there is little information on

(1) Abstracted from a dissertation by the author, Coal Research Laboratory Fellow in the Department of Chemistry, Carnegie Institute of Technology, submitted in partial fulfillment of the requirements for the degree of Doctor of Science, June, 1950.

(2) McArdle Memorial Laboratory, Medical School, University of Wisconsin, Madison, Wisconsin.

(3) J. J. Morgan, "Chemistry of Coal Utilization," H. H. Lowry, Editor, John Wiley and Sons, Inc., New York, N. Y., 1945, pp. 1693-1709.

(4) B. J. C. van der Hoeven, *ibid.*, pp. 1586-1635.

(5) R. M. Barrer, *Proc. Roy. Soc. (London)*, **A149**, 253 (1935); *J. Chem. Soc.*, 1256 (1936); 1261 (1936).

(6) R. M. Barrer and E. K. Rideal, *Proc. Roy. Soc. (London)*, **A149**, 231 (1935).

the direct interaction of carbon monoxide and carbonaceous fuels at elevated temperatures. Previous investigators⁷⁻¹⁰ have studied this reaction as a subsidiary to the carbon dioxide-carbon reaction.

The present paper describes results obtained in a study of the reaction between carbon monoxide and a degassed high temperature coke at temperatures ranging from 700 to 1000° and pressures from 1 to 63 cm. of mercury. The experimental procedure involved continuous recirculation of carbon monoxide over an externally heated coke sample. Equations are proposed for the observed reactions and the three rate constants, which describe the rate at which these reactions proceed, have been evaluated.

Experimental

Apparatus.—Figure 1 is a schematic diagram of the apparatus. Circulation was maintained in the closed cycle ABC of capillary tubing both by the thermal convection of gases passing through the reaction chamber (1), which was situated in a high temperature furnace (2), and by means of a Pyrex pump (3). Circulation minimized differences in gas composition along the flow path resulting from reaction. The gases passed through a gas buret (4) and returned to the reaction chamber (1), with intermediate connections to a precision manometer (5) and a gas sampling device (6). The reaction loop ABC was served by equipment for vacuum production and low pressure measurement (7), gas storage (8) and gas purification (9).

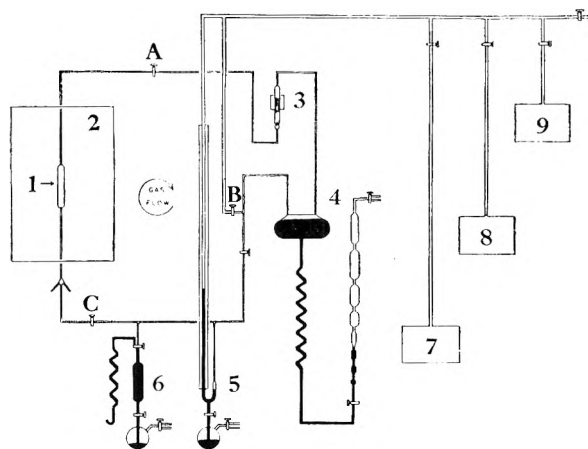


Fig. 1.—Schematic diagram of the apparatus.

Details of the reaction chamber are shown in Fig. 2. It consisted of a quartz chamber E, holding roughly 30 g. of coke. Quartz-Pyrex graded seals at D and D' joined the quartz assembly to the Pyrex capillary of the reaction loop CC'. The leads, N and N', of a platinum-platinum 10% rhodium thermocouple led into the refractory casing G and the junction at F was shielded by cement. The leads N and N' split at I and ran out of the assembly through lead-soldered joints M and M' inside thin cylinders of Kovar metal, attached to the Pyrex by Kovar-Pyrex graded seals at L and L'. Platinum resistance wire was wound on the quartz reaction chamber, HH', acted as one arm of an AC bridge which formed part of a thyatron thermostat. The output of a thyatron controlled by the AC bridge was used to vary the impedance of a saturable reactor, which was connected in series with the Globar heating elements of the furnace (2) and with the power supply. By this means, the over-all

temperature of the reaction chamber was held within $\pm 0.5^\circ$ for the duration of the experiment. Variation in temperature along the reaction chamber was reduced to $\pm 1^\circ$ by means of two manually controlled end heaters, which were calibrated to give temperature uniformity at different temperatures.

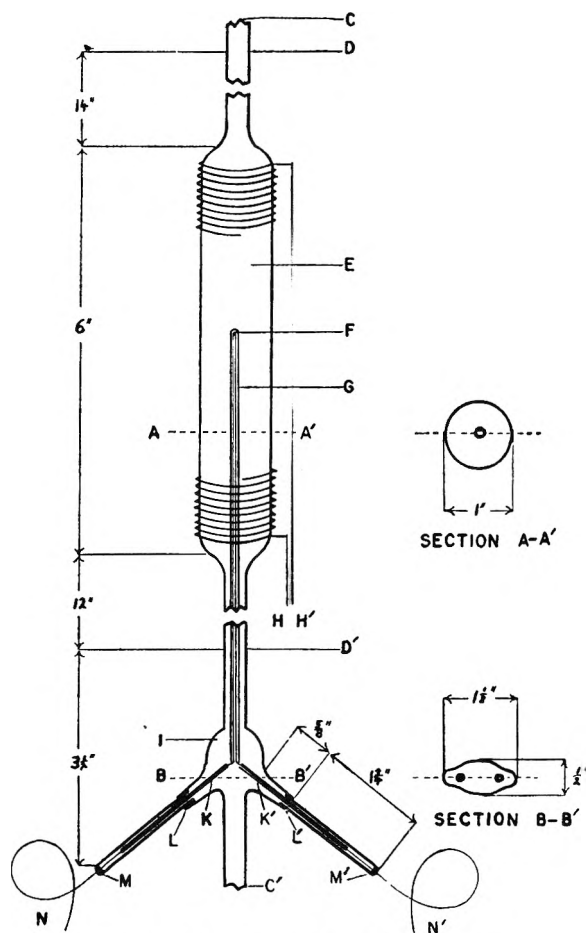


Fig. 2.—Diagram of the reaction chamber.

The pump (3) was constructed from Pyrex precision tubing. Poppet valves ground at the bottom of both piston and cylinder permitted only upward flow of gas. To the inside of the piston was sealed an iron nail encased in Pyrex tubing, whereby the piston could be raised when current activated a solenoid concentric to piston and cylinder. A contact breaker served to cut off the current and drop the piston periodically, a pumping speed of approximately 150 cc./minute being obtained with three breaks of contact a second.

The "gas flow buret" (4) was designed to permit continuous circulation of gas in the reaction loop ABC. It contained a constant mass of mercury, such that when the mercury fell to the lowest mark of the graduated bulbs, it rose in the buret head to a height which just permitted free passage of gas through it. The volume of mercury in the buret head could be varied by known amounts by running mercury into or out of the graduated bulbs.

The precision manometer (5) was fitted with a mirror scale and electrical contacts for zero adjustment, which enabled pressure readings reproducible to ± 0.1 mm. to be taken. The sampling device (6) enabled 85% of the gas in the reaction loop to be transferred into a sampling tube in two operations of filling and emptying its bulb. Vacuum production (7) was accomplished by a mercury diffusion pump backed by a single stage Welch Duo-Seal vacuum pump. The combination gave a vacuum of better than 10^{-5} cm., as measured by a McLeod gage designed to cover the range 10^{-5} to 7 cm. Gas storage (8) was provided by three 5-liter flasks, each connected to a mercury manometer.

Materials.—Helium and nitrogen were bought already purified in sealed 1-liter flasks from the Matheson Company,

(7) W. E. J. Broom and M. W. Travers, *Proc. Roy. Soc. (London)*, **A135**, 512 (1932).

(8) J. Gadsby, F. J. Long, P. Sleightholm and K. W. Sykes, *ibid.*, **A193**, 357 (1948).

(9) A. F. Semechkova and D. A. Frank-Kamenetzky, *Acta Physico-chim. U. R. S. S.*, **12**, 879 (1940).

(10) H. S. Taylor and H. A. Neville, *J. Am. Chem. Soc.*, **43**, 2055 (1921).

Inc., East Rutherford, New Jersey. These flasks were sealed to the apparatus as desired and the seal broken in the usual manner with nail and magnet.

Carbon monoxide was purified in section (9) of the apparatus. Carbon monoxide from a tank was condensed in a trap filled with glass spheres and cooled in liquid nitrogen. The trap was then permitted to warm up, the first half of the distillate being rejected, while the second half was collected: analysis showed this to be 99.9% carbon monoxide. To prevent excessive pressure building up during distillation, a mercury safety valve was incorporated, which would release pressure at 110 cm.

A high-temperature coke was used having an analysis as shown in Table I.

TABLE I

Proximate analysis		ANALYSIS OF COKE		Ash softening
		Ultimate analysis (dry, ash-free basis)		Temperature, °C.
Fixed carbon	89.1	Carbon	96.9	Initial deformation, 1207
		Oxygen	0.5	
Volatile matter	0.6	Hydrogen	0.8	Softening temperature, 1430
		Nitrogen	1.1	
Moisture	0.3	Sulfur	0.7	Fluid temperature, 1450
Ash	10.0			
Total	100.0	Total	100.0	

The coke was ground to under 8 mesh, U. S. standard sieves, and only the 8–12 mesh fraction was used. The sample was initially evacuated and heated for three days at 1000°. The sample did not have to be replaced during all reported experiments since coke was not consumed. There was no visible deposit of carbon on the coke when removed from the furnace after the experiments.

Experimental Accuracy.—The reaction investigated was small in extent and slow in rate, hence accurate measurements and careful calibration of dead space volumes were necessary. The dead space volume of the reaction chamber was calibrated with helium at different temperatures, and since the walls of the reaction chamber were permeable to helium at high temperatures, a correction for helium leak rate was applied. The effective volume of the entire reaction loop was calculated as the sum of the component parts of the system.

The reproducibility of adsorption experiments was determined by performing several duplicate experiments at each temperature investigated. The standard deviation of m , the decrease in volume of gas per gram carbon due to adsorption, was found to be 8.4, 7.1, 7.1 and 14.8% at 1000, 900, 800 and 700°, respectively. Errors in the analysis of the carbon dioxide formed were not of prime importance since the major reaction was the formation of an oxygen complex on the carbon surface.

Experimental Procedure.—Experiments consisted in admitting a measured quantity of carbon monoxide to the coke

sample, measuring subsequent pressure changes and finally analyzing the gas in contact with the coke.

The coke sample was thoroughly degassed by evacuation at a temperature 100–200° higher than that to be used in each experiment. After the temperature of the reaction chamber had been adjusted to the desired value, the sample under vacuum was isolated by means of stopcocks A and C (see Fig. 1). Carbon monoxide gas was then admitted into the reaction loop through stopcock B at a pressure approximately known from the reading of a manometer in the gas storage section (8) of the apparatus. The mass of the gas contained within stopcocks ABC, in terms of the ratio pV/T , was then determined as the mean of three values for three different settings of the gas buret volume (4).

The experiment proper started with the admission of carbon monoxide into the reaction chamber through stopcocks A and C. The pressure inside the reaction loop was then increased to the desired value by adjusting the gas buret volume and the first pressure reading was taken. Readings were continued at suitable time intervals until the end of the experiment. Immediately after the final pressure reading, the gas in the reaction tube was sampled and analyzed for carbon dioxide in an Orsat gas analysis apparatus.

Experimental Results

Adsorption Experiments.—Figure 3 shows the change with time of the volume of gas in the reaction loop, per gram of carbon in the reaction chamber for a typical experiment. Similar curves were obtained for all experiments involving the interaction of carbon monoxide and the degassed coke sample. From such data the decrease in volume of gas (m) per gram of carbon was calculated as the difference between the initial (M_1) and final (M_2) volume of gas

$$m = \frac{M_1 - M_2}{29.015} \quad \text{cc.NTP/g. C} \quad (2)$$

where 29.015 was the gram weight of carbon in the reaction chamber.

Knowing m and the percentage of carbon dioxide in the gas at the end of the experiment, the following quantities could be calculated

$$\text{carbon dioxide formed, } n = \frac{\% \text{ carbon dioxide}}{100} \times \frac{M_2}{29.015} \quad \text{cc.NTP/g. C} \quad (3)$$

$$\text{oxygen adsorbed} = m - n \quad \text{cc.NTP/g. C} \quad (4)$$

$$\text{total carbon monoxide reacted} = m + n \quad \text{cc.NTP/g. C} \quad (5)$$

At each of the four temperatures investigated, two types of experiments were carried out: experiments in which the initial pressure of carbon monoxide was nearly constant and the time of reaction was varied and experiments in which the time of reaction was held constant while the initial pressure of carbon monoxide was varied.

Results for the first type of experiment were corrected from the actual initial pressures to a constant initial carbon monoxide pressure of 60.0 cm. by means of corrections based on slopes in Fig. 5. Correction factors for m were nearly constant at 0.00050 cc./g. C/cm., while for n correction factors had the values 0.00016, 0.00036, 0.00016 and 0.00009 at 700, 800, 900 and 1000°, respectively. The actual initial pressures which were corrected to the standard pressure of 60.0 cm. were usually within 6% of this value.

The results, corrected to constant initial pressure, are plotted in Fig. 4. The curves labeled 'O' give the amount of oxygen adsorbed on the carbon surface, without making any assumptions as to the chemical state of this bound oxygen. The quantity of oxygen adsorbed on the carbon surface approaches a constant value at 700 and 800°, while at 900 and 1000° adsorption continues even after 90 minutes. Experiments at constant time of reaction are shown in Fig. 5. It is seen that oxygen adsorption approaches saturation at an initial carbon monoxide pressure of about 30 cm. The amount of carbon dioxide formed is directly proportional to the initial carbon monoxide pressure. Figure 6 shows that the ratio of carbon dioxide formed to oxygen adsorbed is a linear function of the time of reaction and also directly proportional to initial carbon monoxide pressure.

The data relating the dependence of oxygen adsorbed on

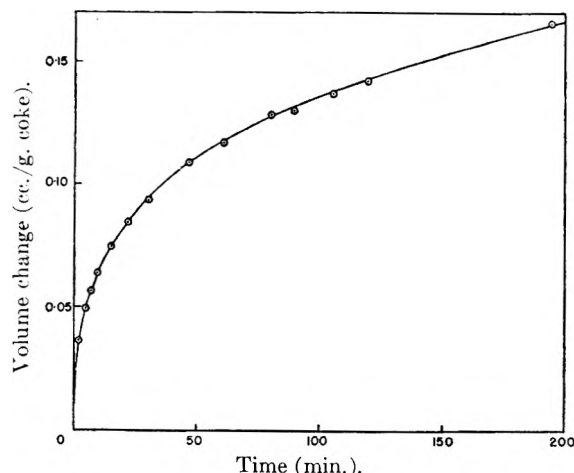


Fig. 3.—Decrease in volume of gas with time (temperature 1000°, initial carbon monoxide pressure 56.40 cm.).

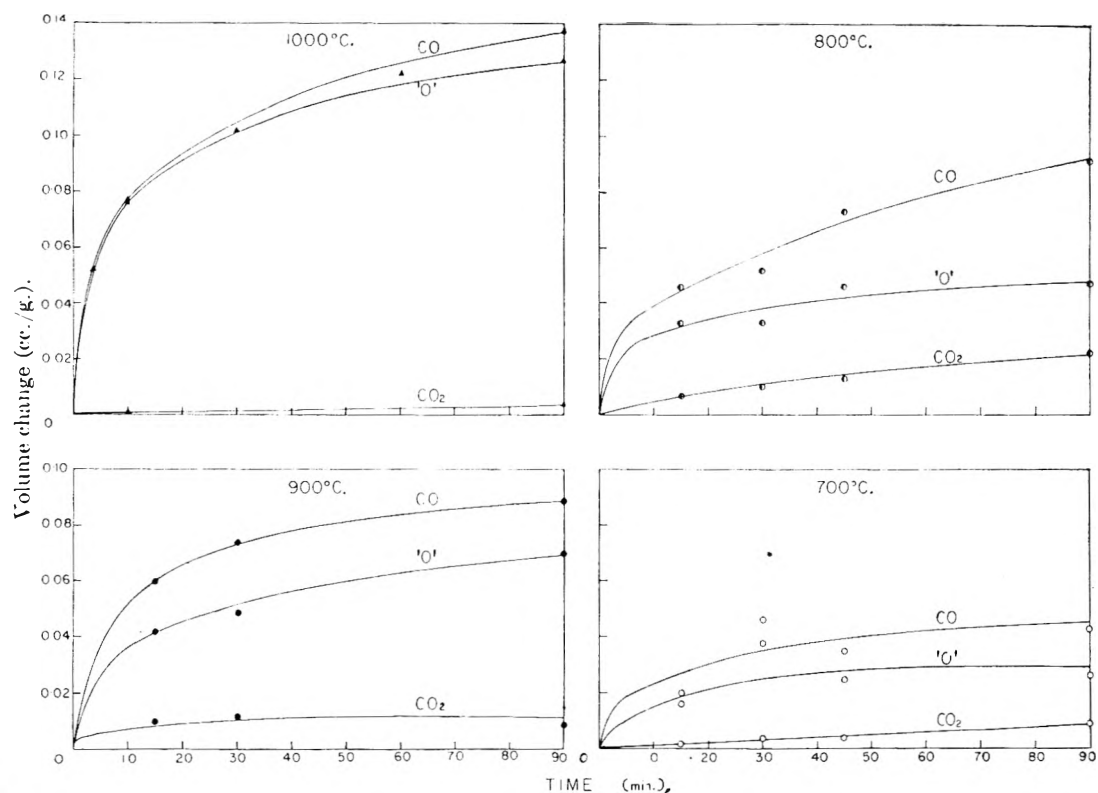


Fig. 4.—Variation of total carbon monoxide reacted, oxygen adsorbed and carbon dioxide formed with time of reaction (initial carbon monoxide pressure 60.0 cm.).

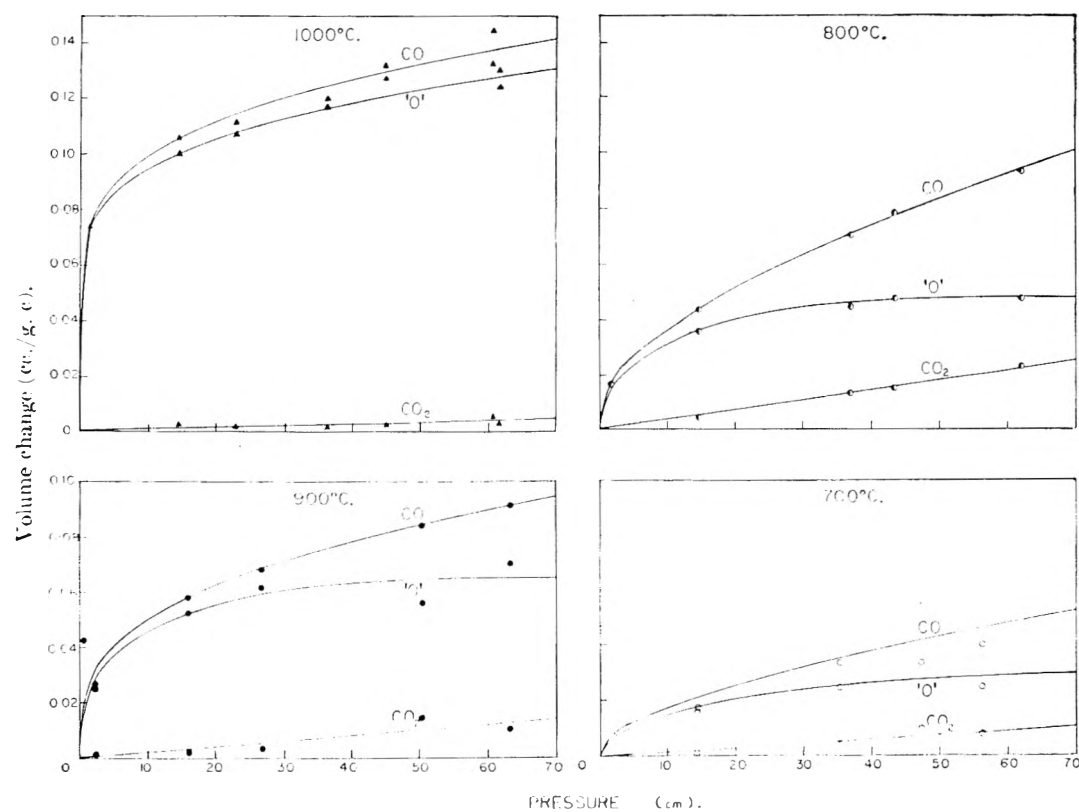


Fig. 5.—Variation of total carbon monoxide reacted, oxygen adsorbed and carbon dioxide formed with initial carbon monoxide pressure (time of reaction 90 minutes).

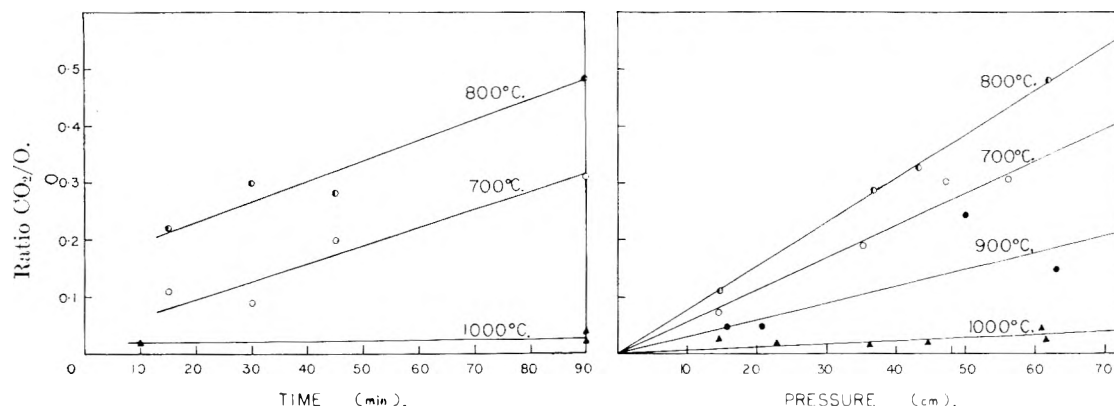


Fig. 6.—Variation of the ratio of carbon dioxide formed to oxygen adsorbed with time (initial carbon monoxide pressure 60.0 cm.) and with initial carbon monoxide pressure (time of reaction 90 minutes).

the initial carbon monoxide pressure at constant time of reaction was treated using Langmuir's adsorption isotherm

$$s = \frac{s_0 K_L p}{1 + K_L p} \quad (6)$$

where s is the gram molecular quantity of gas adsorbed per gram of adsorbent, s_0 is the value of s required to form a monolayer, p is the pressure of adsorbate gas (carbon monoxide) and K_L is the Langmuir adsorption equilibrium constant. Rewriting equation (6) in the form

$$p/s = (1/s_0 K_L) + (p/s_0) \quad (7)$$

it is possible to evaluate s_0 and K_L from a plot of p/s against p , as shown in Fig. 7. Figure 8 indicates that the values of s_0 thus obtained increase exponentially with rise in temperature, and that the maximum quantity of carbon dioxide was formed at around 800°.

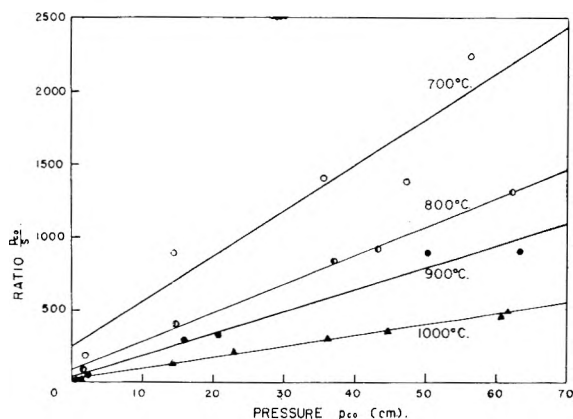


Fig. 7.—Langmuir adsorption isotherm plot.

The equilibrium composition of the carbon dioxide-carbon monoxide-carbon system was estimated from data by Rossini, *et al.*,¹¹ and Austin and Day,¹² as correlated by Wu.¹³ The equilibrium percentage of carbon dioxide is 36.0, 10.5, 2.6 and 0.6% at 700, 800, 900 and 1000°. A comparison of these figures with the percentage of carbon dioxide obtained in experiments at an initial carbon monoxide pressure of 60.00 cm. and after a reaction period of 90 minutes indicates that the ratio of carbon dioxide formed to carbon dioxide at equilibrium was 0.02, 0.17, 0.44 and 0.60 at the respective temperatures. Thus, the equilibrium composition was approached far more rapidly at higher than at lower temperatures.

Desorption Experiments.—Figure 9 shows the rate at which pressure dropped when the system was pumped with

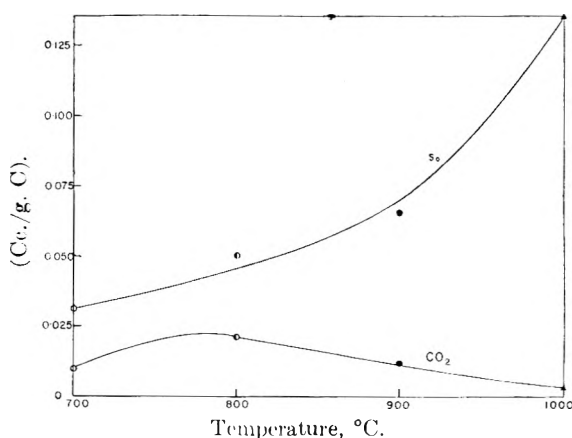


Fig. 8.—Variation of monolayer adsorption of oxygen complex and of carbon dioxide formation with temperature (initial carbon monoxide pressure 60.0 cm., time of reaction 90 minutes).

carbon surfaces previously saturated with carbon monoxide. The rapid drop in pressure with the carbon at 700° is due to the stability of the oxygen complex at that temperature. At higher temperatures, the oxygen complex decomposes more easily, resulting in lower rates of pressure drop with constant pumping speed.

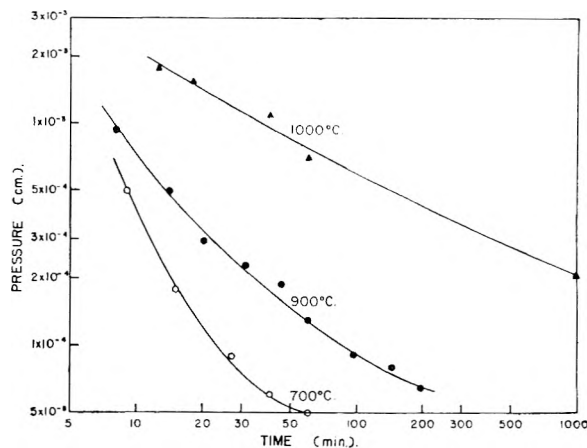


Fig. 9.—Change of pressure with time of evacuation over coke surface saturated with carbon monoxide.

A series of experiments was carried out at 1000, 900 and 800°, in which the carbon surface was saturated with carbon monoxide for 120 minutes. After desorption periods of varying length, carbon monoxide was again admitted for 90 minutes and the fresh adsorption measured. The amount

(11) F. D. Rossini, *et al.*, *J. Research Natl. Bur. Standards R.P.* 1954, **58**, 143 (1945).

(12) J. B. Austin and N. J. Day, *Ind. Eng. Chem.*, **33**, 23 (1941).

(13) P. C. Wu, "The Kinetics of the Reaction of Carbon with Carbon Dioxide," Sc.D. Thesis, Massachusetts Institute of Technology, 1949.

of carbon monoxide readsorbed was assumed equal to that desorbed during the evacuation period. A small correction was applied to compensate for incomplete saturation of the carbon surface during the first adsorption period.

Assuming that the desorption process was a first order reaction expressed by the equation



the desorption rate is given by the expression

$$dx/dt = \alpha(a - x) \quad (9)$$

where (CO) represents an adsorbed carbon monoxide molecule, " α " is a rate constant, " x " is the quantity of carbon monoxide desorbed in time " t " and " a " is the saturation sorption. Values of " α " were determined from sets of four experiments at each temperature investigated. The values obtained were 3.32×10^{-3} , 2.76×10^{-3} and 7.78×10^{-4} , min.^{-1} , at 1000, 900 and 800°, respectively.

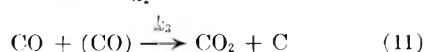
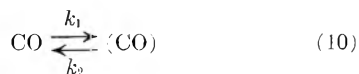
Surface Area Determination.—A quartz bulb holding approximately 25 g. of the same coke sample was attached to the reaction loop and degassed for 18 hours at 230°. Duplicate nitrogen adsorption experiments were performed at 77.4°K., after dead space calibration with helium under identical conditions. The B.E.T. monolayer adsorption was calculated at 0.096 and 0.093 cc./g. coke, corresponding to a mean surface area of 0.38 sq. meter/g. coke, assuming a surface area of 89.6 sq. meter/millimole nitrogen.¹⁴

This value for the B.E.T. monolayer adsorption is of the same order as that for the Langmuir monolayer adsorption s_0 of carbon monoxide, which averaged 0.070 cc./g. coke for the four temperatures investigated. These estimates are in marked contrast to those obtained by Gadsby, *et al.*,⁸ in their study of coconut shell charcoal. They found that the maximum quantity of carbon monoxide adsorbed in experiments at 850°, namely, 0.34 cc./g. carbon, was equivalent to only 0.5% of the surface of the carbon as estimated from an adsorption isotherm with water vapor at room temperature.

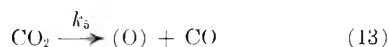
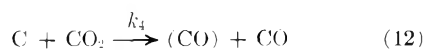
Such differences with previous experience are believed due to differences in characteristics of "carbons." The present investigation was carried out with a high-temperature coke, a fuel having surface characteristics markedly different from either an active carbon or a graphite.

Theoretical

The following equations are proposed to account for the reaction found between the degassed coke and carbon monoxide



The following reactions are assumed to take place only after appreciable quantities of carbon dioxide have been formed



Two types of oxygen complex are postulated in equations (12) and (13), since no evidence is given in this paper, to show whether the complex (CO), formed when carbon monoxide is adsorbed on carbon, is equivalent to the complex (O), formed when carbon dioxide reacts with carbon.

Assuming that equation (10) holds, the ratio k_1/k_2 is equal to the Langmuir adsorption equilibrium constant K_L . The temperature dependence of an equilibrium constant may be expressed in the form

$$K_L = K_{0L} e^{-(E_L/RT)} \quad (14)$$

Figure 10 gives a plot of $\log_{10} K_L$ against $1/T$ from which the non-exponential factor K_{0L} was evaluated as $10^{2.8} \text{ atm.}^{-1}$ and the heat of reaction E_L as 8.0 kcal., with a standard deviation of 0.51 kcal.

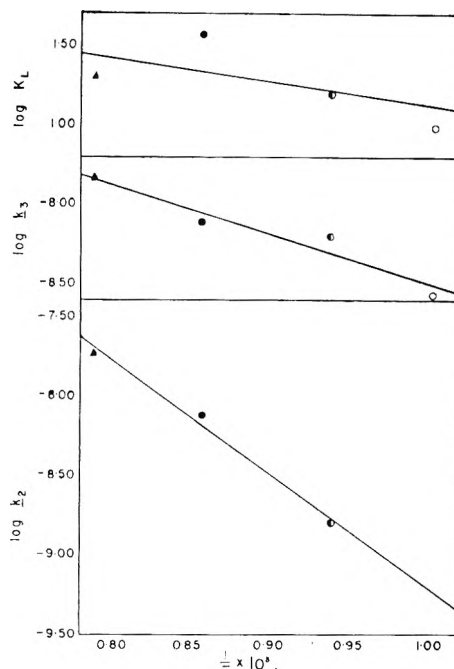


Fig. 10.—Arrhenius plot of the variation of K_L , k_3 and k_2 with temperature.

To evaluate the rate constant k_3 for the formation of carbon dioxide, it may be assumed that the reactions represented by equations (10) and (11) occur exclusively on the carbon surface. At equilibrium, the rate of formation of (CO) will equal its rate of desorption

$$(k_1 P_{\text{CO}} + k_4 P_{\text{CO}_2} + k_5 P_{\text{CO}_2}) (1 - \theta_{\text{CO}}) = (k_2 + k_3 P_{\text{CO}}) \theta_{\text{CO}} \quad (15)$$

where θ_{CO} is the fraction of active surface covered by (CO), whence

$$\theta_{\text{CO}} = \frac{k_1 P_{\text{CO}} + k_4 P_{\text{CO}_2} + k_5 P_{\text{CO}_2}}{k_2 + (k_1 + k_5) P_{\text{CO}} + (k_4 + k_3) P_{\text{CO}_2}} \quad (16)$$

and rate of formation of carbon dioxide is given by

$$R_{\text{CO}_2} = k P_{\text{CO}} \theta_{\text{CO}} - (k_4 + k_5) P_{\text{CO}_2} (1 - \theta_{\text{CO}}) \quad (17)$$

Since $K_L = (k_1/k_2)$, and with $k_3 < k_1$ and P_{CO_2} comparatively negligible

$$\theta_{\text{CO}} = \frac{(k_1/k_2) P_{\text{CO}}}{1 + (k_1/k_2) P_{\text{CO}}} = \frac{K_L P_{\text{CO}}}{1 + K_L P_{\text{CO}}} \quad (18)$$

and

$$R_{\text{CO}_2} = k_3 P_{\text{CO}} \theta_{\text{CO}} \quad (19)$$

If equation (19) holds, R_{CO_2} should be proportional to P_{CO} at constant θ_{CO} . This is shown by Fig. 5. Values of θ_{CO} may be assumed constant for each temperature since the quantity of oxygen adsorbed after 90 minutes increased only at 900 and 1000°, and even at these temperatures continued adsorption was slow.

Estimates of k_3 may be calculated by means of equations (18) and (19), and the values are given in Table II.

(14) S. W. Benson and D. A. Ellis, *J. Am. Chem. Soc.*, **72**, 2095 (1950).

TABLE II
EVALUATION OF RATE CONSTANT k_3

Temp., °C.	θ_{CO}	R_{CO_2}/P_{CO_2} , cc. min. ⁻¹ atm. ⁻¹ g. ⁻¹	k_3 , g. mole min. ⁻¹ atm. ⁻¹ g. ⁻¹
1000	0.932	0.0270	1.437×10^{-8}
900	.930	.0146	$.779 \times 10^{-8}$
800	.894	.0114	$.632 \times 10^{-8}$
700	.806	.0044	$.271 \times 10^{-8}$

A plot of $\log_{10} k_3$ against $1/T$ is also shown in Fig. 10 from which k_{O_3} was evaluated as $10^{-5.6}$ g. mole min.⁻¹ g.⁻¹ and E_3 as 13.2 kcal. with a standard deviation of 0.19 kcal.

The values of the rate constant " α " for the desorption reaction (equation (8)) were converted to the conventional rate constant by means of the equation

$$k_2 = \alpha s_0 \theta_{CO} \quad (20)$$

where s_0 is the monolayer adsorption of carbon monoxide in g. mole g.⁻¹ and θ_{CO} is recorded in Table II. A plot of $\log_{10} k_2$ versus $1/T$ is also shown in Fig. 10. The factor, k_{O_3} , was evaluated as $10^{-2.0}$ g. mole min.⁻¹ and E_2 as 33.6 kcal., with a standard deviation of 0.15 kcal.

From a knowledge of k_2 and K_L , k_1 was evaluated. The non-exponential factor k_{O_1} was $10^{0.8}$ g. mole min.⁻¹ atm. g.⁻¹ and the energy of activation E_1 was 41.6 kcal., with a standard deviation of 0.53 kcal.

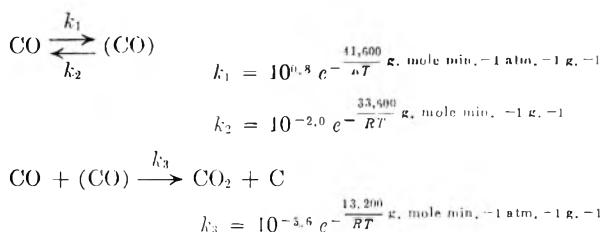
Discussion

In estimating rate constants, the concentration of carbon dioxide was assumed to be negligible. Had this assumption been unwarranted, either of the reactions, expressed by equations (12) or (13), could account for oxygen complex chemisorbed on the carbon surface.

Evidence that carbon monoxide was indeed directly adsorbed when admitted to a degassed coke surface was provided by the initial, relatively rapid decrease in pressure, which fell off with time. In the absence of carbon dioxide in the carbon monoxide initially admitted, carbon dioxide formation

was dependent on previous adsorption of carbon monoxide on the coke surface. At 700 and 800°, the maximum quantities of carbon dioxide formed at the end of a 90-minute reaction period were only 2 and 17%, respectively, of the equilibrium composition values, and adsorption had practically ceased at the end of this period. On the other hand, at 900 and 1000°, respectively, 44 and 60% of the equilibrium carbon dioxide composition was attained within 90 minutes, and adsorption was still appreciable at the end of this time interval.

From these data it is concluded that the initial reaction at all temperatures investigated was the adsorption of carbon monoxide on the degassed coke surface. This initial reaction is represented by the equations



In the course of a 90-minute reaction period, the extent to which carbon dioxide, formed in the course of the reaction, reverted to carbon monoxide was probably small at 700 and 800°. However, at the higher temperatures of 900 and 1000°, the carbon monoxide-carbon dioxide equilibrium was more nearly attained and the slow rates of oxygen adsorption found at the end of the 90-minute period is partly attributed to the reactions expressed by equations (12) and (13).

Acknowledgment.—The author is deeply indebted to Dr. H. H. Lowry, Director of the Coal Research Laboratory, for his direction of the work and to Dr. J. P. Fugassi, Professor of Chemistry, for his good advice. Thanks are due to Dr. A. A. Orning of the Coal Research Laboratory and to Dr. J. T. Kummer of the Mellon Institute for aid in the design of equipment.

THE MECHANISM OF THE CARBON DIOXIDE-CARBON REACTION¹BY ARNOLD E. REIF²*Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh 13, Pennsylvania**Received October 26, 1951*

Experimental evidence is presented to show that the reaction of carbon dioxide with a high temperature coke at 900° and under approximately atmospheric pressure is given by the equations $\text{CO}_2 \rightleftharpoons (\text{C}) + \text{CO}$ and $\text{C} + (\text{O}) \rightarrow \text{CO}$ where (O) represents a molecule chemically bonded to the carbon surface. This mechanism ascribes the inhibition of the carbon dioxide-carbon reaction to the chemical combination of carbon monoxide with oxygen deposited on the carbon surface by carbon dioxide.

Introduction

Research on the kinetic aspects of carbon gasification reactions is progressing concurrently at a number of laboratories the world over. In the United States, work in this field has been carried on for a number of years at the Carnegie Institute of Technology,^{3,4} the Massachusetts Institute of Technology,^{5,6} the Institute of Gas Technology,⁷ the Brookhaven National Laboratory,⁸ the United States Bureau of Mines⁹ and in other laboratories where the work has sometimes been confidential in nature. In England, significant contributions have come from groups at Oxford University^{10,11} and Leeds University.¹² Russian workers¹³ are among the additional research groups active in this field.

Examination of theories proposed for the kinetics of the carbon dioxide-carbon reaction gives a first impression that they differ widely. Similarities and differences between theories stand out clearly only when the proposed mechanisms are restated in uniform nomenclature. It is the purpose of this paper to present experimental and theoretical evidence that has a bearing on these theories.

Reactions which play a part in the mechanism of the carbon dioxide-carbon reaction may be summarized as

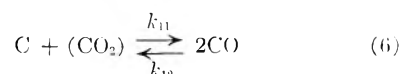
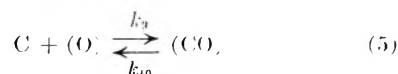
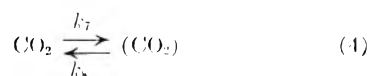
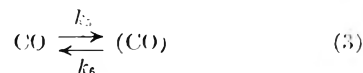
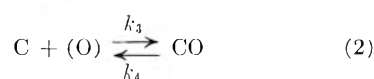
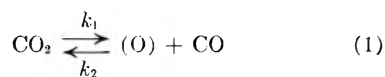


Table I shows some of the various combinations of these equations that have been used to describe the carbon dioxide-carbon reaction. It is possible to eliminate a number of these equations and arrive at a relatively simple mechanism.

TABLE I

Group of workers	Equations used
Russia ¹³	1, 2, 4
Oxford ¹⁰	3, 4, 6 forward
Oxford ¹¹	1 forward, 2 forward, 3
Leeds ¹²	1, 2
M.I.T. ⁶	1 forward, 3, 5, forward

There is general agreement^{6,10-13} that experimental data on the rate of gasification of carbon by carbon dioxide fit an equation of the form

$$\text{rate} = \frac{K_1 p_{\text{CO}_2}}{1 + K_2 p_{\text{CO}} + K_3 p_{\text{CO}_2}} \quad (7)$$

where p_{CO_2} and p_{CO} are, respectively, the partial pressures of carbon dioxide and carbon monoxide, and the constants K_1 , K_2 and K_3 are functions of one or more of the rate constants which characterize equations (1) to (6). Using the assumption that the different steps of the reaction occur exclusively on the carbon surface, equation (7) may be derived on the basis of several combinations of certain of the reactions (1) to (6). The purpose of this paper is to show which of the possible combinations may be the correct one.

It has been shown⁶ that formulating the mechanism by a combination of reaction (2) with the forward reaction of equations (1) and (5) leads to equation (7). Since this required a hypothetical reaction (5), for which no evidence is given, this mechanism can be discounted.

Russian workers¹³ have reported that the adsorption of carbon dioxide by carbon is negligible above 600°, which would mean that at higher temperatures reactions (4) and (6) are not applicable. There would then only remain reactions (1), (2) and (3) from which to choose the correct mechanism.

With the exception of one of several mechanisms

(1) Abstracted from a dissertation by the author, Coal Research Laboratory Fellow in the Department of Chemistry, Carnegie Institute of Technology, submitted in partial fulfillment of the requirements for the degree of Doctor of Science, June, 1950.

(2) McArdle Memorial Laboratory, Medical School, University of Wisconsin, Madison, Wisconsin.

(3) M. A. Mayers, *J. Am. Chem. Soc.*, **61**, 2053 (1939).

(4) A. A. Orning, S. Mallov and M. Neff, *Ind. Eng. Chem.*, **40**, 429 (1948).

(5) W. K. Lewis, E. R. Gilliland and G. T. McBride, *ibid.*, **41**, 1213 (1949).

(6) P. C. Wu, "The Kinetics of the Reaction of Carbon with Carbon Dioxide," Sc. D. Thesis, Chem. Eng., Massachusetts Institute of Technology, 1949.

(7) J. D. Parent and S. Katz, "Equilibrium Compositions and Enthalpy Changes for the Reactions of Carbon, Oxygen and Steam," Research Bulletin, No. 2, Inst. Gas Tech., Chicago 16, Illinois, 1948.

(8) F. Bonner and J. Turkevich, *J. Am. Chem. Soc.*, **73**, 561 (1951).

(9) H. R. Barchelder and J. C. Sternberg, *Ind. Eng. Chem.*, **42**, 877 (1950).

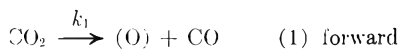
(10) J. Gadsby, C. N. Hinshelwood and K. W. Sykes, *Proc. Roy. Soc. (London)*, **A187**, 129 (1946).

(11) J. Gadsby, F. J. Long, P. Sleightholm and K. W. Sykes, *ibid.*, **A193**, 357 (1948).

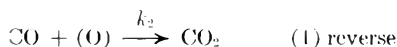
(12) A. Key, Gas Research Board Commun. (London) No. G.R.B. 40 (1948).

(13) A. F. Semechkova and D. A. Frank-Kamenetzky, *Acta Physico-chim. U. R. S. S.*, **12**, 879 (1940).

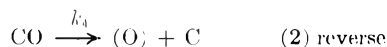
advanced in the first paper¹⁰ by the Oxford group and one of several discussed by the M.I.T. investigator,⁶ there is general agreement as to the mechanism of the gasification process above 600° in the absence of the product of the reaction, carbon monoxide



The retardation process, however, has been formulated in two distinct ways: the Russian¹³ and the Leeds¹² groups represent the retardation mechanism by the equations



and



When these equations are combined with the forward equations (1) and (2), it is found that equation (7) can be derived only if it is assumed that either reaction (1) reverse or reaction (2) reverse predominates.

The second retardation mechanism is advocated in a later publication from Oxford¹¹ and in the work from M.I.T.,⁶ and is represented by equation (3). An investigation of this reaction was undertaken¹⁴ in order to clarify the retardation mechanism of the carbon dioxide-carbon reaction. The reaction expressed by equation (3) was found to occur at a slow rate but no evidence for the reaction expressed by equation (2) reverse was obtained under the experimental conditions studied.

The elimination of equation (2) reverse reduces the choice between possible retardation mechanisms to equation (1) reverse or equation (3). It can, however, be shown that either one of these mechanisms, but not both, can control retardation.

Suppose both retardation mechanisms were active: then equations (1), (2) forward and (3) would describe the carbon dioxide-carbon reaction. If these reactions occur exclusively on the carbon surface, then at equilibrium the rate of formation of the carbon-oxygen complex, (O), on unit effective surface equals the rate at which it is removed from the surface

$$k_1 p_{\text{CO}_2} (1 - \theta_{\text{O}} - \theta_{\text{CO}}) = (k_3 + k_2 p_{\text{CO}}) \theta_{\text{O}} \quad (8)$$

where θ_{O} and θ_{CO} are the respective fractions of carbon surface covered by (O) or (CO), and p_{CO_2} and p_{CO} are the, respective, partial pressures of carbon dioxide and carbon monoxide. Equating the rate of adsorption of carbon monoxide with its rate of desorption, at equilibrium

$$k_2 p_{\text{CO}} (1 - \theta_{\text{O}} - \theta_{\text{CO}}) = k_4 \theta_{\text{CO}} \quad (9)$$

whence

$$\theta_{\text{O}} = \frac{k_1 p_{\text{CO}_2}}{k_3 + k_1 p_{\text{CO}_2} + \left(\frac{k_2}{k_3} + \frac{k_5}{k_6} \right) p_{\text{CO}} + \left(\frac{k_2 k_5}{k_3 k_6} \right) p^2_{\text{CO}}} \quad (10)$$

and, since the rate of carbon gasification, R , is $k_3 \theta_{\text{O}}$

$$R = \frac{k_1 p_{\text{CO}_2}}{1 + \frac{k_1}{k_3} p_{\text{CO}_2} + \left(\frac{k_2}{k_3} + \frac{k_5}{k_6} \right) p_{\text{CO}} + \frac{k_2}{k_3} \times \frac{k_5}{k_6} p^2_{\text{CO}}} \quad (11)$$

(14) A. E. Reif, *THE JOURNAL*, **56**, 778 (1952).

A comparison of equation (11) with the experimentally verified equation (7) reveals that equation (11) possesses an extra term in p^2_{CO} . This term vanishes if p_{CO} is small or if either k_5/k_6 or k_2/k_3 is negligible as compared to the other. Since equation (7) has been shown to hold⁶ for appreciable values of p_{CO} , either $k_5/k_6 \ll k_2/k_3$ or $k_2/k_3 \ll k_5/k_6$. These conditions are satisfied only when either the chemisorption of carbon monoxide on carbon by equation (3), or the chemical reaction of carbon monoxide with chemisorbed (O) to reform carbon dioxide by equation (1) reverse controls retardation.

Experimental

In order to obtain evidence on which of the alternative retardation mechanisms was controlling, experiments were made to test the reaction of carbon monoxide with a carbon surface previously saturated with carbon dioxide or with carbon monoxide. The apparatus, materials and procedure employed have already been described.¹⁴ In addition, carbon dioxide of 99.95% purity was used. It was prepared by sealing into the gas purification line a tube containing solid carbon dioxide cooled in a mixture of Dry Ice and acetone. The tube was then evacuated, the cooling mixture removed and the solid vaporized into an evacuated flask.

The results of experiments are summarized in Table II. Experiments are numbered in the order in which they were made and consecutive experiments are prefixed with the same letter; four series of consecutive experiments are reported. The amount of oxygen "O" adsorbed was calculated from the change in volume and composition of the gases in the reaction chamber, and does not distinguish between oxygen bound to the coke surface as (O), as (CO), or in some other manner. A comparison of the results obtained for experiments A-41 and D-99, which are duplicates except for the evacuation of the sample previous to the experiment, gives an estimate of experimental accuracy.

In Experiment A-41, 0.290 cc. of oxygen (O) was adsorbed per gram carbon by saturating the surface with carbon dioxide. After evacuating for 17 hours and admitting carbon monoxide (Experiment A-42), only 0.011 cc./g. carbon of carbon monoxide was adsorbed in the same period of 90 minutes. Further periods of evacuation (Experiments A-43 and A-44) permitted increasing quantities of carbon monoxide to be adsorbed (0.029 cc./g. carbon and 0.088 cc./g. carbon). These experiments show that the adsorption of carbon monoxide on a carbon dioxide-saturated surface was small.

Experiments D-99 and D-100 show the same effect more conclusively. After saturating the carbon surface with carbon dioxide in Experiment D-99, the surface was evacuated for only 0.3 hour before admitting carbon monoxide to it in Experiment D-100. After a reaction period of 30 minutes, a small amount (0.014 cc./g. carbon) of oxygen was adsorbed on the carbon surface. Almost twice as much (0.025 cc./g. carbon) oxygen was removed from the surface by reaction with carbon monoxide to form carbon dioxide, the net effect being the removal of 0.009 cc./g. carbon of oxygen from the surface. Even if all the adsorption had occurred through equation (3) forward, the effect of equation (1) reverse was almost twice as large. Previous work¹⁴ also indicates that under conditions approaching the carbon dioxide-carbon monoxide equilibrium composition, oxygen complex formation occurs through equation (1) forward rather than through equation (3) forward. Since 80% of the equilibrium carbon dioxide composition was reached in the present case, the bulk of adsorption occurred *via* equation (1) forward. Moreover, since equilibrium was so nearly approached, very little further reaction through equation (1) reverse could occur. Hence, the rate of reaction (1) reverse was probably greater than twice as fast as reaction (3) forward.

Series B records results obtained by saturating a carbon surface with carbon monoxide, evacuating for a short period of time and then readmitting carbon monoxide to the surface. Experiments B-69 and B-70 are similar to Experiments C-71 and C-72, except for the evacuation periods and carbon monoxide pressures used. It is seen that the carbon monoxide-saturated surface behaves as if many active sites are still unoccupied: considerably more carbon monoxide

TABLE II
 THE REACTION OF CARBON MONOXIDE AND OF CARBON DIOXIDE WITH CARBON

Expt. No.	Reactant gas	Reaction temp., °C.	Reaction time, min.	Evacuation temp., °C.	Evacuation time, hr.	Initial volume of gas, cc./g. C	Initial pressure, cm.	Gain in vol. of gas, cc./g. C	Final CO ₂ , %	CO ₂ formed cc./g. C	CO formed cc./g. C	"O" adsorbed cc./g. C	Ratio CO ₂ /O
A-41	CO ₂	900	90	900	3.2	26.51	46.37	0.467	11.75	...	1.223	0.290	0.44
A-42	CO	900	90	900	17	27.08	42.49	-.027	1.74	0.016	...	.011	1.43
A-43	CO	900	90	900	23	25.73	40.62	-.038	1.01	.009	...	.029	0.29
A-44	CO	900	90	1000	17	23.59	40.39	-.096	1.16	.008	...	.088	.10
B-69	CO	900	90	1050	1.3	35.77	45.18	-.082	0.55	.006	...	.075	.08
B-70	CO	900	90	900	0.3	36.31	46.42	-.026	.84	.010	...	.016	.66
C-71	CO	900	90	1050	2.0	36.44	62.70	-.078	.58	.007	...	.072	.10
C-72	CO	900	90	900	0.5	37.39	57.90	-.030	.57	.007	...	.022	.32
D-99	CO ₂	900	90	1000	54	26.11	45.33	.480	8.73	...	1.260	.299	.40
D-100	CO	900	30	900	0.3	34.81	61.51	-.014	2.09	.025	...	-.009	-2.78

can be adsorbed on it and considerably less carbon dioxide is formed, as compared with the carbon dioxide saturated surface. These results are not unexpected, since a comparison of Experiments A-41 and D-99 with Experiments B-69 and C-71 shows that at 900°, carbon dioxide initially deposits 4.0 times as much oxygen on the degassed carbon surface as does carbon monoxide. This result is in agreement with data given by the Oxford group,¹¹ who found this ratio to be 5.8 for a coconut shell charcoal at 750°. In both studies, the rate of decomposition of (O) by carbon dioxide was therefore considerably faster than the rate of adsorption of (CO).

A number of other workers^{5,6,11} give data that show that a small quantity of carbon monoxide admixed to carbon dioxide greatly reduces the rate of gasification of carbon. While this phenomenon is satisfactorily explained by reaction (1) reverse, retardation by chemisorption of carbon monoxide on the carbon surface by reaction (3) would require either the rate of adsorption of (CO) to be much larger than the rate of deposition of (O) by carbon dioxide, or the rate of desorption of (CO) to be much slower than the rate of gasification of the carbon-oxygen complex (O) by reaction (2) forward.

Evidence to show that the rate of gasification of (CO) is similar to the rate of gasification of the carbon-oxygen complex (O) is obtained from a comparison of Experiments B-69, B-70 with Experiments D-99, D-100. In the first case, a carbon surface saturated with carbon monoxide was evacuated for 0.3 hour before carbon monoxide was readmitted, and 0.026 cc./g. carbon was adsorbed in the succeeding 90 minutes. In the second case, a carbon surface saturated with carbon dioxide was evacuated for the same period before carbon monoxide was admitted to it, and 0.014 cc./g. carbon was adsorbed in the succeeding 30 minutes. The amount of adsorption, which is of the same order, is a measure of the desorption of (CO) in one case and the gasification of the carbon-oxygen complex (O) in the other, which took place in the 0.3-hour evacuation period.

Thus, at this temperature of 900°, at which gasification occurs, both the assumptions which would make possible retardation through equation (3) appear to be unwarranted. In addition, the fact that approximately only one-fifth of the carbon surface capable of taking up (O) from carbon dioxide was found to adsorb (CO), makes it difficult to understand how the chemisorption of (CO) could account for the great retardation of gasification caused by carbon monoxide. To make this theory possible, it would be necessary to assume that gasification occurred almost exclusively from sites capable of taking up (CO) molecules.

A study of the reaction of carbon monoxide with a degassed coke surface¹⁴ revealed that at the temperatures of 700, 800 and 1000°, monolayer adsorption of carbon monoxide was, respectively, 49, 74 and 204% of its value at 900°. The increase in monolayer adsorption at 1000° to twice its value at 900° is insufficient to account for a major change in reaction mechanism between these temperatures. The smaller monolayer adsorption values at temperatures lower than 900° decrease the probability that equation (3) controls the retardation mechanism at those temperatures.

Further evidence to show that the chemisorption of carbon monoxide on carbon by equation (3) is unlikely to be the controlling mechanism is contained in Table III. The

non-exponential factor and the energy of activation of the directly determined¹¹ equilibrium constant k_2/k_3 for equation (3) are both different in magnitude or in sign from the values for K_{O_2} and E_2 to which they should correspond when the latter are computed from data by other investigators^{5,6,11} on the assumption that equation (3) controls the retardation mechanism. Even allowing for the difference in carbons used, there is no agreement between directly and indirectly determined equilibrium constants.

Discussion

The conclusion drawn from the evidence presented is that retardation of the carbon dioxide-carbon reaction occurs through equation (1) reverse. This differs from the choice of retardation by equation (3) made by the Oxford group,¹¹ which was based mainly on two sets of experiments.

From six experiments, in which mixtures of carbon dioxide and carbon monoxide in varying proportions were introduced to charcoal at 750° for a period of 20 minutes, after which the quantity of oxygen adsorbed on the surface was determined, they concluded that a wide variation in the final pressure of carbon dioxide was not accompanied by a corresponding change in the amount of oxygen complex adsorbed, which followed more closely the smaller variation in final pressure of carbon monoxide. This led to the conclusion that a large part of the oxygen on the surface at the end of this time interval was probably due to the adsorption of carbon monoxide.

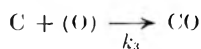
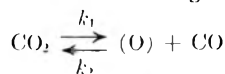
A statistical analysis of the data does not support their interpretation. Straight lines drawn by the method of least squares show that the dependence of adsorbed oxygen on the final partial pressure of carbon dioxide is 1.92 times as great as its dependence on the final partial pressure of carbon monoxide. The standard deviation of points from the former line is only 57% of the standard deviation of points from the latter line. It would seem, therefore, that an opposite conclusion to that drawn by the authors is in better agreement with the data.

It was also pointed out by these authors in support of their mechanism that if their experimental data were interpreted in terms of the alternative mechanism, the energy of activation of reaction (1) reverse would assume the impossible value of -16.8 kcal. It may be seen from Table III, which is an extension of one given in the M.I.T. publication,⁶ that the energy of activation of reaction (1) reverse is the sum of E_2 and $(E_1 - E_3)$.

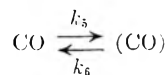
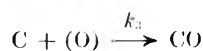
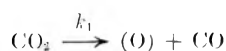
TABLE III
 RATE CONSTANTS FOR THE CARBON DIOXIDE-CARBON REACTION

Group of workers	Carbon sample	K_{O_1}	E_1	K_{O_2}	E_2	K_{O_3}	E_3	K_{O_1}/K_{O_3}	$E_1 - E_3$	$(K_{O_1}K_{O_2})/K_{O_3}$	$E_1 + E_2$	k_{O_2}/k_{O_3}	$E_1 - E_3$
		g. mole min. ⁻¹ atm. ⁻¹ g. ⁻¹		atm. ⁻¹		atm. ⁻¹		g. mole min. ⁻¹ g. ⁻¹		atm. ⁻¹ g. ⁻¹		atm. ⁻¹	
Oxford ¹¹	Coconut shell charcoal	10 ^{3.8}	58.8	10 ^{-7.9}	-45.5	10 ^{6.5}	30.1	10 ^{2.3}	28.7	10 ^{-5.6}	-16.8	..	..
M.I.T. ⁶	New England coke	10 ^{4.8}	47.9	10 ^{-1.9}	-15.4	10 ^{-0.6}	-6.4	10 ^{5.2}	54.3	10 ^{3.3}	38.9	..	..
M.I.T. ⁶	New England coke	10 ^{7.5}	61.7	10 ^{-5.4}	-40.3	10 ^{-1.5}	-6.1	10 ^{9.1}	67.8	10 ^{3.7}	27.5	..	..
	Electrode carbon	10 ^{6.0}	50.1	10 ^{-8.6}	-60.6	10 ^{-0.8}	-6.6	10 ^{6.8}	56.7	10 ^{-1.7}	-2.1	..	..
Reif ¹⁴	High temperature coke	..	..	..	..	..	..	..	..	..	..	10 ^{2.8}	8.0

The rate of reaction of carbon dioxide with carbon may be calculated for any given temperature by the rate equation $\text{rate} = \frac{K_1 p_{CO_2}}{1 + K_2 p_{CO} + K_3 p_{CO_2}}$, where $K_1 = K_{O_1} e^{-1000 E_1/RT}$, $K_2 = K_{O_2} e^{-1000 E_2/RT}$ and $K_3 = K_{O_3} e^{-1000 E_3/RT}$. The rate constants employed in two different representations of the mechanism of the carbon dioxide-carbon reaction may be evaluated from Table IV in the following manner



where $k_1 = K_1$, $k_2 = K_1 K_2 / K_3$, $k_3 = K_1 / K_3$



where $k_1 = K_1$, $k_3 = K_1 / K_3$, $k_5/k_6 = K_2$.

and includes experimental errors made in the separate determination of E_2 and $(E_1 - E_3)$. Since the probable error of -16.8 kcal. derived from the data given by the Oxford group¹¹ was 5.6 kcal. or one-third of its absolute value, it is possible that a positive value is within the limits of experimental error. The average value of this energy of activation obtained in the work at M.I.T. was +21.4 kcal., the positive value indicating that equation (1) reverse is feasible on thermodynamic grounds.

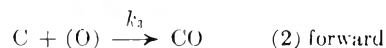
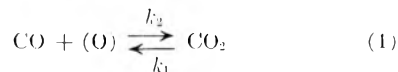
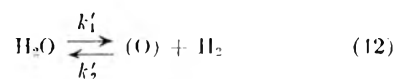
It may be argued that experiments with one type of carbonaceous fuel make it impossible to predict the reaction mechanism with another type of fuel. While there is much evidence to show that the rates of gasification reactions vary widely with composition and reactivity of fuel, there appears to be agreement between experimenters that the same mechanism applies for all types of carbonaceous fuel. Even when different types of carbonaceous fuels were investigated by the same groups of workers,^{5,6,13} only a single mechanism to cover the behavior of all carbonaceous fuels was advanced. Nevertheless, only further experimental work can disprove the possibility that two competing reactions, expressed by equation (1) reverse as opposed to equation (3), may have different relative magnitudes in different types of fuels under different conditions of temperature and pressure.

In the present paper an attempt has been made to compare directly the magnitude of these competing reactions. The reported experiments clearly demonstrate that under the stated conditions the reaction of equation (1) reverse predominates. A detailed study¹⁴ of the rival mechanism of equation (3) showed that this reaction was small in magnitude and slow in rate. Finally, it has been

demonstrated that the data in the literature are largely consistent with the theory that equation (1) reverse controls the retardation mechanism.

It is concluded that the reaction between carbon dioxide and a variety of carbonaceous fuels proceeds according to equations (1) and (2) forward. The rate constants which characterize these equations vary widely with composition and reactivity of the fuel.

If the steam-carbon reaction follows an analogous mechanism to the carbon dioxide-carbon reaction, as suggested by Key,¹² it may be expressed by the equations



An interesting point in this representation is that equations (12) and (1) combine to give the well known water-gas shift reaction, which is known to be catalyzed by carbon. Gasification of carbon by mixtures of steam and carbon dioxide is thus divided into two simple portions: the attainment of the equilibrium composition of the water gas shift equation and the gasification of carbon by equation (2) forward.

Acknowledgment.—The author is very grateful to Dr. H. H. Lowry, Director of the Coal Research Laboratory, and to Dr. J. P. Fugassi, Professor of Chemistry, for their stimulating interest and helpful advice.

KINETICS OF THERMAL DENATURATION OF X-RAYED EGG ALBUMIN

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By the coagulation method, it is shown that X-rayed egg albumin contains different unimolecularly denaturing protein derivatives of decreased thermal stability. Denaturation time curves are given for an irradiated solution at five different temperatures between 29.70 and 59.20° and they are accounted for by three labile species or fractions, characterized by strongly reduced values of both frequency factor and activation energy of denaturation reaction. In the concentration range studied, these structural reactions result from solvent activation and are independent of protein concentration. Data are given for the inhibition of the effect, when the protein was irradiated together with different organic molecules. Similar structural injuries were found when solid egg albumin was X-rayed and subsequently dissolved in water; the yield for the formation of labile protein derivatives was in this case 1.8.

Although it has long been known that proteins, upon exposure to ionizing radiation at low temperature, exhibit the characteristic aggregation reaction of denaturation,¹⁻⁷ more detailed studies are still lacking. It is not known whether denaturation can be defined quantitatively by the coagulate and, if so, whether it takes place primarily or secondarily. In this paper it will be shown that the denaturation of X-rayed egg albumin can be studied by the coagulation method in essentially the same manner as for the intact protein. Under the conditions used, the irradiated systems were found to be initially in the native state, and to contain protein derivatives of greatly reduced thermal stability, characterized by first order denaturation kinetics, as is also the case for the intact protein. We shall, in the following, treat in some detail the various technical problems encountered in such measurements, an example of kinetic data over wide temperature range will be given and, on basis of these, the question of separating the labile species will be dealt with. The work reveals structural injuries which appear important to our understanding of the effect of ionizing radiation on proteins under physiological conditions. It indicates presumably a principal factor in the well known after-effects seen in the irradiation of protein enzymes, which are now beginning to attract quantitative attention.^{8,9}

Technical Procedures

Crystalline egg albumin was prepared from hens eggs with sodium sulfate as the salting-out agent.¹⁰ It was recrystallized four times at pH 4.6-4.7, a concentrated solution was made up and most of the sulfate removed by dialysis at neutral pH near 0°. The solution was adjusted to pH 4.8 and heated briefly at 50°. The precipitate formed was removed and the stock solution thus obtained was stored in frozen form.

In preparing solutions for irradiation, NaOH and H₂SO₄ were used for controlling hydrogen ion activity, which was measured with a glass electrode to an accuracy of pH 0.01, at 25°. The calibration of the pH (pH) scale is based on pH 4.71 for 0.01 M CH₃COOH + 0.01 M CH₃COONa.¹¹

For irradiation of the solid protein, a well dialyzed solution was evaporated to dryness in a vacuum desiccator over sulfuric acid near 0°. The procedure produced only a trace of insoluble material. The preparation contained 8.7% H₂O (drying at 110°) and a negligible amount of Na₂SO₄.

The evacuation chamber and reaction cells earlier described¹² were used for preparing air-free solutions for irradiation. These must be made up from pre-evacuated solvent, in order to prevent foaming and resulting denaturation during the evacuation process.

The exposures were carried out with filtered tungsten radiation, λ_{eff} 0.30 Å. and ca. 10 r./sec. for the solutions, λ_{eff} 0.137 Å. and 40 r./sec. for the solid albumin. Calculations of absorbed energy were based on 0.090×10^{-6} equivalent $\text{Fe}^{++} \rightarrow \text{Fe}^{+++}$ /joule in 1 mM. FeSO₄ in 0.8 N H₂SO₄,^{13,14} taken to be wave length independent in the range of wave length used. The photoelectric absorption was obtained from formulas quoted by Lea¹⁵ the recoil electric absorption from Klein and Nishina.¹⁶ The ionization energy of air was taken to be 32.5 ev.

In the determination of the reaction-time curves, aliquots of the solution under examination were heated in individual flasks, the temperature of the baths being kept constant to within 0.01°. After the removal of a flask from a bath 1% (NH₄)₂SO₄ was added and the solution was kept for one hour to allow coagulation to go to completion, whereafter the coagulate was removed, and the concentration of soluble protein determined by boiling a known volume of the filtrate for 20 minutes. The coagulate was washed with pH 4.8 H₂SO₄ and thereafter with a small amount of water. It was dried to constant weight at 110°.

Owing to the high temperature coefficient of the denaturation reaction, effective zero time should be set rather close to the moment when the solution in a flask reaches bath temperature. This requires usually some 30 seconds and the zero time error may be set at 5 to 10 seconds. Upon removal of a flask from a bath, the reaction was stopped practically instantaneously by cooling in tap or ice-water.

In order to minimize the danger of infection, part of the work was carried out in a cold room, near 0°. Although preservatives cannot be employed, solutions were heated for as long as 72 hours, at the low temperatures, without complication from this source.

Egg Albumin

Thermal denaturation can be studied kinetically by bringing samples of the reacting system rapidly to low temperature and precipitating the denatured protein at its isoelectric point, eventually with help of a suitable salt. By this method, first order denaturation kinetics has been established with considerable accuracy for a variety of proteins.

The principal works on crystalline egg albumin

- (1) L. E. Arnow, *J. Biol. Chem.*, **110**, 43 (1935).
- (2) A. Fernau and W. Pauli, *Biochem. Z.*, **70**, 426 (1915).
- (3) A. Fernau and W. Pauli, *Kolloid. Z.*, **30**, 6 (1922).
- (4) A. Fernau and M. Spiegel-Adolf, *Biochem. Z.*, **204**, 14 (1929).
- (5) B. Rajewsky, *Strahlentherapie*, **33**, 362 (1929).
- (6) M. Spiegel-Adolf, *Arch. Path.*, **12**, 533 (1931).
- (7) P. Wels, *Phys. Arch.*, **199**, 226 (1923).
- (8) R. S. Anderson, *Federation Proc.*, **9**, 6 (1950).
- (9) B. P. Kaufmann, M. R. McDonald and H. Gay, *Carnegie Inst. Wash. Yearbook*, **49**, 173 (1949-50).
- (10) R. A. Kekwick and R. K. Cannan, *Biochem. J.*, **30**, 227 (1936).
- (11) R. G. Bates, *Chem. Rev.*, **42**, 1 (1948).
- (12) H. Fricke, E. J. Hart and H. F. Smith, *J. Chem. Phys.*, **6**, 229 (1938).
- (13) H. Fricke and S. Morse, *Phil. Mag.*, **7**, 129 (1929).
- (14) H. Fricke and E. R. Bronwscome, *J. Am. Chem. Soc.*, **55**, 2358 (1933).
- (15) D. E. Lea, "Actions of Radiations on Living Cells," Cambridge University Press, 1947, p. 347.
- (16) O. Klein and Y. Nishina, *Z. Physik*, **52**, 853 (1929).

are by Chick and Martin¹⁷⁻²⁰ and Lewis.^{21,22} The former authors, who were the pioneers in this field, also made a careful examination of the underlying technical procedures. The reaction was studied in the presence of the $(\text{NH}_4)_2\text{SO}_4$ of the crystalline preparation, under which condition the denatured protein could be brought down quantitatively over a broad range of pH around 4.8, the isoelectric point of egg albumin.

The kinetic study is complicated by the binding of additional hydrogen and hydroxyl ions by the denatured protein, which leads generally to a decrease in rate as the reaction progresses, since the rate is minimum near neutral pH. By taking this effect into account, first order reaction kinetics was established to within a few per cent. change in the velocity constant for 50% change in protein concentration, (initially ca. 1% in all these works) the rate showing a small systematic decrease as the reaction proceeded. The reason for this decrease remained obscure at the time, but a possible explanation can be seen now in view of the electrophoretic heterogeneity of crystalline egg albumin. Although it has not been found possible so far to alter the electrophoretic pattern by denaturation fractionation,²³ a difference of only a few per cent. between the denaturation velocities of the electrophoretic constituents might still be possible.

The present kinetic studies were all carried out in presence of pH 4.85 sodium acetate buffer. Although acetate reacts with the protein, its specific effect on the denaturation rate, if any, is too small to be readily detected, at the rather low concentration needed and has caused no practical difficulties. The concentration of the buffer was always 0.1 M, which kept pH constant to within 0.01, at all protein concentrations used. A change in pH of 0.01 alters the denaturation velocity 4%. The pH of the buffer has a small temperature coefficient ($\Delta\text{pH} +0.01$ to 0.02 per 10° , in the range

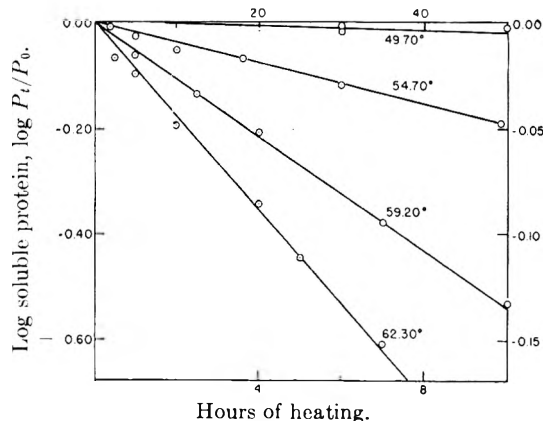


Fig. 1.—Thermal denaturation of 0.46% egg albumin in pH 4.85, 0.1 M sodium acetate buffer + 0.1% Na_2SO_4 —scales: 49.70 and 54.70°, upper, right; 59.20°, lower, right; 62.30°, lower, left.

(17) H. Chick and Martin, *J. Physiol.*, **40**, 404 (1910).

(18) H. Chick and Martin, *ibid.*, **43**, 1 (1911).

(19) H. Chick and Martin, *ibid.*, **45**, 61 (1912).

(20) H. Chick and Martin, *Kolloidchem. Beihefte*, **5**, 49 (1914).

(21) H. K. Cubin, *ibid.*, **23**, 25 (1929).

(22) P. S. Lewis, *Biochem. J.*, **20**, 965 (1926).

(23) L. G. Longworth, R. K. Cannan and D. A. McInnes, *J. Am. Chem. Soc.*, **62**, 2680 (1940).

of temperatures used), which affects the experimental temperature dependence of the reaction. It was not found necessary so far, however, to take this effect into account.

In addition to the buffer, Na_2SO_4 was added (to 0.1%) to all solutions before heating them. In other respects, our experimental procedure was essentially the same as used by the earlier workers. The technical details were set down in the foregoing section.

Observations have been carried out between 0.1 and 1% protein, over which range of concentration the rate was found constant to within 5 to 10%, which is sufficient for our present purpose. There is a tendency toward decreasing rate at the lower concentrations, which cannot be attributed to heterogeneity of the preparation, since it is seen both when time of heating and initial protein concentration are altered.

Data on the effect of initial concentration of protein on the rate are given in Table I.

TABLE I

Effect of dilution on rate of thermal denaturation of intact and irradiated egg albumin. Dosage 33 kr. All solutions were heated at 59.20° with pH 4.85 0.1 M Na acetate + 0.1% Na_2SO_4 , the intact for 12.5 hr., the irradiated for 3 hr.

Concn. heated solution, %	Soluble protein, %	
	Intact	Irradiated
0.46	67.6	66.3
.345	65.9	67.1
.260	68.5	66.5
.195	67.9	68.8
.145	69.4	68.1

Figure 1 shows, in semi-logarithmic plot, reaction time curves for a 0.46% solution at four different temperatures, between 49.70 and 62.30° , the three first of which were obtained as blanks in the irradiation experiments described below. The straight lines shown define the first order velocity constants α , which are used in the analysis.

In Fig. 2, the value of α is plotted against the reciprocal of absolute temperature, each point shown representing the average of different experiments. The points lie practically on a straight line, which passes also approximately through points at higher temperatures, calculated for pH

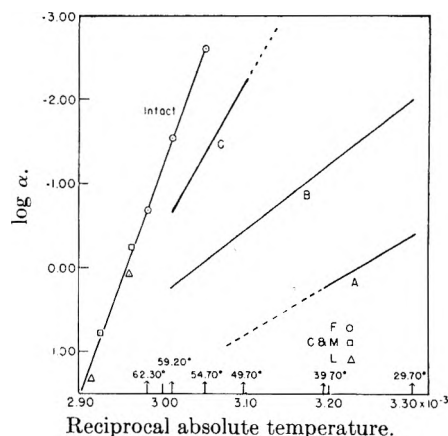


Fig. 2.—Denaturation velocity constant α (h^{-1}) of intact and labile fractions A, B and C of X-rayed 0.46% egg albumin in Arrhenius plot; values from Chick and Martin¹⁷⁻²⁰ and Lewis²² are inserted.

4.85 from observations by Chick and Martin¹⁷⁻²⁰ and Lewis.²² In carrying through this calculation, adjustment was made to the present *pH* (*paH*) scale by adding 0.04 to the *pH* (*psH*) values of these observers.¹¹ It should be noted also that their data refer to solutions containing about 0.4% (NH₄)₂SO₄ while the salt concentration in our solutions was 0.1% Na₂SO₄, in addition to the acetate. At these concentrations and *pH*, electrolytes accelerate the denaturation, but only to a rather small degree.

If we write the Arrhenius equation $\alpha = \nu e^{-E/RT}$ the values obtained for ν and E from the straight line in Fig. 2 are $\nu = 10^{50}$ sec.⁻¹, $E = 129,000$ cal./mole. The mean value of E from Chick and Martins' observations is 134,000, from Lewis 130,000 cal./mole.

Although we have preferred to use the simple Arrhenius equation in this work, the presence of the additional factor T in the equation

$$\alpha = kT/h \times e^{-(\Delta H - T\Delta S)/RT}$$

given by the theory of absolute reaction rate²⁴ tends to improve the fit of the points. The application of this formula leads to the values for the energy (ΔH) and entropy (ΔS) of activation, recorded in Table II.

TABLE II

Data on intact egg albumin and radiation altered protein fractions A, B and C. E and ν are the experimental values of activation energy and frequency factor. ΔH and ΔS are calculated from the theory of absolute reaction rate

A: Reaction rate:

$$0.20 \times 10^{-6} M/1000 \tau = 0.024 \times 10^{-6} \text{ mole/joule; yield} = 0.075$$

$$E = 26000 \text{ cal./mole, } \nu = 10^{15} \text{ sec.}^{-1}$$

$$\Delta H = 25000 \text{ cal./mole, } \Delta S = 8 \text{ cal./degree} \times \text{mole}$$

B: Reaction rate:

$$0.49 \times 10^{-6} M/1000 \tau = 0.061 \times 10^{-6} \text{ mole/joule; yield} = 0.19$$

$$E = 35000 \text{ cal./mole, } \nu = 10^{20} \text{ sec.}^{-1}$$

$$\Delta H = 34000 \text{ cal./mole, } \Delta S = 31 \text{ cal./degree} \times \text{mole}$$

C: Reaction rate:

$$0.88 \times 10^{-6} M/1000 \tau = 0.109 \times 10^{-6} \text{ mole/joule; yield} = 0.34$$

$$E = 81000 \text{ cal./mole, } \nu = 10^{19} \text{ sec.}^{-1}$$

$$\Delta H = 80000 \text{ cal./mole, } \Delta S = 164 \text{ cal./degree} \times \text{mole}$$

Egg albumin:

$$E = 129000 \text{ cal./mole, } \nu = 10^{50} \text{ sec.}^{-1}$$

$$\Delta H = 128000 \text{ cal./mole, } \Delta S = 305 \text{ cal./degree} \times \text{mole}$$

Irradiated Egg Albumin

This section describes experiments on solutions of egg albumin irradiated with dosages below 100 kr./1% protein at 0°, *pH* 4.85 H₂SO₄, in absence of air. The solutions also contained the small amount of (non-reactive) Na₂SO₄ from the stock solution. The exposures caused a slight change in *pH*, which was too small to have any appreciable effect on the reactions.

Irradiation accelerates the coagulation process, without changing its qualitative features. The irradiated systems are quite stable near 0°, around *pH* 4.8 and the only minor complication in measuring the denaturation of these systems by the coagulation

method is, that in some cases the coagulates must be collected at this low temperature. The reaction thus defined is intramolecular, for it is first order, within the experimental accuracy, when protein concentration is changed by dilution (Table I). It shows the typical *pH* dependence of thermal denaturation, although to a less pronounced degree, than for the intact protein. The temperature coefficient is also high, but again markedly decreased as compared to the original.

The following points should be particularly remarked upon. (1) In absence of salt, the *pH* zone of thermal precipitability was the same to within *pH* 0.1, as in the original solution, namely, *pH* 4.5 to 5.2. Although radiation reactions no doubt occur, which alter the isoelectric point of the protein, the shift is, therefore, as would be expected, much too small to affect appreciably the precipitation reaction. This was indicated, also, by the fact stated in (2).

(2) The weight of total denaturable protein, as obtained by brief boiling, was not altered by irradiation. It is well known, that isoelectric egg albumin hydrolyzes to a noticeable degree, if it is subjected to prolonged boiling and it should be noted that this process becomes more pronounced upon irradiation. With the dosages here used, the effect of this secondary process, on the weight of the coagulum, is negligible, during the short time required to bring the coagulation to completion, but it can be detected by examining the filtrate. Thus, after boiling a 0.5% solution for one hour, Folin phenol reagent showed the presence of 20×10^{-6} *M* equivalent tyrosin in the filtrate from the intact protein and 70×10^{-6} *M* equivalent tyrosin after the solution had been treated with 60 kr.

(3) The dilution test indicates that the kinetic observations are not complicated by reactions, during the heating, between the protein and radiation reaction products. That no such effect was present was shown also by dialyzing an irradiated solution before heating it. A possible troublesome reaction product would be H₂O₂, but since the present irradiations were carried out in absence of air, this compound is probably not formed in an appreciable quantity. Direct test of its effect showed that 0.5% egg albumin could be heated with 10^{-4} *M* H₂O₂ for two hours at 49.70°, without coagulation.

Denaturation-Time Curves.—Figure 3 (a-d) records the denaturation time curves at five different temperatures between 29.70 and 59.20°, for a 0.46% egg albumin solution treated with 33.2 kr. The ratio *M/N* of protein molecules in the solutions to ion pairs in air produced by this dosage, is 0.9. From preliminary experiments it was expected that this dosage would be within the range of dosages giving a linear dosage curve, but the final observations showed that this is not the case. The influence of multiple reactions is not negligible, therefore, although the structural injuries observed are essentially those characteristic of small dosages.

Examination of the reaction curves shows that, within the experimental accuracy, they can be accounted for by four first order terms A, B, C and D, the denaturation velocity constant of each of

(24) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, New York, N. Y., 1941.

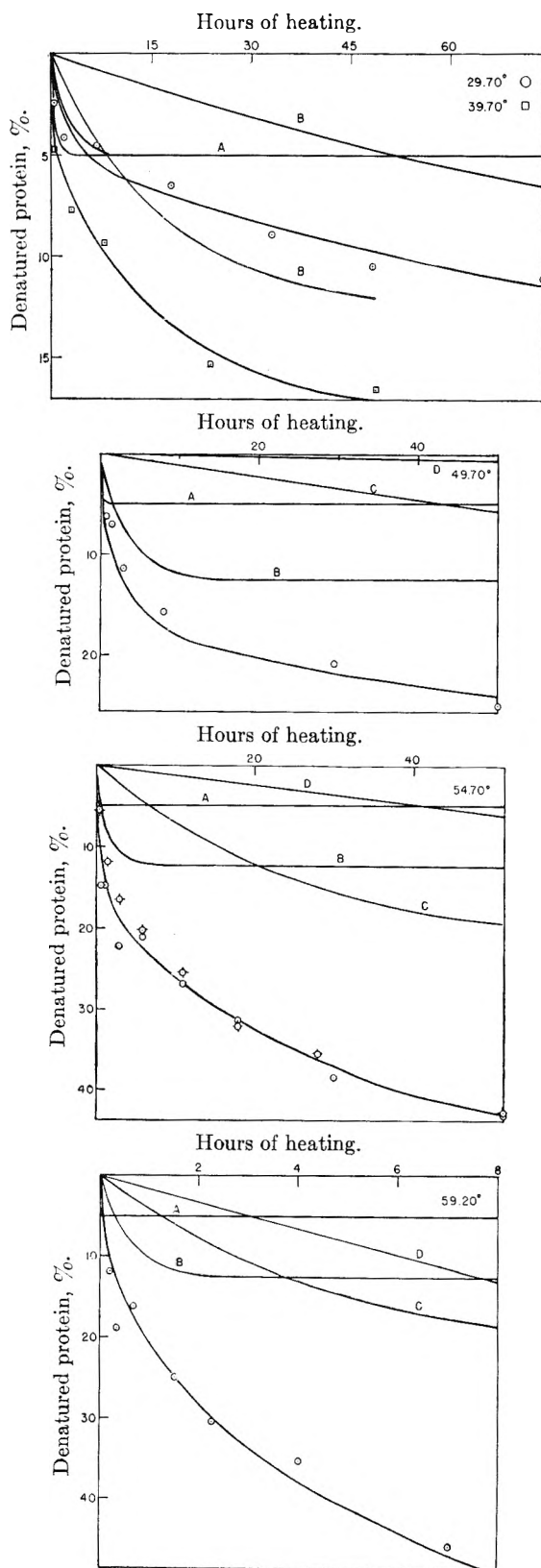


Fig. 3a-d.—Thermal denaturation of X-rayed 0.46% egg albumin and of fractions A, B, C and D; dosage 33.2 kr. The lines are theoretical. $\circ$ - $\circ$ in (c) were obtained in two different irradiations.

which is represented by the Arrhenius equation. Their concentrations are 5, 12.5, 22.5 and 60%,

respectively, and D represents protein having the same denaturation velocity constant (α) as the intact, *i.e.*, the concentration of soluble protein

$$P_t = 0.05e^{-\alpha_1 t} + 0.125e^{-\alpha_2 t} + 0.225e^{-\alpha_3 t} + 0.60e^{-\alpha t} \quad (1)$$

The denaturation velocity constants α_p are given in Fig. 2.

The denaturation of each term is recorded separately in Fig. 3 and the lines drawn through the experimental points are calculated from formula (1). The agreement is satisfactory, but the accuracy is obviously not sufficient to show whether or not these terms represent individual protein derivatives.

At 59.20°, the reaction is shown to 75% completion, at which stage the rates are approximately the same in the irradiated and intact solution, although points measured further out indicate that the irradiated solution contains more labile protein than given by formula (1). The irradiated solution contains apparently no protein derivatives more stable than the original.

The Arrhenius values of frequency factor and energy of activation for the different terms are recorded in Table II. The table contains also values for energy and entropy of activation, as obtained by using the equation of the theory of absolute reaction rate.

Protein Concentration.—Three solutions of concentrations 0.23, 0.46 and 0.92% were treated in one set of experiments with 72 kr./1% protein, in another with 36 kr./1% protein. In each of these sets of experiments, the radiant energy absorbed in the different solutions is practically constant for unit of protein concentration. After irradiation, the solutions of higher concentrations were diluted to that of the weakest, whereafter they were heated at 59.20°. The curves for the different concentrations were found to be practically identical, showing that the observed effect results essentially from solvent activation, and that this mechanism is independent of protein concentration in this concentration range.

Radiation Dosage.—The 0.46% solution was treated with two smaller dosages, *viz.*, 10.0 and 20.0 kr. and the denaturation-time curves were determined at 59.20° (Fig. 4). The vertical distance between a curve for irradiated protein and that of the intact, at the end of the heating period, 10 hours, can be used as an approximate measure, in logarithmic scale, of the fraction of labile protein in the irradiated solution. This quantity is shown as function of dosage in Fig. 4. The slope decreases with increasing dosage, as would be expected, since, as we keep on irradiating a solution, an increasingly greater portion of the radiant energy will be used in altering molecules already sufficiently labile to be recorded in our measurements.

Radiation Reaction Rate.—The fractions A, B and C constitute together 40% of the protein of the irradiated solution. In order to calculate the initial rate of production of these fractions, we make use of the dosage curve in Fig. 2 and obtain 0.0154/kr. Expressed in molar concentration, the initial rate is calculated from

$$k = 0.0154 \times \frac{0.46 \times 10}{45000} = 1.57 \times 10^{-6} M/\text{kr.}$$

The molecular weight of egg albumin is taken to be 45000.²⁵ With reference to the radiant energy absorbed in the protein solution, the rate is 0.19×10^{-6} mole/joule. Using this value, the yield with respect to the ionization in air is 0.60.

The relative concentrations of the radiation altered fractions are 0.05/0.40, 0.125/0.40, and 0.225/0.40, respectively. By multiplying each of these values with the total reaction rate just given, the initial rates of production of these fractions are obtained (Table II).

Nature of Reactions.—The observations made so far indicate that the changes resulting in insolubility of heated irradiated egg albumin are of the same general character as those produced by heating the original protein. Thus, it appears, in view of the strong decrease in both energy and entropy of activation, that irradiation is capable of producing profound structural injuries, about whose exact nature there is, however, hardly any basis at present for expressing any opinion. Many of the chemical changes in the irradiated protein may involve breakage of cross linkages, but the effect on the stability seems likely to be rather small. The effect of oxidation of Cysteine SH should be particularly remarked upon, since the reaction of this group may account for a major part of the chemical radiation effect and the group can be oxidized also by chemical methods. While no quantitative information is available on the effect of its chemical oxidation on the stability, it is known that all (four or five) cysteine groups in an egg albumin molecule can be oxidized, to SS and beyond this stage, without denaturation and apparently without very marked instability.²⁶ The only side group likely to be of great structural importance, is cystine, but this group appears to be rather insensitive to radiation and, moreover, there is only one such group in egg albumin.

If the polypeptide chain were ruptured, the effect on the stability would presumably be very marked. This structure appears to be relatively resistant toward chemical breakage, but might conceivably be broken hydrolytically under the influence of energy liberated during the initial stages in the interaction of the protein with the active water particles. It would be of interest to test this point by irradiating simpler peptides.

If the peptide chain is actually broken, we should expect proteins to fractionate under influence of moderately massive dosages. Svedberg and Brohult²⁷ did in fact find strong fractionation in α -rayed solutions of serum albumin and hemoglobin, when examined in the ultracentrifuge. The dosage was not stated, but it appears to have been of the order of a few hundred thousand equivalent r . With moderate X-ray dosages, there is apparently no fractionation of human serum albumin.²⁸ Its absence, even after the irradiated protein has denatured, in the cases studied by us, may be inferred since, as was pointed out above, the weight

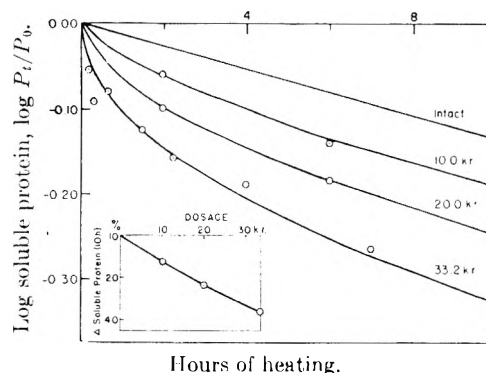


Fig. 4.—The effect of dosage in the thermal denaturation of X-rayed egg albumin; temperature, 59.20°.

of the total heat coagulable protein was not altered upon irradiation.

Effect of Added Organic Substances.—Irradiation of organic mixtures has already been given a good deal of attention in the past as a technically simple method for throwing light on the relative radiation sensitivity of different types of organic grouping.^{12,29} The behavior of a protein in such experiments is of particular interest since, chemically, the constituent amino acids are generally much less reactive than in their free state. All substances reported upon below acted as inhibitors.

The mixtures contained 0.60% egg albumin and were prepared and irradiated at pH 4.85 near 0°. All were treated with a dosage of 22 kr. and some also with 33 kr. The dissolved air was not removed in these experiments; it has only little effect on the reaction in the irradiation of egg albumin by itself.

After irradiation, diffusible substances were removed by dialysis, whereafter the solutions were heated at 62.20° for four hours, which caused a practically complete removal of labile protein from the irradiated solutions. The non-irradiated mixtures were treated in the same manner and, as a further control, solutions prepared by adding intact egg albumin to irradiated solutions of the added substances were also tested. The purpose of these and other tests, which need not be described here, was to guard as far as possible against the possible effect of irreversible reactions between the protein and the added material or its radiation products which might take place during the dialysis. No complications of this kind are believed to be present in the data which follow.

It will be seen by examining Fig. 4, that the value $\log P_0/P_1$ is approximately proportional to dosage, P_0 and P_1 representing soluble protein in the heated solution of intact and irradiated egg albumin, respectively. Consequently, the inhibitory power of an added substance is logically represented by

$$I_h = \frac{\log F_2/P_1}{\log P_0/P_1}$$

P_2 is the fraction of soluble protein in the heated irradiated mixture. The values of I_h obtained with

(25) R. Tristram, *Advances in Protein Chem.*, **5**, 83 (1949).

(26) M. L. Anson, *ibid.*, **2**, 369 (1945).

(27) T. Svedberg and S. Brohult, *Nature*, **143**, 938 (1939).

(28) E. B. Sanigar, L. E. Krejci and E. O. Kraemer, *Biochem. J.*, **33**, 1 (1939).

(29) H. Fricke, *Symposium IV, Chemistry and Physics of Radiation Dosimetry*, p. 24, 1950, U. S. Dept. of Defense & Atomic Energy Commission, Tech. Services, Dept. of Commerce, Washington, D. C.

22 kr. are plotted in Fig. 5, the checks made with 33 kr. showing that these values represent sufficiently well the condition of small radiation dosage.

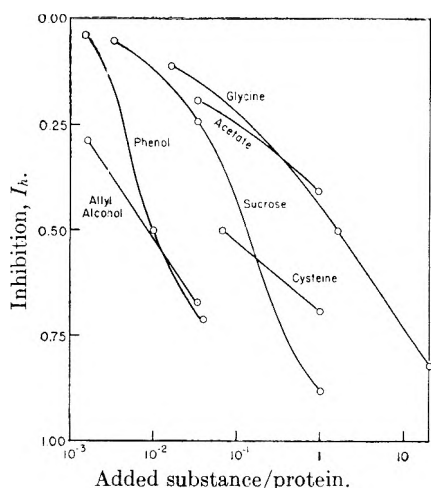


Fig. 5.—Irradiation of mixtures of egg albumin and different organic compounds.

The observations give new examples of the great differences in protective power of different organic substances. Considering its high contents of reactive groupings, the radiation reactivity of egg albumin appears to be relatively low, as would be expected from its behavior toward chemical reagents. Organic compounds of high chemical reducing power have generally been found to have high radiation susceptibility or protective power and the observations obtained agree fairly well with this rule, especially if the comparison is made at low concentrations of the added substance. Cysteine is not as effective as would be expected on this basis, but data were obtained only at rather high concentrations. Examples have been given in the past³⁰ of high protective power of unsaturated aliphatic compounds, although these did not prepare us for the remarkable effectiveness of allyl alcohol in our experiment. It is of interest that the protective power of glycine is not greater than that of acetic acid, although the amino group has in general been found to be relatively reactive compared to the other groups in these two molecules.

Solid Egg Albumin

The protein powder was placed in a flat sealed Pyrex flask and over a period of three days treated with such a dosage (2000 kr.) that the energy absorbed in the standard ferro sulfate solution was 18700 joules/l. On basis of the ionization in air, this dosage ionizes of the order of 25% of the protein molecules.

The drying process was not wholly without effect on the protein, since 1 to 2% was insoluble at pH 4.85. The denaturation rate of the soluble portion was not, however, significantly different from that of the original wet protein.

At pH 4.85 and 0°, in presence of 1% (NH₄)₂SO₄, the amount of insoluble protein in the irradiated material was practically the same as in the original. The residue was filtered off and the filtrate remained

clear for some hours at 0°, but became later opalescent and coagulated rapidly at higher temperatures. On basis of a similar examination as described above for the irradiated solutions, it was concluded that, as before, (1) denaturation is wholly secondary, (2) it can be defined and followed quantitatively at higher temperatures by completing the coagulation process at low temperature, (3) it is first order when concentration is altered by dilution, (4) it is not appreciably affected by reactions between the protein and radiation reaction products and (5) all the radiation altered protein is heat denaturable.

Reaction-time curves were measured at 49.70 and 60.00° for a 0.46% solution (Fig. 6). At 60.00° heating was continued for 10 hours, at which point the slope of the irradiated curve was practically the same as for the intact.

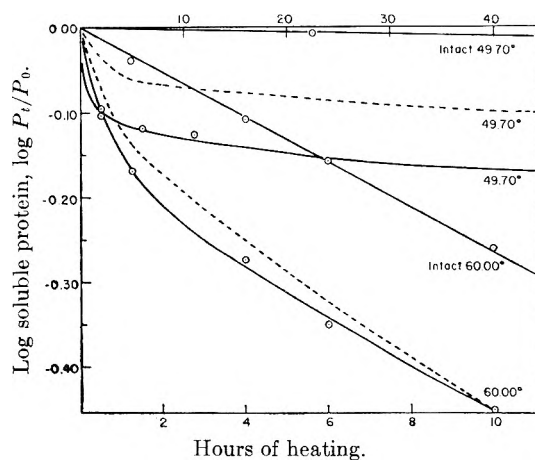


Fig. 6.—Thermal denaturation of a 0.46% solution of X-rayed solid egg albumin at 49.70 and 60.00°; pH 4.85; dosage 2000 kr. The broken lines show denaturation of a 0.46% solution of egg albumin treated with 27 kr. Time scales: upper, 49.70°; lower, 60.00°.

The irradiated system is evidently heterogeneous. The data are insufficient for analysis, but for comparison are shown the denaturation-time curves for 0.46% egg albumin treated with 27 kr. With this dosage, the curves obtained for the two systems at 60.00° coincide approximately at the end of the heating, but the curve for the irradiated solid lies lower at the shorter heating times. This difference is still more pronounced in the curves at 49.70°. The two systems contain, therefore, approximately the same total amount of experimentally labile protein, but this protein fraction is in a more highly injured condition in the irradiated solid, coming down faster and at a rate less dependent on temperature, than in the irradiated solution.

By taking the vertical distance between the 60.00° curves for the irradiated solid and intact albumin, at 10 hours heating time, we obtain the fraction of protein of markedly increased lability in the solution of the irradiated protein. This fraction is 0.35. If we assume that the amount of unaltered protein varies exponentially with dosage, the initial radiation reaction rate is calculated from

$$\frac{\ln 0.65}{17.0 \times 45000} = 0.56 \times 10^{-6} \text{ mole/joule}$$

As before, 45000 is the molecular weight of egg albumin. The value 17.0 is the radiant energy in joule absorbed in 1 g. of the protein. In calculating the latter value, the 8.7% H_2O of the preparation, which must be present as water of hydration, was taken to be part of the protein. The small amount of Na_2SO_4 can be ignored and its elementary composition was taken to be 7% H, 50% C, 15.3% N, 26% O, 0.1% P, 1.6% S.

From the above value for the reaction rate, the yield with reference to the ionization in air is calculated to be 1.8. On basis of existing data on the ionization energy of organic substances in gaseous form, the ionization energy of protein seems likely to be smaller than that of air and the yield referred to the ionization in the protein itself would be, therefore, probably somewhat below 1.8. Due to the cluster effect, more than one activation process (ionization, excitation) must occur in some of the giant protein molecules. The result will be more extensive injury and smaller yield than would have been obtained if the energetic processes had been produced at random.

In considering the significance of the high yield, it should be recognized that, since the structurally

sensitive part of the protein includes presumably the weaker linkages in the molecule, injury by transfer of energy from other parts of the molecule may be an important factor in the induced instability. Moreover, the possibly effective energetic processes include both electronic deficiencies and ejected electrons, as well as electronic excitations, the number of the latter being probably about twice that of the ionizations. The importance of excitation is shown qualitatively by the familiar denaturing effect of the light from a quartz mercury lamp. This light is absorbed chiefly in the aromatic groups, but—based on observations on simple peptides³¹—is often assumed to exert its structural effect by transference of the energy to, and breakage of, the peptide chain. If this be true, excitations in other parts of the protein molecule should be equally effective.

This investigation was supported by research grant, Project R. G. 673, from the Division of Research Grants and Fellowships of the National Institutes of Health. I am indebted to Dr. E. Parker for his assistance during part of the work.

(31) E. K. Ridcal and J. S. Mitchell, *Proc. Roy. Soc. (London)*, **159A**, 206 (1937).

THE DIELECTRIC PROPERTIES OF DISPERSED LIQUIDS. I. THE THEORY OF THE DIELECTRIC CONSTANT

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The dielectric increment of a dilute homogeneous dispersion of a liquid in a medium of lower dielectric constant is given by Equation 9, where V_1 is the volume concentration of the dispersed phase, k_1 and k_2 are the dielectric constants of the dispersed and continuous phases, respectively; a_0 is the droplet radius, E_0 , the field strength, and γ , the interfacial tension. For aerosols, the second term is generally negligible. However, under proper conditions, the dependence of the dielectric increment upon field strength might be detectable, and afford a method of investigating particle size distributions. The distortion of the droplets by the field may be expected to lead to slight anomalies in the dielectric absorption, also dependent upon particle size.

I. Introduction

Among the properties of emulsions and aerosols which have received relatively little recent attention are the dielectric constant and dielectric absorption. Perhaps the most thorough studies have been carried out by Pickara²⁻⁸ and by Guillien,⁹ although the latter concentrated his interest on solid dispersions primarily. Both of these series of investigations, however, were carried out with conventional, relatively insensitive instruments, and were accordingly restricted to quite concentrated dispersions. The recent application of microwave techniques to the meas-

urement of dielectric properties¹⁰⁻¹⁷ has permitted a great increase in the sensitivity of dielectric constant determinations. The microwave refractometer described by Birnbaum¹⁰ is particularly useful, since it is primarily intended for measuring minute differences in dielectric constant.

This improvement in available instruments has prompted a new investigation of the dielectric properties of liquid dispersions. The experiments will be conducted principally upon aerosols, although the calculations to be reported in this paper should be equally applicable to dilute dispersions

(1) Contribution No. 538.

(2) A. Pickara, *Bull. intern. acad. polon. sci., classe sci. math. nat.*, **45**, 20 (1918).

(3) A. Pickara, *Kolloid-Z.*, **49**, 97 (1929).

(4) A. Pickara, *Compt. rend. soc. polon. phys.*, **4**, 251 (1929).

(5) A. Pickara, *Physik. Z.*, **31**, 579 (1930).

(6) A. Pickara, *Kolloid-Z.*, **52**, 179 (1930).

(7) A. Pickara, *ibid.*, **58**, 283 (1932).

(8) A. Pickara, *ibid.*, **59**, 12 (1932).

(9) R. Guillien, *Ann. phys.*, **16**, 205 (1941).

(10) G. Birnbaum, *Rev. Sci. Instruments*, **21**, 169 (1950).

(11) G. Birnbaum and J. Franeau, *J. Applied Phys.*, **20**, 817 (1949).

(12) G. Birnbaum, S. J. Kryder and H. Lyons, *ibid.*, **22**, 95 (1951).

(13) B. Bleany, J. H. N. Loubser and R. P. Penrose, *Proc. Phys. Soc. (London)*, **59**, 185 (1949).

(14) C. M. Crain, *Phys. Rev.*, **74**, 691 (1948).

(15) H. Lyons, G. Birnbaum and S. J. Kryder, *ibid.*, **74**, 1210(A) (1948).

(16) R. L. Sproul and E. G. Linder, *Proc. Inst. Radio Engrs.*, **34**, 305 (1946).

(17) C. W. Tolbert and A. W. Straiton, *Rev. Sci. Instruments*, **22**, 162 (1951).

of liquids in any medium of lower dielectric constant.

As a preliminary to experimental studies in this field, a theoretical analysis has been made of the dependence of the dielectric constant upon the concentration, the particle size, and the properties of the substances involved. The results of this analysis are reported in this paper.

II. Calculations

Pickara's studies have indicated that the dielectric properties of dispersions in highly polar media are anomalous, probably because of the formation of double layers of indefinite properties surrounding the droplets. To avoid this difficulty, we will treat only the case where the dielectric constant of the medium is less than that of the dispersed phase. This restriction also simplifies the treatment of the change in dielectric constant with field strength. We will also neglect the problem of the internal field in dielectrics, confining our attention to suspensions so dilute that interactions between the droplets can be neglected. For more concentrated dispersions, appropriate modifications in the internal field may be made by whatever theory seems preferable. Neither of these restrictions will be serious in the case of aerosols, the type of dispersion of primary interest to us.

The major problem which we must solve is the determination of the effective electric moment of a droplet in an electric field. In the absence of the field, the droplet will be spherical, due to interfacial tension. The field, however, tends to distort the droplet into a spheroid, with the axis of revolution parallel to the field. For moderately low field strengths, when the dielectric constant of the medium is less than that of the droplet, the spheroid will be prolate, with eccentricity, e , given by the limiting law¹⁸

$$e_2 = \frac{9a_0\epsilon_2(\epsilon_1 - \epsilon_2)^2}{4\gamma(\epsilon_1 + 2\epsilon_2)^2} E_0^2 \quad (1)$$

where

$$e = \sqrt{1 - (b/a)^2} \quad (2)$$

b being the minor axis and a the axis of revolution of the spheroid, a_0 the radius of the undistorted droplet, γ the interfacial tension between the two phases, and E_0 the field strength. In more concentrated dispersions, E_0 may be modified appropriately to account for interactions between droplets. The inductive capacities of the dispersed and continuous phases are, respectively, ϵ_1 and ϵ_2 .¹⁹

A spheroid of volume $4\pi a_0^3/3$, and of eccentricity e in a field of strength E_0 , can be shown to have a net polarization, above that of an equal volume of dispersion medium

$$p_1 = \frac{4\pi a_0^3}{3} (\epsilon_1 - \epsilon_2) E_0 \left\{ 1 + \frac{\epsilon_1 - \epsilon_2}{2\epsilon_2} \frac{(1 - e^2)}{e^2} \left[\frac{1}{e} \ln \frac{(1 + e)}{(1 - e)} - 2 \right] \right\}^{-1} \quad (3)$$

or, neglecting terms of order e^4

$$p_1 = 4\pi a_0^3 \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} \right) \epsilon_2 E_0 \left\{ 1 + \frac{2(\epsilon_1 - \epsilon_2)}{5(\epsilon_1 + 2\epsilon_2)} \frac{e^2}{e^2} \right\} \quad (4)$$

If we insert the limiting law, Eq. (1), we find

$$p_1 = 4\pi a_0^3 \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} \right) \epsilon_2 E_0 \left\{ 1 + \frac{9\epsilon_2(\epsilon_1 - \epsilon_2)^3}{10(\epsilon_1 + 2\epsilon_2)^3} \frac{a_0 E_0^2}{\gamma} \right\} \quad (5)$$

In a dilute suspension, in which we can neglect the interaction among the different droplets, the total polarization will be the sum of the polarization of the dispersion medium and of the dispersed phase. For a dispersion containing n_1 droplets, all of the same radius, a_0 , per cubic centimeter, the total polarization will be

$$P = (\epsilon_2 - \epsilon_0) E_0 + n_1 p_1 \quad (6)$$

The apparent macroscopic inductive capacity, ϵ , of the dispersion may be calculated from the definition

$$\epsilon = (P/E_0) - \epsilon_0 \quad (7)$$

where ϵ_0 is the inductive capacity of free space (unity in the case of electrostatic units). Remembering that $4\pi a_0^3$ is three times the volume of a droplet, we obtain as our expression for ϵ

$$\epsilon = \epsilon_2 + 3V_1\epsilon_2 \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} \right) \left\{ 1 + \frac{9\epsilon_2(\epsilon_1 - \epsilon_2)^3}{10(\epsilon_1 + 2\epsilon_2)^3} \frac{a_0 E_0^2}{\gamma} \right\} \quad (8)$$

where V_1 is the volume of the dispersed phase per cubic centimeter of dispersion.

The dielectric constant, κ , of a material is the ratio of its inductive capacity to that of free space, so that for c.g.s. electrostatic units we may write for the dielectric increment of the dispersion

$$\Delta\kappa = \kappa - \kappa_2 = 3V_1\kappa_2 \left(\frac{\kappa_1 - \kappa_2}{\kappa_1 + 2\kappa_2} \right) \left\{ 1 + \frac{9\kappa_2(\kappa_1 - \kappa_2)^3}{10(\kappa_1 + 2\kappa_2)^3} \frac{a_0 E_0^2}{\gamma} \right\} \quad (9)$$

The coefficient of $a_0 E_0^2/\gamma$ is always less than κ_2 . Thus, the magnitude of the second term in brackets, and of the higher order terms which we have neglected, can be disregarded when $a_0 E_0^2/\gamma$ is less than $0.01/\kappa_2$ without causing an error of more than one per cent. Since the dielectric strength of air is about 100 statvolts per centimeter, the maximum effect for aerosol droplets with surface tension 10 dynes per centimeter and one micron radius will be less than 10%. For the low field strengths customarily used in dielectric constant measurements, the effect of particle size can safely be ignored over the entire size range, and we can use the approximate equation

$$\Delta\kappa = 3\kappa_2 \left(\frac{\kappa_1 - \kappa_2}{\kappa_1 + 2\kappa_2} \right) V_1 \quad (10)$$

III. Discussion

Equation (10) offers a basis for a rapid and continuous measure of the volume concentration of the dispersed phase of any colloid if a sufficiently sensitive method of measuring the dielectric increment is available. For aerosols of high dielectric constant, the concentrations can be determined

(18) C. T. O'Konski and H. C. Thacher, Jr., to be published.

(19) The most convenient source for the electrostatic results used in this calculation is Stratton.²⁰ We will follow his nomenclature, in general, and will also follow his example in using rationalized equations throughout. However, since interfacial tensions are commonly expressed in c.g.s. units, the field strength appears as statvolts per centimeter.

(20) J. A. Stratton, "Electromagnetic Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

to about three times the precision in measuring the dielectric increment. The Birnbaum microwave refractometer is said to be sensitive to changes in the dielectric constant as low as 4×10^8 , and should thus be capable of measuring aerosol concentrations as low as two parts per hundred million by volume.

If we assume that the density in the dispersed phase is the same as in the bulk, the sensitivity amounts to about 60 micrograms per liter of dioctyl phthalate smoke, and approximately the same concentration of other common smoke agents. Experimental work is now in progress in this Laboratory to verify this conclusion.

Although the change in dielectric constant of aerosols with field strength is beyond detection by present instruments, it may be detectable in emulsions where the drop size may be larger, the interfacial tension lower, and where high field strengths are possible without sparking. Since the effect is approximately linear in the drop radius, it may afford a convenient method of studying particle size distributions in emulsions.

Another possible source of information on the drop spectrum, and a phenomenon of interest in its own right, is the dielectric relaxation. If a droplet is allowed to come to equilibrium in a steady field, and the field is suddenly removed,

the droplets will execute damped oscillations about a spherical shape, with frequency given by the Rayleigh formula²¹

$$\omega_0^2 = 8\gamma/\rho_1 a_0^3 \quad (11)$$

and a damping factor²²

$$\tau = a_0^2 \rho_1 / 5\eta \quad (12)$$

The polarizability of the droplets will also show this variation, so that we may expect a form of dielectric absorption near the resonant frequency, which, for colloidal droplets, falls in the megacycle range. This absorption will be of an unusual type, since unlike that due to the relaxation of polar molecules, the displacement will drop immediately to zero when the field is removed, while the "dielectric constant" will show damped oscillations about its zero-field value.

Development of a quantitative theory of this effect will be hampered both by the non-linearity of the dependence of the polarizability upon the field strength, and by the electrical and hydrodynamic problems involved. However, the existence of such an effect seems assured, and its dependence upon the drop radius seems highly probable.

(21) H. Lamb, "Hydrodynamics," Dover Publishing Co., New York, N. Y., 1945, p. 475.

(22) H. Lamb, *ibid.*, p. 640.

COLLISION DIAMETERS OF SOME GASES AS FUNCTIONS OF TEMPERATURE

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The collision diameters calculated from viscosity data for oxygen, nitrogen, argon and air are given over the range of temperature from 200 to 2500°K.

Kinetic theory states that, when a gas is assumed to be composed of smooth, rigid, elastic, spherical molecules of diameter σ , the viscosity is given by the relationship

$$\mu = 0.1792 (kmT)^{1/2} / \sigma^2$$

where μ is the viscosity; m the mass of the molecule; k , Boltzmann's constant; and T , the absolute temperature. The accurate derivation of this relationship is straightforward and is given in its entirety by Chapman and Cowling.¹ With accurate viscosity data this relationship provides a convenient means for the determination of molecular size. Diameters, so calculated, are regarded as equivalent ones and are very useful for many sorts of approximate calculations and for comparison with size determinations by other methods. Several authors have calculated diameters by this method, but only at 0°. (Chapman and Cowling¹ give values for helium up to 800°, but these seem to be the only data for a range of temperature.) Discrepancies between values obtained by other calculators are shown below.

In this work, the molecular diameters of nitrogen, oxygen, argon and air using the latest available viscosity data and the latest accepted values of the fundamental constants are given; the variation of the diameter with temperature given by the relationship used is shown; and the values obtained with previous similar determinations are compared with values determined by completely different methods.

Recently there have been published by Vasilescu² extensive viscosity data for air, nitrogen and argon. These determinations cover a complete range of temperatures, going as high as 2900°F., and seem to be the most accurate and complete work on viscosity done up to this date. Vasilescu's results were statistically analyzed by the personnel of the Air Materiel Command Heat Transfer Project at The Johns Hopkins University and published in a convenient tabular form in a recent report.³ Included in this report were values for oxygen analyzed in the same manner as the other gases, but

(2) V. Vasilescu, *Ann. Phys.*, **20**, 137, 292 (1945).

(3) August 31, 1948, Report, Air Materiel Command Project, Dept. of Chem. Eng., The Johns Hopkins University.

(1) S. Chapman and T. C. Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge Press, 1939, pp. 168, 220, 221, 229.

from much more sparse data⁴ than Vasilescu had presented.

These data plus the values given by Birge⁵ as the latest accepted values of the fundamental constants were used in this work.

Calculations and Results

The values of the fundamental constants used are

$$n = \text{Avogadro's number} = 6.0228 \times 10^{23} \text{ mole}^{-1}$$

$$k = \text{Boltzmann's constant} = 1.38047 \times 10^{-16} \text{ erg deg.}^{-1}$$

The molecular weights are given in Table I, which also shows the calculation of the mass of the molecule. In Table II the results for the viscosity and

TABLE I
CALCULATED MOLECULAR MASSES

Gas	Mol. wt.	$m \times 10^{24}$, g.	$m^{1/2} \times 10^{12}$, g.
N ₂	28.016	45.5166	6.820
A	39.944	66.321	8.144
O ₂	32.000	53.131	7.289
Air	(28.96)	48.084	6.934

collision diameter of N₂, A, O₂ and air, respectively, are given. Figure 1 shows the variation of collision diameter with temperature.

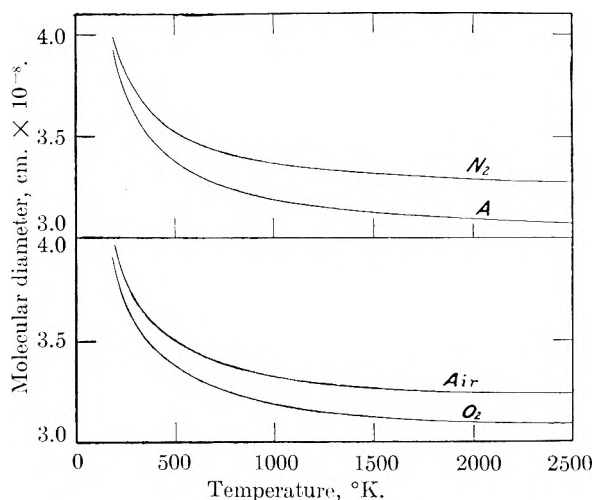


Fig. 1.—Molecular diameter of nitrogen, oxygen, argon and air as a function of temperature.

Discussion

The decrease of molecular diameter with temperature is interesting. All four gases considered show a decrease of approximately 20% over the complete range of temperature, 200–2500°K. Chapman and Cowling¹ offer the explanation of this effect by considering molecules centers of repulsive forces, not hard spheres.

In Table III a comparison of the values obtained at 0° with values taken from other sources is given.

Chapman and Cowling used the viscosity data of Schmitt⁶ for their calculation on nitrogen and oxygen and the data of Schultze⁷ for argon. Kennard used the data of Trautz⁸ on nitrogen, oxygen and

(4) P. J. Rigdon, *Phil. Mag.*, **25**, 961 (1938).

(5) R. T. Birge, *Rev. Modern Phys.*, **13**, 223 (1941).

(6) Schmitt, *Ann. Physik*, **30**, 398 (1909).

(7) Schultze, *ibid.*, **5**, 165 (1901); **6**, 310 (1901).

(8) Trautz and Zink, *ibid.*, **7**, 427 (1930); Trautz and Baumann, *ibid.*, **2**, 733 (1929); Trautz and Sorg, *ibid.*, **10**, 81 (1931); Trautz and Melster, *ibid.*, **7**, 409 (1930); Trautz and Binkele, *ibid.*, **5**, 561 (1930).

TABLE II

COLLISION DIAMETERS AND VISCOSITIES AS A FUNCTION OF TEMPERATURE

Temp., °K.	Nitrogen		Argon		Oxygen		Air	
	$\times 10^6$	$\times 10^8$	$\times 10^6$	$\times 10^8$	$\times 10^6$	$\times 10^8$	$\times 10^6$	$\times 10^8$
200	129.0	3.968	160.5	3.887	147.1	3.841	133.1	3.939
250	155.1	3.826	195.4	3.725	178.3	3.688	160.3	3.795
273	166.3	3.776	210.5	3.665	191.5	3.632	172.0	3.741
298	177.9	3.733	226.3	3.617	205.9	3.587	184.2	3.699
300	178.8	3.730	227.4	3.614	207.0	3.584	185.1	3.697
400	221.0	3.605	285.0	3.469	258.1	3.460	229.2	3.569
500	257.9	3.529	335.8	3.379	303.2	3.364	267.8	3.477
600	291.1	3.476	381.5	3.318	343.7	3.307	302.6	3.438
700	321.4	3.428	423.3	3.274	380.8	3.265	334.3	3.399
800	349.4	3.409	462.0	3.240	415.0	3.234	363.5	3.371
900	375.5	3.387	498.2	3.213	447.0	3.209	390.9	3.347
1000	400.0	3.369	532.2	3.192	477.0	3.190	416.6	3.329
1100	423.3	3.354	564.3	3.175	505.5	3.176	440.9	3.314
1200	445.4	3.342	594.9	3.160	532.6	3.159	464.1	3.301
1250	456.0	3.337	609.7	3.153	545.6	3.154	475.3	3.296
1300	466.5	3.332	624.1	3.147	558.4	3.148	486.2	3.290
1400	486.7	3.323	652.1	3.137	583.2	3.138	507.4	3.281
1500	506.2	3.315	679.1	3.127	607.0	3.129	527.8	3.273
1600	525.2	3.308	705.0	3.119	630.0	3.120	547.5	3.266
1700	543.2	3.302	730.1	3.112	652.2	3.115	566.5	3.260
1750	552.0	3.299	742.4	3.108	663.0	3.112	575.7	3.257
1800	560.7	3.297	754.4	3.105	673.7	3.109	584.9	3.254
1900	577.7	3.292	777.8	3.100	694.4	3.104	602.6	3.250
2000	594.4	3.287	800.9	3.094	714.8	3.099	620.1	3.245
2500	671.4	3.270	907.1	3.074	808.9	3.080	700.7	3.22

argon and the data of Kellstrom⁹ for air. Loeb does not discuss the source of data for his calculations, neither does the Handbook. Both only repeat that the determinations were from viscosity data. Strong takes his data from Kaye and Laby.¹⁰

The values calculated in this paper agree well with those of Chapman and Cowling, even though they are very slightly higher (approximately 0.4%). Kennard's viscosity data were 4% higher than the viscosity data used in this paper and this difference is reflected in the final answer. The difference (0.7%) between the 1941 value of k and that previously accepted caused another minor deviation.

In an effort to obtain comparison with the molecular diameter calculated by assuming tetrahedral packing in the liquid, the low temperature portion of the N₂ curve was replotted as σ vs. $(1/T^\circ\text{K.})$ and extrapolated to the boiling point. The reciprocal temperature plot gave a much flatter curve which lent itself more readily to extrapolation. The value of σ at the boiling point of N₂ (-195.8°) was 4.93×10^{-8} cm., compared to the value of 4.30×10^{-8} calculated from the area covered by a molecule assuming close packing of liquid molecules.¹¹

Table IV compares the values obtained in this paper with diameters calculated from other methods. The values were taken from Loeb¹² and the Handbook.¹³

As can readily be seen, the viscosity results here

(9) Kellstrom, *Nature*, **136**, 682 (1935).

(10) G. W. C. Kaye and T. H. Laby, "Tables of Physical and Chemical Constants and Some Mathematical Functions," Longmans, Green and Company, New York, N. Y., 1936.

(11) P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, **59**, 1553 (1937).

(12) L. B. Loeb, "The Kinetic Theory of Gases," McGraw-Hill Book Co., Inc., New York, N. Y., 1934, p. 643.

(13) "Handbook of Chemistry and Physics," 30th Ed., Chemical Rubber Publishing Company, Cleveland, Ohio, 1940.

TABLE III

COLLISION DIAMETERS ($\sigma \times 10^8$ CM.) AT 0°

Gas	Chapman and Cowling ¹	Kennard ¹⁴	Loeb ¹²	Strong ¹⁵	Handbook ¹³	This work
N ₂	3.756	3.75	3.16	3.50	3.15	3.773
A	3.664	3.64	2.86	3.36	2.88	3.665
O ₂	3.620	3.61	2.98	3.39	2.98	3.632
Air		3.72				3.741

(14) E. H. Kennard, "Kinetic Theory of Gases," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, p. 149.

(15) J. Strong, "Procedures in Experimental Physics," Prentice-Hall Publishers, Inc., New York, N. Y., 1938, p. 96.

TABLE IV

 $\sigma \times 10^8$ CM. AT 0°

Gas	van der Waals	Gas isotherms	Molecular refraction	Present viscosity
N ₂	2.94	2.98	2.40	3.773
O ₂	2.98	2.65	2.34	3.632
A	3.15	2.42	2.96	3.665

reported are higher than other values but it must be realized that the assumptions made in each particular method of calculation make an analytical comparison difficult.

A JACOBIAN METHOD FOR THE RAPID EVALUATION OF THERMODYNAMIC DERIVATIVES, WITHOUT THE USE OF TABLES

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The method of Shaw, which makes use of Jacobians to calculate easily the thermodynamic derivatives, is presented in such a way that no tables are necessary. With it, any of the first partial derivatives may be set down rapidly from memory.

Many students of thermodynamics are familiar with the Bridgman method² for finding the first partial derivatives of the thermodynamic functions, because it is the Bridgman table of Jacobians that appears in most textbooks. Few have learned how to use the method given by Shaw,³ usually called the "Method of Jacobians." This scheme has the advantage of being more general and hence more flexible than Bridgman's system, although it requires learning a few simple properties of Jacobians. Using the Bridgman table, one obtains an expression in which T and P are always the independent variables. This feature is inherent in the structure of the table. In Shaw's method, alternate expressions containing other pairs of variables are readily derived. However, in the method as it is usually presented, one must get accustomed to five extra symbols, which are used as abbreviations for the six Jacobians formed from the state variables, P , V , T and S .

In the following outline, the additional symbols of Shaw will not be necessary. The table used in his system is usually reprinted in the form of a ten-by-ten array. It can be condensed to a five-by-five form which is extremely easy to duplicate from memory. However, with the aid of a few simple rules, any of the Jacobians may be set down immediately without the aid of a table. Only a knowledge of the four fundamental equations is required. This gives ready access to some 720 first partial derivatives which arise from the ten thermodynamic variables used in the method, with many possibilities for alternate expressions.

Those not already familiar with the Jacobian method will find it helpful to refer to the more

complete treatments given below.⁴ Otherwise the advantages of this method may not at first appear to be worth its consideration. The brief summary of the properties of Jacobians is given here so that anyone may take advantage of the device after a few practice calculations.

The Jacobian is defined as

$$J(x, y/r, s) = \frac{\partial(x, y)}{\partial(r, s)} = \frac{(\partial x/\partial r)_s (\partial y/\partial s)_r}{(\partial x/\partial s)_r (\partial y/\partial r)_s} = \left(\frac{\partial x}{\partial r}\right)_s \left(\frac{\partial y}{\partial s}\right)_r - \left(\frac{\partial x}{\partial s}\right)_r \left(\frac{\partial y}{\partial r}\right)_s \quad (1)$$

The independent variables r and s may be any desired, and for the purposes of a single problem are usually taken as implied. That is, one usually writes down only $J(x, y)$. The following relations come from the definition and should be recognized on sight after use

$$J(x, x) = 0 \quad (2)$$

$$J(x, y) = -J(y, x) \quad (3)$$

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{\partial(x, z)}{\partial(y, z)} = \frac{J(x, z)}{J(y, z)} \quad (4)$$

The last relation (4) is used to evaluate any desired derivative.

Shaw proceeded by defining five new symbols for the basic Jacobians $J(V, T)$, $J(P, V) = J(T, S)$, $J(P, S)$, $J(P, T)$ and $J(V, S)$. He then calculated the Jacobians for 100 pairs of variables in terms of P , V , T , S and the five symbols listed above. These were collected in a ten-by-ten array which has been reprinted in the references cited.^{3,4} The

(4) (a) O. A. Hougen and K. M. Watson, "Chemical Process Principles," Part II, John Wiley and Sons, Inc., New York, N. Y., 1947, pp. 465-471.

(b) T. K. Sherwood and C. E. Reed, "Applied Mathematics in Chemical Engineering," McGraw-Hill Book Co., Inc., New York, N. Y., 1939, pp. 170-182.

(c) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1943, pp. 17-24.

(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) P. W. Bridgman, "Condensed Collection of Thermodynamic Formulas," Harvard University Press, Cambridge, Mass., 1926.

(3) A. N. Shaw, *Phil. Trans. Roy. Soc. (London)*, **A234**, 299 (1935).

Jacobians listed are for the pairs of variables formed from the quantities $P, V, T, S, E, H, A, F, Q(\text{rev})$ and $W(\text{rev})$. Actually only 45 independent relations are present because of equations (2) and (3). The purpose of the table was to give access to the more complex Jacobians which contain either one energy variable and one state variable, or two energy variables. This made it unnecessary to recalculate them when using the system, but the table is clumsy and not always available.

With the aid of the following rules, any of the Jacobians may be set down in a matter of seconds.

(I).—Those Jacobians containing P, V, T or S are left untouched or are transformed by one of the following relations

$$J(P, V) = J(T, S) \quad (5)$$

This relation arises from the cross-differentiation of any of the four fundamental equations⁵ and is very useful. It can be remembered by noting that the intensive variables are paired with the extensive, and that the two intensive variables occupy the same relative positions (*i.e.*, if P appears first, T appears first).

$$J(T, V) J(P, S) + J(P, T) J(V, S) + J(V, P) J(T, S) = 0 \quad (6)$$

This relation is sometimes conveniently used to eliminate any one of the simple Jacobians, but is not necessary. It is equivalent to the definition (1).⁶

(II).—Those Jacobians containing one each of an energy variable ($E, H, F, A, Q(\text{rev})$ or $W(\text{rev})$) and a state variable (P, V, T or S):

One needs to remember the two undifferentiated state variables occurring with each energy differential in the fundamental equations. These two are set down, and each is followed by a Jacobian containing first, the conjugate of the state variable in that term (that is, the variable appearing as a differential) and second, the state variable in the desired Jacobian. For example, to find $J(A, S)$: from the relation $dA = -SdT - PdV$ write down $-SJ(T, -PJ(V, V)$, and then add S to obtain $J(A, S) = -SJ(T, S) - PJ(V, S)$.

(III).—Those Jacobians containing two energy variables: these are the most complex. As a rule, they contain from three to four terms, and each term consists of two state variables and one Jacobian. Because it is irksome to derive them when needed, Shaw felt that a table was desirable. An

example will be given to assist in the formulation of the rule.

Suppose it is required to find $J(H, A)$. First recall that T and V occur with H , and that $-S$ and $-P$ occur with A . Then mentally multiply these two pairs together as though they were two binomials, only making sure to put down the variables associated with H first. That is, write down

$$-TS \quad -TP \quad -VS \quad -VP$$

leaving a space. Then after each pair write down the Jacobian containing the conjugate pair, keeping the same order and leaving the sign intact. Thus, $-TS$ is followed by $J(S, T)$. Next, $-TP$ is followed by $J(S, V)$ etc. The complete expression is

$$J(H, A) = -TS J(S, T) - TP J(S, V) - VS J(P, T) - VP J(P, V)$$

Now suppose one wants to evaluate $(\partial H / \partial S)_A$. The expression just obtained is used, along with

$$J(S, A) = -J(A, S) = S J(T, S) + P J(V, S) \\ \left(\frac{\partial H}{\partial S} \right)_A = \frac{J(H, A)}{J(S, A)} = \frac{-TS J(S, T) - TP J(S, V) - VS J(P, T) - VP J(P, V)}{S J(T, S) + P J(V, S)}$$

Dividing through by $J(S, T)$ or $-J(P, V)$ results in

$$= \frac{TS - TP \frac{J(S, V)}{J(P, V)} - VS \frac{J(P, T)}{J(P, V)} - VP}{-S + P \frac{J(V, S)}{J(V, P)}}$$

But

$$\frac{J(V, S)}{J(V, P)} = \frac{J(V, S) J(V, T)}{J(V, T) J(V, P)}$$

It is also clear that

$$\frac{J(V, S)}{J(V, T)} = \frac{J(S, V)}{J(T, V)} = \left(\frac{\partial S}{\partial T} \right)_V = \frac{1}{T} C_v$$

Then

$$\left(\frac{\partial H}{\partial S} \right)_A = \frac{TS - PC_v \left(\frac{\partial T}{\partial P} \right)_V - VS \left(\frac{\partial T}{\partial V} \right)_P - VP}{S - \frac{PC_v}{T} \left(\frac{\partial T}{\partial P} \right)_V}$$

This rather complicated derivative, which has been derived here in a short space, would take some time to obtain accurately by ordinary means. It is true that derivatives of such complexity are seldom required. But it is also true that many refrain from adopting short cuts and learning easier methods because they are often of limited utility. It is hoped that this simplification will encourage more students and teachers of thermodynamics to adopt the Shaw system. To anyone wishing a proof or justification of the above rules, it is suggested that a condensation of the original table be attempted.

(5) The four fundamental equations of thermodynamics referred to here are $dE = TdS - PdV$, $dH = TdS + VdP$, $dF = -SdT + VdP$ and $dA = -SdT - PdV$.

(6) To put down (6) easily from memory, write any one of the variables (in this case S) in the same relative position in each of the three terms (here the last position). Then permute the remaining three among the rest of the positions so that each appears but once in any term and none occupies the same relative position in the three terms.

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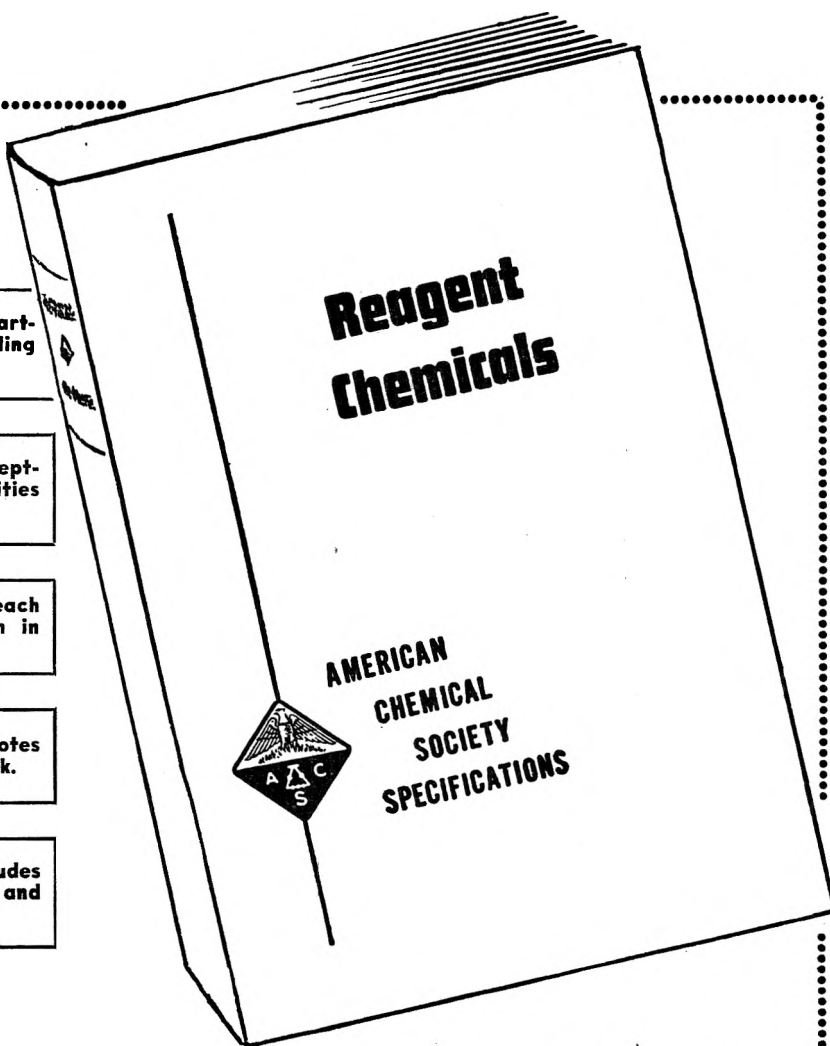
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