

THE JOURNAL OF PHYSICAL CHEMISTRY

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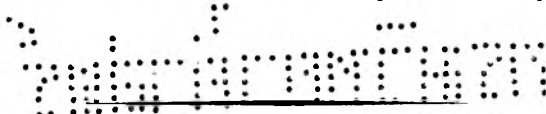
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TRACER ELECTROPHORESIS. I. FREE LIQUID METHOD¹

BY HORST W. HOYER,² KAROL J. MYSELS AND D. STIGTER

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Received February 12, 1953

A precise and relatively simple method of using tracers in the determination of electrophoretic mobilities is described. It is free of boundary anomalies, and needs no special electrodes. It uses only open tubes and is thus free of surface effects. Under certain conditions it permits the determination of mobility of a component which is in dynamic equilibrium with others. The method is based on the analytical determination of the volume swept by a boundary between two otherwise identical solutions, one tagged, the other tracerless. The stability of the boundary in a narrow horizontal tube is satisfactory even at room temperature. The method has been adapted especially to the measurement of mobility of micelles of association colloids tagged with water-insoluble dyes. Systematic errors are avoided, the accuracy of the method is of the order of 0.3% and is limited by the analytical error.

The need for perfect electrodes in the Hittorf method, and the occurrence of boundary anomalies and the presence of foreign leading ions in moving boundary methods, are among difficulties encountered in conventional determinations of electrophoretic mobility. Tracer methods may obviate these difficulties, but introduce so many others that only one precision tracer method, that of Brady,³ seems to have been described. This method uses a fritted glass disc which may introduce systematic errors due to surface effects.

We have developed a different method which uses only open tubes and hence is not subject to this objection. It uses much higher relative changes in the measured concentrations and hence gives a higher precision for the same analytical error. For purposes of intercomparison we have also used a modified Brady method which will be described later. The two methods agree within their precision (Fig. 4) but the open tube method appears both more accurate and more precise.

The absence of a stabilizing density difference across the boundary between tagged and tracerless solution is always a source of complication in tracer electrophoresis. Electrosmotic flow, which is unavoidable, rapidly renders parabolic an

originally straight boundary.⁴ Diffusion destroys original sharpness, and unless one works at the temperature of maximum density, thermal convection currents introduce distortions. Thus a well defined plane boundary cannot be maintained in tracer electrophoresis. This prevents the use of moving boundary methods but not of analytical methods. In the latter, one needs to define only a surface being crossed by the analytically determined specie. This surface is formed by the electrode in the Hittorf method, by a porous membrane in Brady's method, and by the plane of a stopcock (2, Fig. 1) of a horizontal capillary in our work.

In the study of micelles of detergents tagged⁵ with water-insoluble dyes, we encountered additional difficulties due to the interaction of solution with lubricants. On the other hand, the develop-

(4) H. W. Hoyer and K. J. Mysels, *THIS JOURNAL*, **54**, 966 (1950).

(5) The term "tagged," "labeled" or "tracer" particles should be applied to any particle which is substantially identical with other particles in the process studied yet can be distinguished by an appropriate analytical method. Isotopic atoms are commonly used as tracers because in most processes different atomic weights cause only minute differences, yet the analytical determination is easy. However, other labeling methods are possible and may have advantages. Thus isotopic tracers are useless if it is desired to label the micelle of an association colloid which is in dynamic equilibrium with other species present. We are using⁴ for this purpose dyes of small molecular weight which are insoluble in water but combine with the micelles (probably by dissolving in their hydrocarbon center). The dye is thus attached to a micelle probably without significantly affecting its properties⁶ and can be detected readily colorimetrically. Hence it acts as an excellent tracer or tag permitting the determination of the properties of the micelle alone.

(1) Most of this material as well as its early development is reported in the Ph.D. thesis of Horst W. Hoyer, University of Southern California, 1951, and was presented at the XIIth International Congress of Pure and Applied Chemistry, New York, September 13, 1951.

(2) Bristol-Myers Company Fellow, 1949-1951.

(3) A. P. Brady, *J. Am. Chem. Soc.*, **70**, 911 (1948).

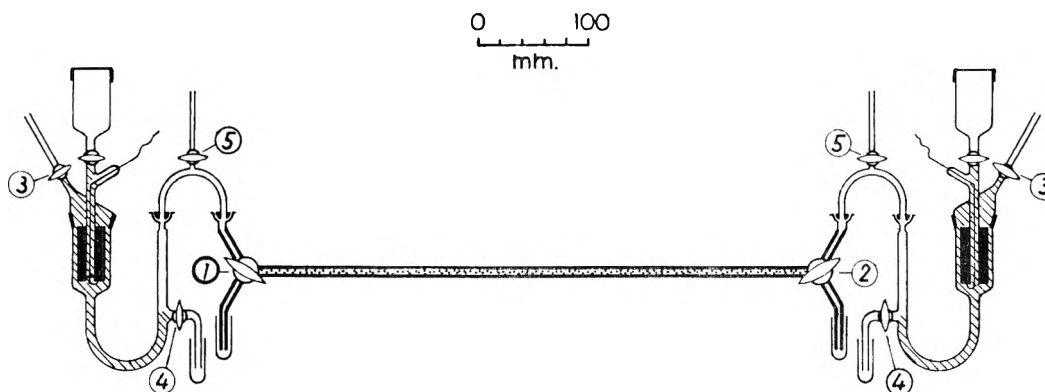


Fig. 1.—The free liquid tracer electrophoresis cell: dots indicate the portion occupied by the tracer solution at the beginning of a run and crosshatches that occupied by concentrated sodium chloride; the clear portion contains the untagged solution.

ment of this and of a related diffusion method⁶ was greatly facilitated by the direct visibility of the tracer, although both methods are fully applicable to radioactive and other tracers.

Experimental

Cell and Procedure.—The cell used is shown schematically in Fig. 1. Its heart is the central horizontal capillary tube limited by three-way stopcocks 1 and 2. This is filled with the tracer solution while the adjoining tubes on both sides are filled with untagged solution. Concentrated sodium chloride solution extends to the silver-silver chloride electrodes, each having an area of 400 cm.², which complete the circuit.

The electrode vessels are filled with salt solution through the funnels. The central tube is filled quantitatively with tracer solution *via* the downward tubes of stopcocks 1 or 2 by suction applied to stopcock 5. Then the arching tubes are filled with untagged solution in a similar way and sharp liquid junctions are formed at the levels of the stopcocks 4. Finally all downward outlets are immersed in mercury cups, and after balancing pressures, the corresponding stopcocks are closed while stopcocks 5 are opened. The apparatus is brought to temperature equilibrium in an air thermostat. This takes about 1.5 hours and is checked by observing the level of liquid above one of the stopcocks 5 with a cathetometer. Then stopcock 5 near the cathode is closed, the three-way stopcocks 1 and 2 opened, and the current switched on.

A run lasts between 2 and 4 hours. The current flowing through the cell is measured at frequent intervals. The absence of leaks, temperature fluctuation or gassing is ascertained by observation of the liquid level.

Upon completion of a run, the solution is removed from the three-way stopcocks and adjacent tubes on both sides, then the contents of the horizontal capillary are collected quantitatively with washings of untagged solution, weighed and their optical density determined. An alternate procedure, particularly useful at low tracer concentrations is to disconnect the central part of the cell, carefully clean and dry the stopcock bores and side tubes, then homogenize the contents of the horizontal tube by tilting, and determine the optical density of a part of the homogenized solution without any dilution.

Lubricants.—Stopcock greases caused serious difficulties with our detergent solutions. None tried would consistently prevent leakage of detergent solution between openings (*i.e.*, around the barrel) of a stopcock which had to be turned several times. Elimination of pressure drop across the barrel by mercury cups, as suggested to us by Dr. R. J. Williams, finally overcame this difficulty. Two greases, Dow Silicone vacuum grease and Peters-Van Slyke grease of the Fisher Scientific Co., prevented leakage to the outside along the barrel and this only when the stopcocks were pressed in by pressure adapters. The silicon grease, however, emulsified strongly in the solutions and gave a turbidity which was difficult to take into account in determining optical densities. The Van Slyke grease did not emulsify

but dissolved much larger amounts of the tracer dye from the tagged solution. To minimize this cause of error, the greased stopcocks were exposed overnight to the tagged solution before actual use. The grease is thus saturated with dye and the most easily accessible part of it washed away. The use of the Van Slyke grease about doubled the reproducibility of results and permitted the making of some six runs without dismantling and regreasing the cell.

Auxiliary Determinations.—A Beckman spectrophotometer served to determine the concentration of the tracer dye.

The current at 200–325 volts was supplied by a constant voltage source (Model 25, Lambda Electronics Corporation) and measured to 0.1% by potentiometric determination of the potential drop across a 300–3000-ohm resistor in series with the cell.

The conductivity of the solutions was measured to 0.1% with a Jones-Dyke⁷ bridge with extrapolation to infinite frequency to compensate for polarization errors.

The volume between stopcocks 1 and 2 was determined with mercury and with tracer solution in blank runs. The two determinations agreed to 0.5% and the more precise values obtained with mercury were used in the calculation.

Computation.—If the reference surface is indicated schematically by 2 in Fig. 2, the amount of tracer crossing this surface is equal to the decrease of the total amount of tracer in front of plane 2 during the experiment. If all the tracer is present originally between planes 1 and 2, determination of the amounts present between these planes before and after electrophoresis gives the desired quantity, provided that no tracer has crossed plane 1 and the tracer concentration just in front of plane 2 remains unchanged throughout the experiment. Experimentally, stopcocks 1 and 2 (Fig. 1) serve to define the corresponding planes.

The quantities measured are

- v , vol. of the tube between stopcocks (cc.)
- i , av. current flowing through the cell (amp.)
- C_0 , concn. of tracer in original solution
- C , av. concn. of tracer between stopcocks at end of expt.
- t , time of duration of the expt. (sec.)
- κ , conductivity of the soln. (mho/cm.)

If μ (cm.²/v. sec.) is the electrophoretic mobility of the tagged species, s (cm./sec.) its actual velocity, Δv (cm.³) the volume of solution swept by the particles crossing the plane of the stopcock, E (v./cm.) the potential drop and X (cm.²) the cross-section of the tube, one obtains

$$\mu = \frac{s}{E} = \frac{\kappa s}{i/X} = \frac{\kappa \Delta v / X t}{i/X} = \frac{\kappa \Delta v}{i t} = \frac{\kappa}{i t} \times \frac{(C_0 - C)v}{C_0}$$

This computation depends on the equality of κ for both solutions. We have always found these to agree within the error of measurement.

Joule Heating.—The passage of electric current causes the temperature of the solution to rise above that of the air thermostat until the rate of heat dissipation is equal to that of heat production. The heating occurs mainly in the narrow tubes of the apparatus where about 80% of the resistance is located and the dissipating surface is least. Hence

(6) K. J. Mysels and D. Stigter, *This Journal*, **57**, 104 (1953).

(7) P. H. Dyke, *Rev. Sci. Instr.*, **2**, 379 (1931).

the change in resistance of the cell with time gives a good basis for calculating the temperature rise in the capillary. As expected, the steady state of current and hence temperature are approached exponentially and reached within 10% in 15 minutes. The steady state temperature rise is proportional to the power dissipated per unit length of the capillary and amounts to about 1° per 5 milliwatts/cm.

Under steady state conditions the bulk of the temperature gradient occurs at the glass-air interface and most of the rest in the glass. This may be seen from the following estimates, assuming the liquid to be completely stationary so that all heat transport is by conduction. The maximum temperature difference within the liquid is given by

$$T_{\text{center}} - T_{\text{wall}} = \frac{W}{4\pi K_W}$$

and that between the two glass surfaces by

$$T_{\text{inner}} - T_{\text{outer}} = \frac{W}{2\pi K_{gl}} \ln \frac{r_0}{r_i}$$

where W is the power (mw.) dissipated per cm. of tube length, K_W and K_{gl} the heat conductivities of solution and wall (0.0015 and 0.0018 cal./cm./ $^\circ\text{C}$./sec., respectively), r_0 and r_i the inner and outer radii of the tube (0.14 and 0.40 cm., respectively). Therefore, the power input required to raise the temperature of the solution by 1° corresponds to a temperature difference of about 0.06° within the liquid and of about 0.1° between the two surfaces of the capillary so that the temperature difference between the air of the thermostat and the outside of the capillary is about 0.87° . Since convection currents in the liquid will reduce temperature gradients, this calculation gives the maximum value for the temperature difference within the tube.

We use an air thermostat⁸ whose temperature fluctuates by less than 0.1° . The main reason for using an air thermostat is to avoid electrical leaks with our detergent solutions. It has also the advantages of convenience and cleanliness. Its disadvantage is the poor cooling of the capillary which limits the current intensities used. A water thermostat would improve the cooling by a factor of 5 or 10 and might be preferable for the study of solutions more easily controlled by stopcocks. The cell of Fig. 1 could be used without changes.

Effect of Temperature Rise.—The temperature rise increases the mobility of the ions in the solution, but as a first approximation causes no error in the computation of the mobility. This is because the transport number of any specie is independent of temperature, to the extent that temperature affects equally the mobility of all ions. Therefore, using κ measured at, say 25° , one computes μ at 25° , no matter what the actual temperature of the solution. However, since temperature may affect the structure of the micelle so that the assumption of equal effect on all ions might lead to erroneous results, we prefer to adjust the temperature of the thermostat so that the steady state temperature of the capillary is close to 25° .

Current Intensity.—High values of i permit faster completion of experiments, reduce dangers from density differences of solution, require higher voltages and cause greater heating. The last effect increases with the square of i and generally is the limiting factor if it is desired to keep the temperature rise of the solution within 1 or 2° . In solutions of low conductivity, the available potential is the limiting factor, but these experiments are of short duration anyhow.

Temperature rises up to 3° do not seem to have any effect on the functioning of the cell, as may be seen from data of Table I in which the only variable is the current intensity. $\Delta v/v$ is close to 0.6 and the temperature of the air thermostat 25° .

TABLE I

0.75% SODIUM LAURYL SULFATE IN 0.05 M SODIUM CHLORIDE (ORANGE OT TRACER)

W, mw./cm.	Temp. rise, $^\circ\text{C}$.	$\mu \times 10^4$
5.7	1.25	3.555
9.6	1.75	3.545
17.	3.1	3.57

(8) To be described shortly by K. J. Mysels.

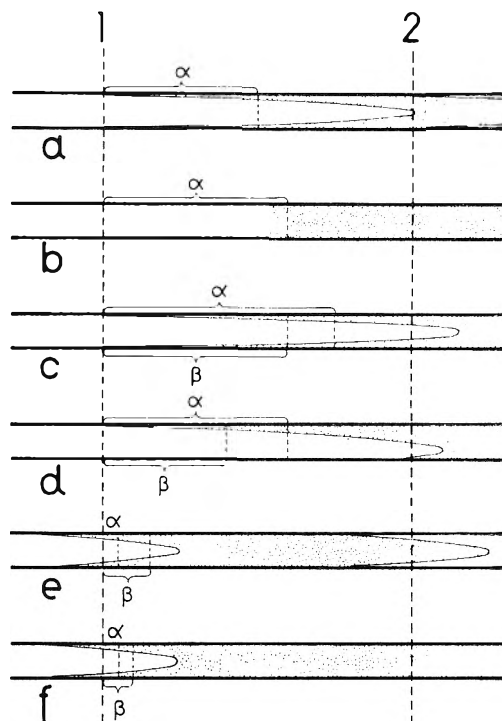


Fig. 2.—Schematic shape of the boundary under various conditions: shaded part is the tracer solution. The volume between 1 and 2 is originally occupied by the tracer solution. α indicates the proportion of that volume actually swept by the tracerless solution and β indicates the proportion computed: a, no convection or diffusion; b, effect of diffusion and convection; c, too large transport; d, density difference; e, high electroosmotic velocity; f, same with tracer solution beyond 2.

Size and Shape of Horizontal Tube.—For our colorimetric method of measuring tracer concentrations, about 3 ml. seems to be the minimum volume of the capillary. Smaller volumes would be preferable since small diameters reduce heating but require more sensitive analytical methods. We have generally used tubes 3.0 mm. i.d. and 43 cm. length for the more conducting solutions and 3.5 mm. i.d. and 28 cm. length for the more dilute ones, but have noticed no difference in results when these were interchanged.

Volume Transported.—As the volume Δv , swept by the untaged particles passing the first stopcock increases, the change in concentration between stopcocks $(C_0 - C)/C_0$ increases and the analytical error decreases in importance. When Δv becomes large, some of the untaged particles pass the second stopcock, escape detection, as shown in Fig. 2c, and thus give an erroneously low value of μ . The point at which this becomes significant depends on the shape of the boundary and determines the highest permissible value of Δv .

If the electroosmotic velocity at the wall were equal to $-\mu$ and other influences were neglected, the boundary would remain sharp and assume the shape of a paraboloid of revolution whose base remains at the first stopcock and whose tip reaches the second when $\Delta v = 0.5v$, as shown in Fig. 2a. If this value of Δv is exceeded, the computed value of μ decreases rapidly, as shown by curve A in Fig. 3. If the electroosmotic velocity is lower, the paraboloid becomes less elongated and Δv has a higher limit.

Two factors favor a higher limit of Δv . One is diffusion, which tends to blur the boundary uniformly; and the other is thermal convection due to the lower temperatures on the periphery of the tube, which causes a symmetrical up and down motion in a plane perpendicular to the axis of the tube. Both tend to shift the rapidly moving particles at the tip of the paraboloid into slower streamlines and the stationary ones at its base into faster streamlines. This shortens the paraboloid, as shown in Fig. 2b, and permits higher Δv values. In the limiting case where electroosmotic velocity is zero, diffusion and thermal convection have little effect,

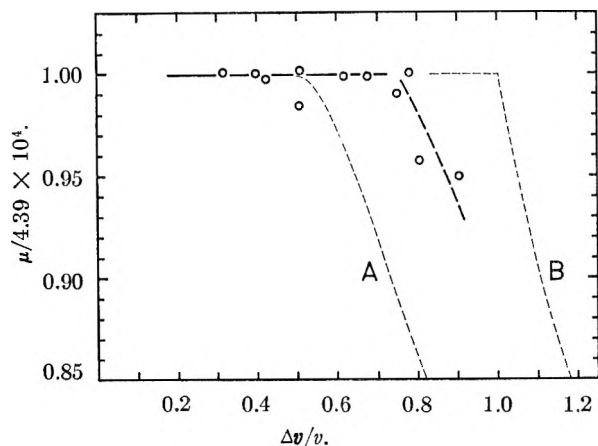


Fig. 3.—Effect of volume transported on the computed mobility. 0.75% sodium lauryl sulfate, Orange OT tracer: curve A corresponds to Fig. 2a and c; curve B to Fig. 2b idealized.

and Δv up to v would be permissible. Line B in Fig. 3 shows for this case the change in μ as Δv exceeds v .

Any difference in the density between the two solutions will cause an unsymmetrical distortion of the boundary, as shown in Fig. 2d, and thus reduce the permissible value of Δv . Diffusion and convection tend, of course, to counteract such layering of the solutions, and with our colored tracers it is easy to see when it occurs. Care in preparing the solutions obviates any difficulty from this source.

Experimentally, the boundary observed in our cell was generally diffuse, covering a range of some 10 cm., *i.e.*, about one-quarter of the tube, and was slightly skewed by density gradients. Figure 3 shows results obtained under otherwise constant conditions for different Δv values. It shows that only above $\Delta v/v = 0.7$ is there any perceptible systematic error.

In principle an electroosmotic velocity larger than $-\mu$ would lead to the movement of some tracer to the left of the original boundary, as shown in Fig. 2e and 2f. In practice,⁹ however, this will not occur because of the effectiveness of diffusion and convection in shortening the paraboloid except under exceptional conditions of wide tube, very slowly diffusing particles and low conductivity of the solution.

Results.—From a qualitative point of view it may be mentioned that we never observed two separate boundaries. It is therefore apparent that if there are two or more species of solubilizing micelles they are either very similar or interconvert rapidly compared to our measurements.

Figure 4 shows micellar mobilities of potassium laurate obtained by the present method at an early date when leakage, large heating effects and turbidity caused by silicone grease prevented highest accuracy. The data nevertheless have an average deviation of only 1% from the line and agree with those obtained by the modified¹ Brady diaphragm method within the uncertainty of the latter. Figure 3 shows the micellar mobility of sodium lauryl sulfate obtained at a later date after the above difficulties have been overcome.

(9) Should such a case be encountered, the liquid in front of the first stopcock would be analyzed for tracer. If the solution beyond the second stopcock is originally tracerless (Fig. 2e), twice the amount found would be added to that remaining between the stopcocks; if the solution beyond the second stopcock is originally also tagged (Fig. 2f) only once this amount would be added.

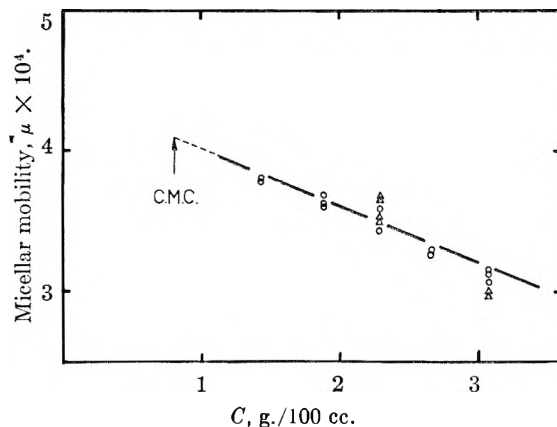


Fig. 4.—Electrophoretic mobility of micelles of potassium laurate containing 4 mole % of potassium hydroxide, Sudan IV tracer: \circ , open tube; Δ , diaphragm.

Points below $\Delta v/v = 0.7$ give six values of $\mu \times 10^4$ cm.²/v. sec. between 4.38 and 4.40, av. dev. 0.15%, and one stray value at 4.32 whose inclusion raises the av. dev. to 0.35%, which is well within the precision (0.15%) of the colorimetric determination. In recent routine applications of the method less than 10% of the runs had to be discarded because of experimental difficulties.

Interpretation of these results is not simple because of the inadequacy of present theories and lack of additional data on these micelles. There is no good way of accounting for the mobility of a micelle in the presence of other micelles. Extrapolation to the critical micelle concentration gives the mobility of a micelle in the presence of only a low concentration of simple ions. This is within the realm of Booth's theory¹⁰ if the radius of the micelle is known. Assuming a radius equal to the length of the laurate anion, *i.e.*, 20.5 Å., and extrapolating the values of Fig. 4 to a mobility of 4.1×10^{-4} at the C.M.C. gives¹¹ a zeta potential of 90 mv. This value is not very sensitive to variations in micellar size and hence should be close to reality. In contrast, charge calculations are very sensitive to the radius chosen and cannot be reliable. The zeta potential is high enough and ionic strength low enough to make important the relaxation effects taken into account by Booth. The potential calculated by Henry's¹² procedure gives a value of only 75 mv. and by the simple Smoluchowski equation 52 mv.

Acknowledgment.—This work was begun with the help of the Bristol-Myers Company and much of it conducted as part of Project NR 356-254 of the Office of Naval Research for which this forms the second technical report. We are also grateful for the Fulbright Travel Grant which enabled D. Stigter to come to Los Angeles.

(10) F. Booth, *Proc. Roy. Soc. (London)*, **A203**, 514 (1950). In this paper X_1^* (b) should be replaced by $2/3X_1^*$ (b) on p. 530, line 17.

(11) Using (Booth's notation) $\kappa a = 1$ and $q^* = 1.4$.

(12) D. C. Henry, *Proc. Roy. Soc. (London)*, **A133**, 106 (1931).

MEASUREMENT OF HEAT OF DISSOCIATION OF FLUORINE BY THE EFFUSION METHOD¹

BY HENRY WISE

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Received August 24, 1953

The heat of dissociation of fluorine has been measured by means of the gas effusion method. These determinations were carried out in a nickel tube housing a thin-edged circular orifice made of the same material. The rate of gas effusion was determined over the temperature range from 500 to 800°K. at a total pressure of 4×10^{-4} mm. The results of these measurements yield for the reaction $F_2(g) = 2F(g)$ a value of $\Delta H_{298}^0 = 37.6 \pm 0.8$ kcal./mole.

Introduction

A wide range of values has been reported² for the energy of dissociation of the fluorine molecule. Estimates of this fundamental physical parameter based on the continuous absorption spectrum show wide disagreement with those obtained by thermochemical considerations for the ClF molecule and the measurement of the equilibrium pressure of F_2 at elevated temperatures.³

For a direct determination of the heat of dissociation of fluorine the gas effusion method⁴ is particularly suitable since the experimental measurements are performed at low pressures (molecular-flow region) and therefore a measurable degree of dissociation is attained at relatively low temperatures. Such a method has been employed in the determination of the thermal dissociation of iodine and bromine.⁵ The experimental measurements to be described were carried out in a nickel tube housing a thin-edged circular orifice made of the same material and heated to the desired temperature by means of a furnace. The rate of gas effusion as a function of orifice temperature was determined from the rate of pressure change in a Pyrex vessel containing fluorine gas at room temperature and a pressure of 10^{-4} mm. which was joined to the nickel tube on the upstream side of the orifice.

Theoretical Analysis

For a gas passing through an orifice with thin edges, the diameter of which is small in comparison with the mean-free path of a molecule, the ratio of mass flow rates of a partially dissociated diatomic gas at temperature T_2 and an undissociated gas at temperature T_1 is given by

$$\frac{\dot{m}_2}{\dot{m}_1} = \frac{P_2 a_2}{P_1 a_1} \sqrt{\frac{T_1}{T_2}} (1 + 0.414\alpha)/(1 + \alpha) \quad (1)$$

where subscripts 1 and 2 refer to the conditions prevailing at temperatures T_1 and T_2 , respectively.⁵ In deriving equation 1 the assumption is made that the individual components of the gaseous mixture effuse independently and that the attainment of the equilibrium composition in the non-effused

portion of the gas is rapid relative to the rate of effusion.⁶

By rearrangement of equation 1 one obtains therefore for the degree of dissociation

$$\alpha = \frac{1 - \left(\frac{\dot{m}_2 P_1 a_1}{\dot{m}_1 P_2 a_2} \sqrt{\frac{T_1}{T_2}} \right)}{\left(\frac{\dot{m}_2 P_1 a_1}{\dot{m}_1 P_2 a_2} \sqrt{\frac{T_1}{T_2}} \right) - 0.414} \quad (2)$$

In the present study, the conditions prevailing at 298°K. are chosen as the reference state since the degree of dissociation of fluorine at that temperature is negligibly small. As an index of the rate of mass flow of gas through the orifice the rate of pressure change in a storage vessel kept at room temperature on the upstream side of the orifice is determined (Fig. 1). Such an analysis is strictly applicable only if the mean free path of the molecules is less than or comparable to the diameter of the connecting tube. Therefore, the rate of mass efflux \dot{m} (in g. sec.⁻¹) is proportional to the rate of pressure change in the system upstream of the orifice. Based on equation 2 the degree of dissociation may therefore be expressed as

$$\alpha = \frac{1 - \left(\frac{a_1}{\sqrt{T_1}} \frac{d \ln P_2}{d \ln P_1} \sqrt{\frac{a_2}{T_2}} \right)}{\left(\frac{a_1}{\sqrt{T_1}} \frac{d \ln P_2}{d \ln P_1} \sqrt{\frac{a_2}{T_2}} \right) - 0.414} \quad (3)$$

where a = cross sectional area of orifice (cm.²), \dot{m} = mass flow rate (g. sec.⁻¹), P = pressure of gas on upstream side of orifice (dynes cm.⁻²). Since the rate of change of pressure represents the dependent experimental variable as required by equation 3, the slope of the pressure-time curve was evaluated in the pressure region from 4.5×10^{-4} to 3.5×10^{-4} mm. over the entire temperature region studied.⁷ In this small pressure interval very little variation in flow rate with pressure was observed, and the average pressure was chosen for the calculation.

Experimental Measurements

1. **Description of Apparatus.**—A schematic drawing of the apparatus is shown in Fig. 1. A nickel cylinder B (3 cm. in diameter and 50 cm. in length) houses the sharp-edged circular orifice (0.0185 cm. in diameter). The entire unit is contained inside a cylindrical furnace whose temperature can be accurately controlled and maintained by means of an external variable resistance. A thermocouple junction (chromel-alumel) located on the outer wall of the

(6) F. E. Harris and L. K. Nash, *Anal. Chem.*, **22**, 1552 (1950).

(7) This slope was calculated from a series of consecutive pressure decrements over time intervals sufficiently small so that the mass effused during such an interval represented only a small portion of the total mass of gas present in the system.

(1) This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory under U. S. Army Ordnance Department Contract No. DA-04-495-ORD 18.

(2) L. Haar and Ch. W. Beckett, Natl. Bur. Stand. Report No. 1435 (Feb. 1, 1952).

(3) R. N. Doeschner, *J. Chem. Phys.*, **19**, 1070 (1951).

(4) M. Knudsen, *Ann. Physik*, **29**, 179 (1909), A. C. Egerton, *Phil. Mag.*, **33**, 53 (1917), and *Proc. Roy. Soc. (London)*, **103A**, 469 (1923).

(5) Th. DeVries and W. H. Rodebush, *J. Am. Chem. Soc.*, **49**, 656 (1927).

nickel tube next to the orifice is used for temperature measurement. Fluorine gas enters the nickel system from the Pyrex vessel A (about 1000-ml. capacity), which is maintained at 298°K. by surrounding it with a thermostated oil-bath. The glass vessel is also provided with a Pirani gage, the output of which is transmitted to a recording Speedomax.⁸ By this means, the rate of effusion of gas through the orifice at elevated temperatures can be determined from the variation of pressure with time in vessel A kept at 298°K.

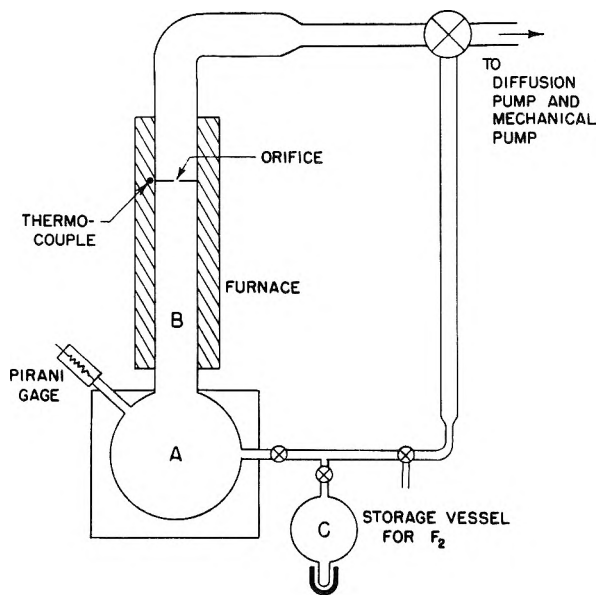


Fig. 1.—Apparatus for measurement of heat of dissociation of fluorine by the effusion method.

As shown in the diagram (Fig. 1), fluorine is supplied to vessel A from the Pyrex storage flask C in which the gas at a pressure of several hundred mm. is kept during the entire investigation. The purity of this material was found to be in excess of 98.7 weight per cent.⁹ In order to diminish the contamination of F₂ caused by interaction of the gas with the container on prolonged storage, vessel C is surrounded by a liquid N₂ trap. Another such trap is placed between containers C and A in order to reduce further contamination of the gas during its passage from one vessel to the other.

A fluorinated hydrocarbon¹¹ "Halocarbon Stopcock Grease" is used on all stopcocks coming in contact with fluorine. This stopcock lubricant proved very satisfactory in high-vacuum work (10⁻⁶ mm.) after a short period of evacuation, during which the more volatile constituents of this product were removed. On the downstream side of the orifice, a mercury diffusion pump backed by a mechanical pump is located. A McLeod gage and another Pirani gage are also employed in the calibration of the apparatus.

2. Calibration of Apparatus.—Since the rate of effusion of gas through the orifice is determined by the rate of pressure change in vessel A, an accurate calibration of the Pirani gage to fluorine is required. A commercial type of Pirani gage,¹² together with a conventional bridge circuit is employed for these measurements. In order to reduce the reaction rate between the fluorine gas and the filament of the Pirani gage, the heating current for the gage is reduced from 100 milliamperes to 85 milliamperes. At this current setting, the Pirani circuit was found to yield rapid response and sensitivity over a pressure range from 10⁻⁶ to 10⁻³ mm. in a calibration of the instrument with nitrogen gas.

(8) A self-balancing potentiometer manufactured by Leeds and Northrup, Inc., Philadelphia.

(9) The analysis¹⁰ showed 0.8 weight % O₂, 0.3% N₂, and 0.1% HF.

(10) R. H. Kimball and L. E. Tufts, U. S. Atomic Energy Commission Report MDDC 195.

(11) A product of Halocarbon Products Corp., North Bergen, N. J.

(12) Type R-1111, Sylvania Products, Emporium, Pa.

Because of the reactivity of F₂ with mercury, the McLeod gage cannot be utilized as a primary standard for the calibration of the Pirani gage to fluorine gas. Thus, it became necessary to evaluate the response of the Pirani circuit to F₂ by a capillary flow method. The rate of gas flow through such a glass capillary into vessel A was measured for several inert gases at a constant upstream pressure. Next, fluorine gas at the same upstream pressure was substituted for the reference gas and the rate of response of the Pirani due to accumulation of F₂ in vessel A was determined. From these data the current output of the Pirani circuit could be correlated with pressure of fluorine gas after the necessary corrections were made for variation in capillary flow with molecular weight and viscosity,¹³ as given by the Poiseuille equation. During the course of the investigation, numerous checks of the Pirani gage with an inert gas such as argon showed no variation in response of the instrument after prolonged periods of contact with F₂ at low pressures.

In addition, the orifice area and its temperature coefficient were determined by passing a non-dissociating gas of known molecular weight through the apparatus. It is obvious that the orifice area a may be evaluated from measurements of the effusion rate \dot{m} of such an inert gas as given by equation 1. If the rate of change of gas pressure in vessel A is taken as an index of the rate of effusion through the orifice located in the reactor B (Fig. 1), the following equation applies for an ideal gas in the non-isothermal case in which the temperature of the orifice T_B is different from that of the storage vessel T_A

$$\left(\frac{a}{V}\right)_{T_B \neq T_A} = \frac{(dP/dt)_A}{P_B} \left(\frac{2\pi M_i T_B}{RT_A^2}\right)^{1/2} \quad (4)$$

where M_i = molecular weight of inert gas, R = gas constant (ergs mole⁻¹ deg.⁻¹), T = temperature (°K.), V is the volume of the apparatus upstream of the orifice, P_A is the instantaneous pressure in A at T_A and P_B that near the orifice at temperature T_B . Because of the phenomenon of thermal transpiration $P_B < P_A$ since $T_B < T_A$. This pressure gradient caused by thermal transpiration is difficult to evaluate from theoretical considerations. It therefore becomes more expedient to calibrate empirically an effective orifice area defined as

$$\left(\frac{a}{V}\right)_{\text{eff.}} = \left(\frac{dP/dt}{P}\right)_A \left(\frac{2\pi M_i T_B}{RT_A^2}\right)^{1/2} \quad (5)$$

For the purpose of calibration argon was chosen since some of its physical properties¹³ closely resemble those of fluorine.

Analysis of Results

The results of the experimental measurements are summarized in Table I. From the measured rate of pressure change in vessel A the degree of dissociation of fluorine α at a given temperature is calculated according to equation 3. In the evaluation of the equilibrium constant K_p for the reaction $1/2\text{F}_2(\text{g}) = \text{F}(\text{g})$ (Table II) as given by

$$K_p = \frac{2\alpha P_B^{1/2}}{(1-\alpha^2)^{1/2}} \quad (6)$$

a correction must be applied to the total pressure of the gas P measured in vessel A because of thermal transpiration between the orifice and vessel A (Fig. 1). To a first approximation the pressure ratio P_B/P_A varies as $\sqrt{T_B/T_A}$. Since the equilibrium constant is a function of \sqrt{P} the effect of this correction term on K_p will be proportional to $(T_B/T_A)^{1/4}$. Thus the degree of uncertainty in the final results due to this approximation will be relatively small.

Graphical analysis of the experimental results in a plot of the logarithm of the equilibrium constant versus the reciprocal absolute temperature yields the curve shown in Fig. 2. From the slope

(13) J. H. Simons, "Fluorine Chemistry," Academic Press, Inc., New York, N. Y., 1950.

of this curve, as evaluated by the method of least squares, the average heat of dissociation over the temperature range studied is 19.0 ± 0.4 kcal. per half mole of fluorine. Combined with the available entropy data¹⁴ for this system, ΔH_{298}^0 is found to be 37.6 kcal./mole with a standard deviation of 0.8 kcal./mole for the reaction $F_2(g) = 2F(g)$.

TABLE I

EXPERIMENTAL RESULTS FOR THE DEGREE OF DISSOCIATION OF F_2 AS A FUNCTION OF TEMPERATURE

T , °K.	$d \log P/dt$ sec. ⁻¹ $\times 10^4$	$(a/V)_{eff.}$, cm. ⁻¹ $\times 10^7$	α^a
298	11.00 \pm 0.15	2.146 \pm 0.005	0
356	10.68	2.258	0
422	10.29	2.389	0
477	10.34	2.499	0
513	9.93	2.580	0.007
550	9.84	2.643	.023
565	9.75	2.673	.035
572	9.76	2.689	.034
604	9.39	2.750	.097
609	9.41	2.760	.091
619	9.35	2.780	.099
658	8.71	2.857	.247
677	7.70	2.896	.588
733	7.51	3.007	.674
781	7.35	3.132	.744
790	7.35	3.120	.749

^a See equation 3.

TABLE II

EQUILIBRIUM CONSTANT FOR REACTION $1/2F_2(g) = F(g)$

T , °K.	α	P^a , atm. $\times 10^7$	K_p , atm. ^{1/2}
298	0	5.27	...
513	0.007	6.89	1.16×10^{-5}
550	.023	7.13	3.88×10^{-6}
565	.035	7.23	5.96×10^{-6}
572	.034	7.28	5.90×10^{-6}
604	.097	7.47	1.68×10^{-4}
609	.091	7.51	1.58×10^{-4}
619	.099	7.56	1.73×10^{-4}
658	.247	7.80	4.50×10^{-1}
677	.588	7.92	1.29×10^{-3}
733	.674	8.23	1.66×10^{-3}
781	.744	8.55	2.06×10^{-3}
790	.749	8.60	2.10×10^{-3}

^a Corrected for thermal transpiration; $P = P_{298} (T/298)^{1/2}$.

It is worthwhile to note that the experimental error of the reported measurements is reduced by the procedure employed in the evaluation of the degree of dissociation. Instead of calculating the average molecular weight of the gas mixture from the effusion rate, the degree of dissociation of the fluorine molecules is found from the relative change in effusion rate as given by equation 3. By this method inherent experimental errors will tend to cancel each other, thereby increasing the accuracy with which α may be computed over and above the precision measure with which the individual parameter may be measured. Thus, the over-all accuracy of the data is estimated to be $\pm 2.5\%$.

(14) L. C. Cole, M. Farber and G. Elverum, *J. Chem. Phys.*, **20**, 586 (1952).

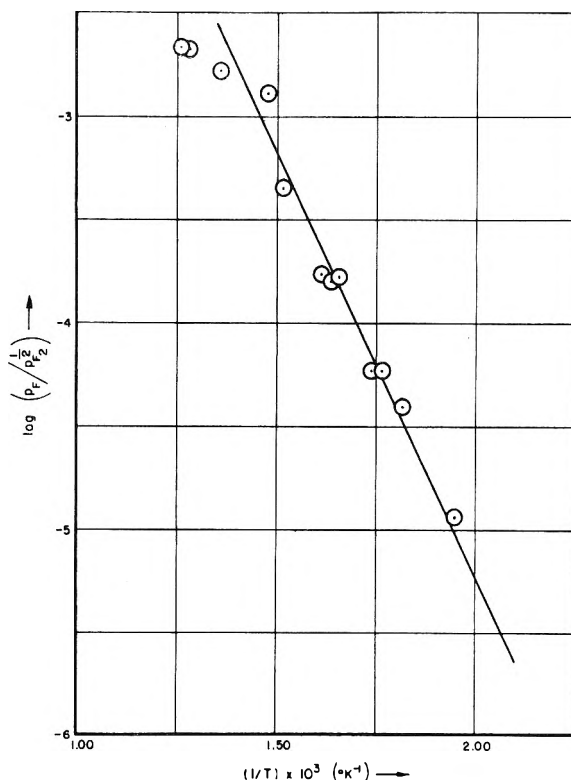


Fig. 2.—Equilibrium constant for reaction $1/2F_2(g) = F(g)$ as a function of temperature.

However, it is to be noted that at temperatures above 700°K., the experimental results deviate in excess of the experimental error from the curve shown in Fig. 2. At these elevated temperatures, the measured rate of efflux of gas from the storage vessel is abnormally high suggesting a smaller dissociation energy than observed at lower temperatures. At first this discrepancy was believed to be caused by an increase in orifice area due to corrosion of the nickel by fluorine at these elevated temperatures. However, subsequent calibration of the orifice diameter with inert gases indicated no change in the dimensions of the opening. On the other hand, in this temperature range interaction between the fluorine and the walls of the metal vessel was observed. Thus a continuous decrease in pressure was recorded in the system when fluorine was admitted to the nickel tube without effusion through the orifice. On prolonged contact between the gas and the walls of the vessel, an equilibrium condition could not be attained at these elevated temperatures. This phenomenon was absent at lower temperatures. In the computation of the heat of dissociation of fluorine (Fig. 2) the empirical data observed above 700°K. have consequently not been included.

The results of these experiments tend to confirm the dissociation energy calculated from thermochemical data¹⁵ [$D_0(F_2) = 40$ kcal.] which are based on the heat of formation of Clf of 11.6 kcal./mole. It is also in good agreement with the results [$D_0(F_2) = 36.5 \pm 1$ kcal.] reported in the direct measurement of the pressure variation with temperature.³

(15) A. Eucken and E. Wicke, *Naturwissenschaften*, **10**, 233 (1950).

THE DIELECTRIC CONSTANTS, POLARIZATIONS AND DIPOLE MOMENTS OF SOME ALKYL BENZENES

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The dielectric constants of 26 alkylbenzenes have been determined at 20 and 30°, and their molar polarizations and dipole moments have been calculated. Comparison was made of the present results with previous values available in the literature for 14 of the compounds, and some discrepancies among the values are discussed. The atomic polarizations of alkylbenzenes were calculated as a function of the number of side chain carbon atoms. Dipole moments of these hydrocarbons, calculated from the Onsager equation, are discussed in relation to the moments found in the gaseous state. The quantities $g^{1/2\mu}$, calculated from the Kirkwood equation, are given; these proved to agree more closely with the gas moments than do the moments calculated from the Onsager equation.

Although much work has been done upon the preparation of highly purified alkylbenzenes and upon the determination of some of their physical properties by NBS and API Project 44,¹ NACA,² and others,³ little work appears to have been done upon the dielectric constants of alkylbenzenes. Timmermans,³ using ± 0.1 to $\pm 0.2\%$ accuracy as a criterion, lists the dielectric constants of only benzene, toluene and *p*-xylene.

It is a purpose of this paper to report measurements of ± 0.1 to $\pm 0.2\%$ accuracy on the dielectric constants of 26 alkylbenzenes. These data were employed in the calculation of the molar polarizations, atomic polarizations and dipole moments⁴⁻⁶ resulting from the application of various theories of polarization.^{4,6} It appears that the Kirkwood equation⁶ is more satisfactory than the Onsager equation⁴ even for the calculation of the dipole moments of slightly polar compounds.

Experimental

The hydrocarbons employed were prepared or purified at this Laboratory.² Despite the fact that the hydrocarbons were stored in the dark in brown bottles with ground glass stoppers, some autoxidation had occurred. To remove these impurities the hydrocarbons were passed through silica gel columns until the dielectric constants remained constant. As a further check on the purity, the densities and refractive indices were then determined⁷ and it was found that the average differences between the NBS values¹ or the NACA values² previously reported and those found in this investigation were two units and one unit in the fourth decimal places for the densities and refractive indices, respectively. The benzene employed for standardization of the dielectric constant cell was distilled from a Podbielniak column having in excess of 150 theoretical plates and was dried over calcium hydride. The density and refractive index were 0.87904 and 1.5010 (NBS, d^{20} , 0.87903; n^{20}_D

1.5011). The dielectric constant values used for benzene were 2.284 at 20° and 2.265 at 30°.⁸

The dielectric constants were determined with a Schering Bridge apparatus (General Radio 716-C). The oscillator employed was a Hewlett-Packard (M-200D) operated at 1000 cycles/sec. The detector circuit consisted of a decade amplifier, 1000 cycles/sec. band pass filter and a vacuum tube voltmeter. A complete worm-gear correction was employed with the precision condenser. The accuracy of the data obtained is estimated to be 0.1 to 0.2%, while the reproducibility of results is better than 0.1%.

The dielectric constant cell⁹ consisted of four nickel cylinders connected in pairs and rigidly connected to an inner glass piece through which the leads passed to sealed-in metallic leads for external connection. The inner piece had a ground glass joint and fit into an outer test-tube. The air capacity was 50.75 micro-microfarads and the residue capacity was 4.33 micro-microfarads.

Temperature control was maintained by pumping water from a large constant temperature bath through a stainless steel water jacket surrounding the glass cell. The temperature was regulated to within $\pm 0.1^\circ$ of the desired temperature.

Results and Discussion

The dielectric constant results of this investigation are listed in columns 2 and 3 of Table I and the values listed in column 2 of Table I (ϵ^{20}) are also given in Table II where they are compared with the most probable values given by Maryott and Smith in the N.B.S. compilation of the dielectric constants of liquids.¹⁰ All of the N.B.S. values not at 20° were extrapolated to 20° for comparison with the values obtained in the present investigation.

As can be seen from Tables I and II, only 15 out of the 27 hydrocarbons have been measured previously. Values for seven of the hydrocarbons listed in column 2 of Table II represent the results of a single previous investigation or the results of quite old work. In some instances where differences exist, which are larger than the experimental errors estimated, the hydrocarbons employed in very old measurements used in the N.B.S. compilation because of a lack of more recent values, may not have been of the highest purity owing to the absence of present day purification methods.

By far the largest discrepancy in Table II is the difference between the value of 2.33 at 20° given for 1-methyl-4-*t*-butylbenzene which comes from the

(1) National Bureau of Standards, "Selected Values of Properties of Hydrocarbons," American Petroleum Project 44, NBS Circular C 461, United States Government Printing Office, Washington, D. C., 1947.

(2) (a) L. C. Gibbons, *et al.*, *J. Am. Chem. Soc.*, **68**, 1130 (1946); (b) J. V. Karabinos, K. T. Serijan and L. C. Gibbons, *ibid.*, **68**, 2107 (1946); (c) C. M. Buess, J. V. Karabinos, P. V. Kunz and L. C. Gibbons, NACA Technical Note No. 1021, 1946; (d) J. V. Karabinos and J. M. Lambert, NACA Technical Note, No. 1019, 1946; (e) T. W. Reynolds, *et al.*, *Ind. Eng. Chem.*, **40**, 1751 (1948); (f) K. T. Serijan, H. F. Hipsher and L. C. Gibbons, *J. Am. Chem. Soc.*, **71**, 873 (1949).

(3) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950.

(4) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

(5) A. P. Altshuller, *THIS JOURNAL*, **57**, 538 (1953).

(6) J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

(7) I. A. Goodman and P. H. Wise, *J. Am. Chem. Soc.*, **72**, 3076 (1950).

(8) (a) F. van der Maesen, *Physica*, **15**, 481 (1949); (b) A. S. Brown, P. M. Levin and E. W. Abrahamson, *J. Chem. Phys.*, **19**, 1226 (1951); (c) W. M. Heston, Jr., and C. P. Smyth, *J. Am. Chem. Soc.*, **72**, 99 (1950); (d) L. Mouradoff-Fouquet, *Compt. rend.*, **226**, 1970 (1948); (e) J. Hadamard, *ibid.*, **204**, 1234 (1937).

(9) Purchased from J. C. Balsbaugh, Cambridge, Massachusetts.

(10) A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," NBS Circular 514, Aug. 1951.

TABLE I
 DIELECTRIC CONSTANTS, MOLAR POLARIZATIONS AND MOLAR REFRACTION OF SOME ALKYL BENZENES

Compound	ϵ^{20}	ϵ^{30}	P_{CM}^{20}	R_D^{20}	$P_{CM}-R_D$	\bar{n}_D^{25}	$P_{CM}-R_\infty$	$[P_0]_D^{25}$	$[P_0]_\infty^{25}$	$[P_0]_0$
Benzene	2.284 ^a	2.265 ^a	26.65	26.2	0.45	25.15	1.5	0.45	1.55	0.0
Methylbenzene	2.385	2.364	33.55	31.1	2.45	29.9	3.65	2.5	3.75	2.0
Ethylbenzene	2.403	2.381	39.05	35.75	3.3	34.45	4.6	3.3	4.7	2.7
1,2-Dimethylbenzene	2.574	2.544	41.55	35.8	5.75	34.45	7.1	5.9	7.25	5.25
1,3-Dimethylbenzene	2.367	2.347	38.45	35.95	2.5	34.6	3.85	2.5	3.9	1.9
1,4-Dimethylbenzene	2.269	2.250	36.65	36.0	0.65	34.65	2.0	0.65	2.0	0.0
Propylbenzene	2.372	2.351	43.75	40.45	3.3	39.0	4.75	3.35	4.8	2.6
<i>i</i> -Propylbenzene	2.384	2.363	44.05	40.4	3.65	39.0	5.05	3.65	5.1	2.9
1-Methyl-2-ethylbenzene	2.595	2.566	47.4	40.45	6.95	38.95	8.35	7.15	8.65	6.45
1-Methyl-3-ethylbenzene	2.365	2.347	43.5	40.65	2.85	39.15	4.35	2.85	4.4	2.2
1-Methyl-4-ethylbenzene	2.265	2.247	41.4	40.7	0.7	39.2	2.2	0.7	2.2	0.0
1,2,3-Trimethylbenzene	2.636	2.609	47.45	40.45	7.00	39.0	8.4	7.2	8.75	6.55
1,2,4-Trimethylbenzene	2.378	2.359	43.2	40.7	2.5	39.2	4.0	2.55	4.1	1.9
1,3,5-Trimethylbenzene	2.279 ^b	...	41.55	40.8	0.75	39.3	2.25	0.7	2.25	0.0
Butylbenzene	2.359	2.338	48.65	45.1	3.55	43.55	5.05	3.6	5.15	2.7
<i>i</i> -Butylbenzene	2.319	2.298	48.05	45.2	2.85	43.65	4.4	2.85	4.45	2.0
<i>s</i> -Butylbenzene	2.364	2.345	48.65	45.0	3.65	43.5	5.15	3.7	5.25	2.80
<i>t</i> -Butylbenzene	2.366	2.346	48.45	45.0	3.45	43.45	5.0	3.5	5.1	2.65
1,2-Diethylbenzene	2.594	2.565	52.9	45.05	7.85	43.5	9.4	8.05	9.65	7.20
1,3-Diethylbenzene	2.369	2.350	48.65	45.3	3.35	43.7	4.95	3.4	5.00	2.55
1,4-Diethylbenzene	2.259	2.244	46.0	45.4	0.6	43.8	2.2	0.65	2.3	0.0
1-Methyl-4- <i>i</i> -propylbenzene	2.253	2.236	46.1	45.35	0.75	43.6	2.5	.8	2.55	0.0
1,3-Dimethyl-5-ethylbenzene	2.275	2.257	46.3	45.5	0.88
Tetralin	2.773	2.744	50.65	42.9	7.75	41.25	9.4	8.1	9.85	7.40
1-Methyl-3- <i>t</i> -butylbenzene	2.330	2.313	52.6	49.9	2.7	2.75
1-Methyl-4- <i>t</i> -butylbenzene	2.250	2.234	50.55	49.9	0.65	48.0	2.55	0.6	2.65	0.0
1-Methyl-3,5-diethylbenzene	2.264	2.251	50.9	50.2	0.765
1,3,5-Triethylbenzene	2.256	2.243	55.6	55.0	0.556

^a Values obtained from reference 8. ^b F. H. Muller, *Physik. Z.*, **38**, 283 (1937).

TABLE II

COMPARISON OF DIELECTRIC CONSTANT VALUES AT 20°

Compound	N.B.S. values ^{a, b}	Present investigation
Methylbenzene	2.389	2.385
Ethylbenzene	2.412	2.403
1,2-Dimethylbenzene	2.568	2.574
1,3-Dimethylbenzene	2.374	2.367
1,4-Dimethylbenzene	2.270	2.269
Propylbenzene	2.36(9) ^c	2.372
<i>i</i> -Propylbenzene	2.38(0) ^c	2.384
1,2,4-Trimethylbenzene	2.41 ^c	2.378
1-Methyl-4-ethylbenzene	2.25(0) ^c	2.265
<i>i</i> -Butylbenzene	2.34 ^c	2.319
<i>t</i> -Butylbenzene	2.38 ^c	2.366
1-Methyl-4- <i>i</i> -propylbenzene	2.24(3)	2.253
Tetralin	2.757	2.773
1-Methyl-4- <i>t</i> -butylbenzene	2.33 ^c	2.250

^a A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," N.B.S. Circular 514, Aug. 1951.

^b N.B.S. values listed to four figures are considerably accurate to 0.5% or better. Values listed to three figures are probably accurate to 2% or better. Figures in parentheses are not to be counted in estimating accuracy. ^c These values are based on a single determination or on very old work.

work of Le Fevre, Le Fevre and Robertson¹¹ and the value of 2.250 from the present investigation. A dielectric constant of 2.33 for this *p*-dialkylbenzene is much higher than the values for the other *p*-dialkylbenzenes all of which fall in the range from 2.25

to 2.27 units. The dielectric constant value for 1-methyl-4-*t*-butylbenzene given by Le Fevre, *et al.*, is quite close to the value obtained for 1-methyl-3-*t*-butylbenzene in the present investigation. Furthermore, the density given by these investigators for 1-methyl-4-*t*-butylbenzene is intermediate between the values reported for the 1,4- and 1,3-isomers by Serijan, Hipsher and Gibbons.^{2f} Probably the 1-methyl-4-*t*-butylbenzene used in the measurement of Le Fevre, *et al.*, was considerably contaminated with the 1,3- and possibly the 1,2-isomer.

In columns 4 through 11 of Table I a number of molar polarizations, molar refractions and their differences are given for the aromatic hydrocarbons investigated. The quantity P_{CM}^L refers to the molar polarizations of the liquids calculated by the Clausius-Mosotti equation and R_D^L to the molar refractions of the liquids employing the sodium D-line. The differences in these quantities for non-polar alkylbenzenes range from 0.45 to 0.8 cm.³ with the values for all the *p*-dialkylbenzenes being 0.7 ± 0.1 cm.³ The quantity R_∞^L is given in column 7 and was calculated employing n given by Forziati.¹² The differences between \bar{P}_{CM}^L and R_∞^L are given in column 8. These differences would represent the atomic polarizations plus the orientation polarization if the Clausius-Mosotti equation were valid for slightly polar compounds. The use of n_D , instead of a n (effective) which includes all of the infrared contribution to the polarization, results in

(11) C. G. Le Fevre, R. J. W. Le Fevre and K. W. Robertson, *J. Chem. Soc.*, 480 (1935).

(12) A. F. Forziati, *J. Research Natl. Bur. Standards*, **44**, 373 (1950).

0.67–0.75 P_A being accounted for. In column 9 the polarization, $[P_0]_D$, is calculated using the Onsager equation^{4,5} with n_D used for the refractive index. It may be seen that $[P_0]_D$ is about equal to $P^{L_{CM}} - R^{L_D}$ for the non-polar hydrocarbons, 0.1 to 0.2 cm.³ larger for hydrocarbons with dipole moments between 0.3 and 0.6 D , and up to 0.35 cm.³ larger for hydrocarbons with moments around 0.6 to 0.7 D . In column 10 the values of $[P_0]_\infty$ are given. These values are calculated employing n_∞ .^{2,4} This quantity should equal the orientation plus the atomic polarization, and it may be seen that $[P_0]_\infty$ is equal to or very slightly larger than $P^{L_{CM}} - R^{L_\infty}$ for the non-polar alkylbenzenes, but becomes increasingly larger than $P^{L_{CM}} - R^{L_\infty}$ with increasing polarity of the hydrocarbons up to differences of 0.45 cm.³ owing to the failure of the Clausius-Mosotti equation for polar liquids.

For benzene, the *p*-dialkylbenzenes and the *sym*-trialkylbenzenes $[P_0]_\infty = P_A$. The *p*-dialkyl compounds in which the two alkyl groups are different have the same $[P_0]_\infty$ as do the corresponding compounds with identical alkyl groups and with the same number of side-chain carbons. (This fact would cast some doubt upon the possibility that the *p*-dialkylbenzenes with dissimilar groups have finite dipole moments.) Employing the $[P_0]_\infty$ values for benzene, 1,4-dimethylbenzene, 1-methyl-4-ethylbenzene, 1,4-diethylbenzene, 1,3,5-trimethylbenzene, 1-methyl-4-*i*-propylbenzene and 1-methyl-4-*t*-butylbenzene, the quantity P_A was related to n , the number of side-chain carbons, by the least squares equation

$$P_A = (1.56 \pm 0.05) + (0.22 \pm 0.01)n \quad (1)$$

In Table III are given the atomic polarizations

TABLE III

ATOMIC POLARIZATIONS OF SOME HYDROCARBONS

Compound	P_A (liquid) ¹³	P_A (gas) ¹⁴
<i>n</i> -Paraffins	0.22 + 0.076 n ¹⁵	0.01 + 0.07 n ¹⁵
Cyclohexane		0.7
Decalin		0.7
Butene-2		1.5
Acetylene		1.3
Benzene	1.55	1.9, 1.1 (ave. 1.5)
Toluene	1.75	2.5, 0.9 (ave. 1.7)
1,4-Dimethylbenzene	2.0	2.0
1-Methyl-4-ethylbenzene	2.2	
1,3,5-Trimethylbenzene	2.2	2.2
1,4-Diethylbenzene	2.45	
1-Methyl-4- <i>i</i> -propylbenzene	2.45	
1-Methyl-4- <i>i</i> -butylbenzene	2.65	
Naphthalene		2.4
Biphenyl		2.8

of a number of hydrocarbons in the liquid and gas-

(13) Liquid values for alkylbenzenes from least-squares equation.

(14) Gas values from Landolt-Börnstein, "Numerical Values and Functions from Physics, Chemistry, Astronomy, Geophysics, and Technology," Vol. I, "Atomic and Molecular Physics," Part III, Springer Verlag, Berlin, 1951, p. 515.

(15) A. Audsley and F. R. Goss, *J. Chem. Soc.*, 2989 (1950).

ous states. The atomic polarizations of aromatic hydrocarbons are larger than those of the *n*-paraffins because of both the higher atomic polarization of the benzene nucleus and the large increment for the CH₂ group in the aromatic series. This increase in atomic polarization with unsaturation is to be noted also with an alkene, butene-2 and an alkyne, acetylene. In both cases, inserting a single multiple bond results in an atomic polarization about equal to that of benzene. Cyclization has no effect on the atomic polarization as is shown by the values for cyclohexane and decalin.

The atomic polarizations derived from gas measurements of the dielectric constant are in fairly good agreement with those found in the liquid state in the present investigation. The gas atomic polarization may actually be slightly lower than the liquid values, if the same differences between the liquid and gas values exist as in the *n*-paraffins. It should be remembered, however, that even a highly accurate gas measurement will result in an uncertainty of ± 0.3 to 0.4 cm.³ in P_A , and measurements of moderate accuracy may result in uncertainties from ± 0.5 to 1 cm.³ in P_A , while the polarizations calculated from dielectric constant measurements on the liquid are accurate to ± 0.05 to 0.1 cm.³. In view of the experimental uncertainties the agreement in the table is quite good.

The values for the two polynuclear hydrocarbons, naphthalene and biphenyl, are also of some interest. If the value given for naphthalene is correct, the additional unsaturation in this fused ring system does not increase the atomic polarization over that of the corresponding alkylbenzene with four side-chain CH₂ groups. The biphenyl molecule appears to have about twice the atomic polarization of benzene. Again this is not the result of additional unsaturation but may be accounted for if we take $P_A = 1.56 + 6(0.22) = 2.88$. Thus it would appear that the presence of an unsaturated linkage somewhere in the hydrocarbon molecules increases the atomic polarization by about one cm.³, but further unsaturation appears to have no corresponding effect. The atomic polarization in both the aliphatic and aromatic series increases linearly with the increase in CH₂ groups.

The values of $[P_0]_0$ in column 11 of Table I are obtained by subtracting the appropriate P_A from $[P_0]_\infty$. If it is assumed that the atomic polarization of a slightly polar hydrocarbon is the same as the atomic polarization of the isomeric non-polar hydrocarbon then the differences, $[P_0]_\infty - P_A$, should be the orientation polarization obtainable from the Onsager equation. This procedure is similar to employing a n (effective), which includes all of the infrared contributions to the refractive index, in the Onsager equation.

In Table IV are listed the dipole moments calculated from the Onsager equation using $n_D(\mu_1)$, the dipole moments calculated by the equation $\mu = (\epsilon - n_D^2) \times 10^{18}$ previously considered,⁵ (μ_2), the dipole moments calculated from Onsager's equation completely corrected for atomic polarization (from $[P_0]_\infty - P_A$), (μ_3), the values of $g^{1/2}\mu_4$ calculated from the Kirkwood equation,⁶ and finally the mo-

TABLE IV
 DIPOLE MOMENTS OF AROMATIC HYDROCARBONS

Compound	μ_1	μ_2	μ_3	$g^{1/2}\mu_4$	μ_{KHS}
Benzene	0.15	0.18	0.0		0.0 ¹⁶
Methylbenzene	.35	.38	.31	0.52	.37 ¹⁷
Ethylbenzene	.40	.41	.36	.59	.58 ¹⁷
1,2-Dimethylbenzene	.53	.55	.50	.69	.62 ¹⁸
1,3-Dimethylbenzene	.35	.35	.30		
1,4-Dimethylbenzene	.18	.18	.0		.0 ¹⁸
Propylbenzene	.40	.38	.35		
<i>i</i> -Propylbenzene	.42	.40	.37	.62	.65 ¹⁷
1-Methyl-2-ethylbenzene	.59	.58	.56		
1-Methyl-3-ethylbenzene	.37	.35	.33		
1-Methyl-4-ethylbenzene	.18	.17	.0		
1,2,3-Trimethylbenzene	.59	.59	.56		
1,2,4-Trimethylbenzene	.35	.34	.30		
1,3,5-Trimethylbenzene	.20	.18	.0		
Butylbenzene	.42	.37	.36		
<i>i</i> -Butylbenzene	.37	.33	.31		
<i>s</i> -Butylbenzene	.42	.38	.37		
<i>t</i> -Butylbenzene	.41	.37	.36	.63	.70 ¹⁷
1,2-Diethylbenzene	.62	.58	.59		
1,3-Diethylbenzene	.40	.36	.36		
1,4-Diethylbenzene	.17	.16	.0		
1-Methyl-4- <i>i</i> -propylbenzene	.19	.17	.0		
1,3-Dimethyl-5-ethylbenzene	.20	.18	.0		
Tetralin	.62	.63	.60		
1-Methyl-3- <i>t</i> -butylbenzene	.36	.31	.32		
1-Methyl-4- <i>t</i> -butylbenzene	.17	.15	.0	.0	.39 ¹⁷
1-Methyl-3,5-diethylbenzene	.18	.15	.0		
1,3,5-Triethylbenzene	.17	.14	.0		

ments calculated from gas measurements. The Kirkwood equation was employed in the form

$$g^{1/2}\mu_4 = \left[\frac{3(2\epsilon + nD^2)}{(2\epsilon + 1)(nD^2 + 2)} \right] \left(\frac{9kT}{4\pi N} \right)^{1/2} [P_0 - P_{E+A}]^{1/2} \quad (2)$$

The quantity g is a parameter which indicates the magnitude of the hindering effect of a molecule on neighboring molecules. The quantity P_0 is an orientation polarization.

The values of the dipole moments for μ_1 and μ_2 are in good agreement. The average difference is 0.02 D with the values for μ_2 being slightly lower than the values for μ_1 for the higher molecular weight hydrocarbons. The complete correction for atomic polarization reduces the dipole moments as much as 0.05 D compared with μ_1 . The use of nD in the Onsager equation when calculating μ_1 does account for 0.67 to 0.75 of the atomic polarization, but the remaining correction is of some significance for dipole moments below 0.50 D .

The values of $g^{1/2}\mu_4$ are in better agreement with the moments calculated from gas measurements than are μ_1 , μ_2 , μ_3 . The value of $g^{1/2}\mu_4$ for toluene of 0.52 D is anomalously high, but the remaining values of $g^{1/2}\mu_4$ agree within about 0.05 D with the gas values (excepting 1-methyl-4-*t*-butylbenzene).

(16) *Trans. Faraday Soc.*, 30 (1934), Appendix A—Table of Dipole Moments from page 904.

(17) J. W. Baker and I. G. Groves *J. Chem. Soc.*, 1144 (1939).

(18) E. C. Hurdis and C. P. Smyth, *J. Am. Chem. Soc.*, 64, 2212 (1942).

It appears that the Onsager equation gives dipole moment values from 0.1 to 0.3 D too small for alkylbenzenes. A small improvement could be made if an ellipsoidal model rather than a spherical model were assumed for the alkylbenzenes,¹⁹ but the improvement would hardly be more than 0.05 D for this class of compounds. It is of interest to note that the Onsager moments for aromatic halides are also 0.1 to 0.4 D unit lower than the gas moments.²⁰ Both types of molecules would show dipole association which might be expected to be contra-association in both.²¹ The Onsager moments might be improved by extrapolation of the values of μ to $1/T = 0$,²² but it is questionable whether the discrepancies will entirely disappear.

It appears that even in the case of only slightly polar compounds the Kirkwood equation will give values in better agreement with the gas values than the Onsager equation. That this should be so for molecules which show no hydrogen bonding and only weak dipole-dipole interactions further indicates the very approximate nature of the Onsager treatments.

Acknowledgment.—The author wishes to thank Mrs. Virginia Fenn for determining the densities and refractive indices of the alkylbenzenes employed.

(19) Th. G. Scholte, *Physica*, 15, 437 (1949).

(20) W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, *J. Am. Chem. Soc.*, 72, 2071 (1950).

(21) J. N. Wilson, *Chem. Revs.*, 25, 377 (1939).

(22) J. D. Hoffman, *J. Chem. Phys.*, 20, 740 (1952).

COMBUSTION CALORIMETRY OF ORGANIC CHLORINE COMPOUNDS. HEATS OF COMBUSTION OF CHLOROBENZENE, THE DICHLORO- BENZENES AND *o*- AND *p*-CHLOROETHYLBENZENE¹

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A method is described for determining the heats of combustion of organochlorine compounds in a conventional bomb calorimeter. Hydrazine dihydrochloride solution, supported on a glass filter cloth lining, is used in the bomb to reduce to chloride ion the free chlorine formed in the combustion reaction. The following values in kcal. mole⁻¹ are reported for the heats of formation, ΔH_f , of some chlorinated aromatic compounds from graphite and gaseous hydrogen and chlorine: chlorobenzene (l), +2.5₅; *o*-dichlorobenzene (l), -4.2₆; *m*-dichlorobenzene (l), -4.8₅; *p*-dichlorobenzene (s), -10.1₂; *o*-chloroethylbenzene (l), -12.8₅; and *p*-chloroethylbenzene (l), -12.3₁.

When organic chlorine compounds undergo combustion in a bomb charged with oxygen, hydrochloric acid and free chlorine are usually formed. The equilibration of a mixture of these two states of chlorine with water proceeds slowly; hence, a combustion process yielding such a mixture is not suitable for high precision combustion calorimetry. In 1891 Berthelot and Matignon³ used arsenious oxide solution in the bomb to reduce the free chlorine to chloride ion. Since that time Smith,^{4a,b} Smith and Schjånberg,^{4c} and Schjånberg^{4d,e} have studied the use of this reductant and have pointed out that unless precautions are taken, the chlorine may not be completely reduced during a normal calorimetric reaction period. However, they have been able to increase the rate of reduction by supporting the reducing solution on quartz fibers. Their method, which has been called the "quartz-wool" or "quartz-spiral" method, has been used extensively at the University of Lund for the determination of the heats of combustion of more than a hundred organochlorine compounds.^{4,5} Popoff and Schirokich⁶ increased the rate of reaction between As₂O₃ solution and free chlorine by agitation of the bomb contents. This was accomplished with a "moving-bomb"⁷ calorimetric system.

Because of the relative simplicity of the "static" quartz-wool method it was adopted in this Laboratory as a starting point in the study of the combustion calorimetry of organochlorine compounds. A modification of the method has been developed which includes (a) the use of hydrazine dihydrochloride solution as the reductant and (b) the use of a

coarsely woven glass filter cloth to support the reductant. Application of the modified method has been only partially successful and other procedures are contemplated. However, the results are of general interest and utility and will be presented here.

Experimental

Apparatus.—The calorimetric system used for this investigation, with the exception of the bombs, has been previously described.⁸ Two bombs were used. The first, Pt 1, employed in the early part of this investigation and for most of the combustions, was made of high-carbon steel and lined with platinum (0.02 in. thick). The internal volume of the bomb was 0.384 liter. The electrodes and other internal parts were made of platinum. The bomb used for the *o*- and *m*-dichlorobenzene experiments, Ta 1, was machined from stainless steel and lined with tantalum (0.02 in. thick). The internal volume of the bomb was 0.340 liter. Tantalum was also used for the electrodes, crucible support and valve inlet fittings. A platinum crucible and a ¹/₁₆-inch Teflon (polytetrafluoroethylene) sealing gasket were used with both bombs.^{9,10} The upper portions of the bomb walls were lined with coarsely woven glass filter cloth which was used to support the reducing solution.

A change was made in the orientation of the bomb when the tantalum bomb was put into use. Because the corrosion of the platinum bomb occurred entirely on the crucible, the electrodes, and the ceiling of the bomb, which parts are directly in or above the combustion zone, the bomb was inverted and the crucible supported from beneath as shown in Fig. 1. This arrangement also made it simple to line the ceiling of the bomb with the solution impregnated glass

(8) W. N. Hubbard, J. W. Knowlton and H. M. Huffman, *J. Am. Chem. Soc.*, **70**, 3259 (1948).

(9) The corrosion of platinum in the platinum bomb by the products of combustion was such that a quantitative determination of the chloroplatinic acid formed was necessary in order to apply appropriate thermal corrections. In addition, the chloroplatinic acid formed causes other difficulties when hydrazine dihydrochloride is used as the reducing agent in the bomb (see later discussion). Hence, an effort was made to find another material for lining the bomb that would either reduce the amount of corrosion or yield corrosion products of a less troublesome nature.

Since preliminary experiments indicated that tantalum coupons placed against the ceiling of the bomb might be more resistant to corrosion than platinum, the tantalum-lined bomb was constructed. Tantalum could not be used for the crucible as a coupon of tantalum placed in the crucible was completely oxidized in a trial combustion experiment. An attempt was also made to use a quartz crucible, but this was not successful since combustions performed in even very thin crucibles (3 g.) tended to leave traces of carbon. However, the use of a platinum crucible in the tantalum bomb was reasonably satisfactory. The thermal effect of attack on the crucible was only about 1/2 cal. per combustion. Furthermore, the platinum dissolved came entirely from the crucible, and the amount could be determined as a loss in weight of the crucible, thus making unnecessary the analysis of the bomb solution for platinum.

(10) Teflon occasionally fails when used in combustion experiments with the usual upright bomb.

(1) Presented in part at meetings of the American Chemical Society in Chicago, April, 1948 (two papers), and San Francisco, March, 1949.

(2) Deceased.

(3) M. P. E. Berthelot and C. Matignon, *Ann. chim. phys.*, [6] **23**, 507 (1891).

(4) (a) L. Smith, *Svensk. Kem. Tidskr.*, **40**, 297 (1928); (b) L. Smith, *ibid.*, **41**, 272 (1929); (c) L. Smith and E. Schjånberg, *ibid.*, **43**, 213 (1931); (d) E. Schjånberg, Thesis, University of Lund, Berlingska Boktryckeri, Lund, Sweden, 1934; (e) E. Schjånberg, *Z. physik. Chem.*, **A172**, 197 (1935).

(5) (a) G. Sjöström, *Svensk. Kem. Tidskr.*, **48**, 121 (1936); (b) E. Efring, Thesis, University of Lund, Carl Bloms Boktryckeri, Lund, Sweden, 1938; (c) K. J. Karlsson (now Karrman), Thesis, University of Lund, Carl Bloms Boktryckeri, Lund, Sweden, 1941.

(6) M. M. Popoff and P. K. Schirokich, *Z. physik. Chem.*, **A167**, 183 (1933).

(7) The words "static" and "moving" are used to differentiate between the conventional bombs and those in which agitation of the bomb contents is achieved by mechanical rotation or oscillation of the bomb.

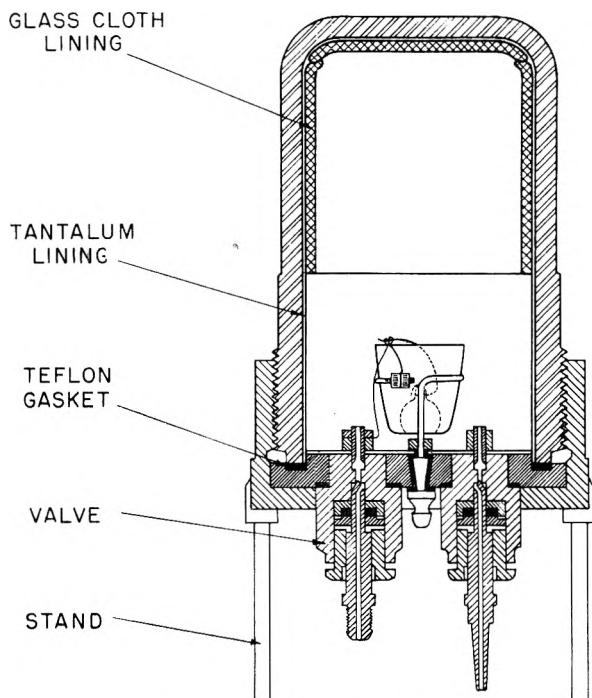


Fig. 1.—Combustion bomb.

cloth, and thereby protect this area from the combustion blast.

Calibration.—The energy equivalent of the calorimeter was determined by the combustion of NBS benzoic acid, 39f, in the bomb (without glass cloth lining) to which 0.1 ml. of water had been added. The heat of combustion, $-\Delta U_B$, of benzoic acid (certified to be 6317.83 cal. g.⁻¹ for standard conditions) was corrected to 6317.16 and 6317.11 cal. g.⁻¹ for the platinum and tantalum bombs, respectively. The difference in the contents of the bomb in the calibration and combustion experiments was accounted for in the usual calculation of the combustion reaction to isothermal conditions. The values obtained for the energy equivalent of the calorimetric system, C_{cal} (calor.), are given in Table I.

Procedures.—Each sample was contained in a thin-walled, soft-glass, flat-bottomed ampoule, the stem of which had been drawn to a very fine capillary and bent down (see Fig. 1). Ampoules were filled shortly before the combustion experiments in an apparatus similar to that previously described¹¹ except that the receiver that held the ampoules had a depression in which the inverted ampoules were placed.

In preparation for a combustion experiment the following procedure was used. An ampoule was removed from the filling system receiver. Two drops of liquid sample were forced out of the ampoule by warming in an oven and touching the drop to filter paper. In this way the level of the liquid in the ampoule was brought below the fine capillary and into the stem. A weighed strip of filter paper with a hole in one end was used as the fuse. After the ampoule was weighed, the hole in the fuse was placed over the capillary and on to the stem of the ampoule. A small weighed amount of auxiliary hydrocarbon oil was placed on the fuse at the stem of the ampoule. The other end of the fuse was inserted in a loop in the platinum ignition wire.

Prior to placing a combustion sample in the bomb the glass cloth lining was positioned in the bomb. It was placed in as close contact with the walls as possible since experiments showed that a loosely fitting cloth delayed attainment of thermal equilibrium. An appropriate volume and concentration of hydrazine dihydrochloride solution was then added to the glass cloth. The concentration and amount of the reductant were adjusted so that at least a 25% excess was present. Otherwise equilibration was slow or incomplete.

(11) G. B. Guthrie, Jr., D. W. Scott, W. N. Hubbard, C. Katz, J. P. McCullough, M. E. Gross, K. D. Williamson and G. Waddington, *J. Am. Chem. Soc.*, **74**, 4662 (1952).

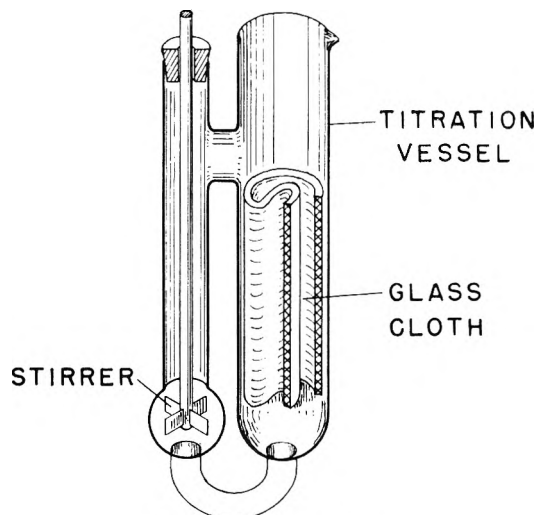


Fig. 2.—Titration vessel.

After the weighed sample and reducing solution had been placed in the bomb, the bomb was sealed and, after residual air had been swept out, it was charged with oxygen to a pressure of 30 atmospheres. The calorimetric observations were carried out in the usual way.^{2,8} In each experiment the combustion was initiated at 24.00° and an increase in temperature of approximately 2° was obtained. Experiments showed that no significant amount of sample was volatilized through the fine capillary of the ampoule in the length of time elapsing between weighing the sample and firing of the combustion. At the conclusion of the experiment the combustion gases were discharged through starch-iodide solution in order to test the completeness of the reduction of free chlorine.

To establish the extent of the side reactions that occurred in the bomb and to carry through the thermochemical corrections, the following analyses of the final bomb solution were necessary: (1) determination of the amount of hydrazine dihydrochloride unreacted; (2) determination of ammonium ion; (3) determination of dissolved platinum; and (4) determination of nitrate ion.

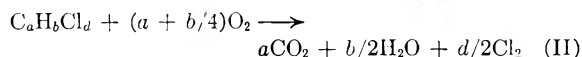
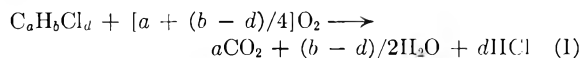
The analytical scheme used was as follows. After the bomb was disassembled, the filter cloth lining was placed in a special titration vessel, Fig. 2, which was so arranged that the solution in the vessel was vigorously circulated through the cloth during the titration. Those parts of the bomb to which chloroplatinic acid was adhering were then washed and these washings kept separate.¹² The remaining interior parts of the bomb were then washed, and these washings were added to the filter cloth lining in the titration vessel where the excess hydrazine dihydrochloride in the solution was titrated with iodine according to the direct iodine method.¹³ After the titration was complete, the solution was poured from the titration vessel and combined with the chloroplatinic acid washings. This mixture was then divided into two equal parts. Platinum was determined in one of these by precipitation with formic acid. The other portion was used to determine (1) ammonium ion by Kjeldahl distillation and (2) immediately following in the same apparatus, nitrate ion by Devarda's method.¹⁴

(12) When hydrazine dihydrochloride is used as the reductant, it is necessary to keep separate the bomb washings that contain chloroplatinic acid (formed by attack of the bomb by chlorine) from those that contain the hydrazine dihydrochloride-hydrochloric acid solution. Otherwise, the chloroplatinic acid would be reduced by the hydrazine. However, since the parts upon which the chloroplatinic acid occur are the ceiling, the electrodes and the crucible, these parts may be washed separately from the cup of the bomb in which all the reductant is contained. With the tantalum lined bomb, the only part of the bomb that has any chloroplatinic acid on it is the crucible. Here it is even simpler to maintain the necessary separation.

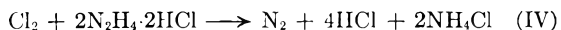
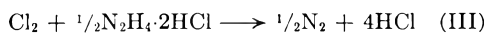
(13) R. A. Penneman and L. F. Audieth, *Anal. Chem.*, **20**, 1058 (1948).

(14) When the tantalum lined bomb was used, no analysis of platinum was necessary, so the entire bomb solution following the determination of excess hydrazine could be used for both the ammonium and nitrate ion determinations.

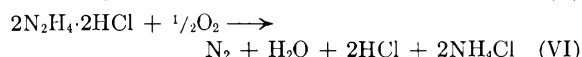
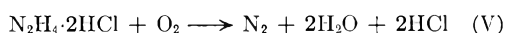
Thermochemical Corrections.—When compounds containing carbon, hydrogen and chlorine undergo combustion in a bomb in the absence of a reductant, reactions I and II occur.



When free chlorine is reduced by hydrazine dihydrochloride, reactions III and IV occur.

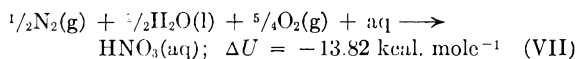


When compounds containing carbon, hydrogen and chlorine undergo combustion in a bomb in the presence of a sufficient excess of hydrazine dihydrochloride, chlorine does not appear among the products of combustion. The compound of interest is then converted quantitatively to carbon dioxide, water and hydrochloric acid. From an examination of the stoichiometric relations given above, it can be shown that a quantitative description of the reactions occurring is given by considering that all of the chlorine compound reacts according to reaction I and that all hydrazine consumed follows either reaction V or VI. From the

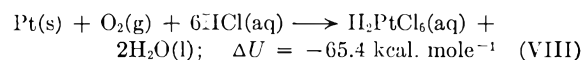


analytical results which give the extent of reactions V and VI, and the appropriate thermochemical data for these reactions, it is possible to compute the energy quantities associated with reaction I.

Corrections for the oxidation of hydrazine dihydrochloride were applied by use of the thermochemical quantities: reaction V, $\Delta U = -131.5$ kcal. mole⁻¹^{15a}; and reaction VI, $\Delta U = -60.9$ kcal. mole⁻¹^{15a}. The states to which the foregoing values apply are N₂H₄·2HCl(aq), NH₄Cl(aq), HCl(aq), O₂(g), N₂(g), and H₂O(l). Further corrections were applied for the formation of nitric acid by oxidation of gaseous nitrogen during the combustion process^{15b}



and the corrosive attack of the platinum^{15a}

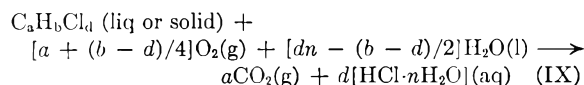


Materials.—Samples of chlorobenzene, *o*- and *p*-chloroethylbenzene and *o*-, *m*- and *p*-dichlorobenzene were made available to this Laboratory through the courtesy of Dr. D. A. Stull of the Dow Chemical Company, Midland, Michigan. The purity of the samples by the freezing point method and their infrared spectra were investigated in the Dow Laboratories. Values of purity in mole % were: C₆H₅Cl, 99.99+; *o*-C₆H₄Cl, 99.78; *p*-C₆H₄Cl, 99.84; *o*-C₆H₄Cl₂, 99.88; *m*-C₆H₄Cl₂, 99.87; and *p*-C₆H₄Cl₂, 99.55. The infrared spectra showed that the impurities present in the samples were isomeric; consequently their effect on the heat of combustion values obtained was probably negligible compared to other experimental uncertainties.

Results.—The data obtained in this investigation are summarized in Tables I, II and III. Table I gives somewhat detailed experimental data for the individual combustions. Table II gives the derived data. Table III compares the heats of combustion obtained in this investigation with values obtained by other investigators.

The columns of Table I list: the series and number designation of each experiment; the mass (wt. *in vacuo*) of compound that underwent combustion, *m'*; the increase in temperature of the calorimeter,

corrected for heat transfer and stirring energy during the reaction period, $\Delta T'_c$; the correction for the combustion of the auxiliary oil, q_{oil} ; the same for the fuse, q_{fuse} ; the corrections for the oxidation of the reductant, q_{hyd} , according to equations V or VI; the correction for the formation of H₂PtCl₆, q_{Pt} ; the correction for the formation of HNO₃, q_{HNO_3} ; the correction for the energy equivalent of the contents of the bomb, *C*, which reduces the results to isothermal conditions¹⁶; and the energy, $-\Delta U_B/M$ of the isothermal bomb process for reaction IX



The change in energy of the combustion reaction under bomb conditions, $-\Delta U_B/M$, is calculated from the data according to eq. X in which the ignition energy, q_{ign} , was always 1.28 cal.

$$-\Delta U_B/M = [C_{eff.}(\text{calor.})\Delta T'_c + C - q_{ign} - q_{oil} - q_{fuse} - q_{hyd} - q_{Pt} - q_{HNO_3}]/m' \quad (X)$$

The results of the combustion experiments are expressed in terms of the defined calorie (4.1840 abs. joules) and refer to the isothermal process at 25° and to true mass. For reduction of weights to vacuum, the density values given in Table I were used. The molecular weights were computed from the 1951 International Atomic Weights.¹⁷

All combustion experiments with chlorobenzene, *o*-chloroethylbenzene and *o*-dichlorobenzene were satisfactory. In two combustions of *p*-chloroethylbenzene, A2 and A5, violent shattering of the ampoule occurred, and carbon deposits indicative of splattering were observed. Another combustion of this compound, A1, was rejected because of calorimetric uncertainties. The first experiment, A1, on *m*-dichlorobenzene yielded a value for $-\Delta U_B/M$ of 4828.6 cal. g.⁻¹. This unexplained high result was also rejected. Two experiments on *p*-dichlorobenzene, A2 and A4, have been omitted from the tables because of calorimetric uncertainties.

In Table II the derived data are given. To obtain ΔU_R from ΔU_B the Washburn¹⁸ corrections were not made rigorously for lack of necessary data, but they were approximated by assuming that the values for the solubility and heat of solution of the bomb gases in the bomb solutions are the same as in water. To calculate the heats of formation of the compound, the heats of formation of CO₂(g) and H₂O(l) were taken to be $\Delta H_f^\circ = -94.0518$ ^{19a} and -68.3174 ^{19b} kcal. mole⁻¹, respectively, and the following values were taken for the heat of formation

(16) $C = C_{eff.}^i(\text{cont.})(25 - t_i) + C_{eff.}^f(\text{cont.})[\Delta t_c - (25 - t_f)]$ in which $C_{eff.}^i(\text{cont.})$ and $C_{eff.}^f(\text{cont.})$ are the energy equivalents of the initial and final contents of the bomb and t_i is the temperature of the calorimeter at the beginning of the reaction period. In computing *C* the following values were taken for the energy equivalent of the initial and final bomb solutions: chlorobenzene combustions, 0.98 and 0.94 cal. g.⁻¹; *o*- and *p*-chloroethylbenzene combustions, 0.98 and 0.96 cal. g.⁻¹; *o*-, *m*- and *p*-dichlorobenzene combustions, 0.97 and 0.90 cal. g.⁻¹. The heat capacity of the glass cloth lining was taken as 0.172 cal. g.⁻¹ deg.⁻¹.

(17) E. Wichers, *J. Am. Chem. Soc.*, **74**, 2447 (1952).

(18) E. W. Washburn, *Bur. Standards J. Research*, **10**, 525 (1933).

(19) (a) E. J. Prosen, R. S. Jessup and F. D. Rossini, *J. Research Natl. Bur. Standards*, **33**, 447 (1944); and (b) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *ibid.*, **34**, 143 (1945).

(15) (a) From F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936; and (b) F. D. Rossini and E. J. Prosen, *J. Research Natl. Bur. Standards*, **33**, 264 (1944).

of $\text{HCl} \cdot n\text{H}_2\text{O}$ from hydrogen, chlorine and water: for $n = 74$, -39.55 kcal. mole $^{-1}$; for $n = 105$, -39.61 kcal. mole $^{-1}$; for $n = 35.5$, -39.35 kcal. mole $^{-1}$; and for $n = 38.5$, -39.38 kcal. mole $^{-1}$. The uncertainties given cannot be taken as a strict measure of the accuracy of the measurements because there is no way of evaluating some of the other uncertainties connected with the method which are discussed later.

Table III gives a comparison of the data obtained

TABLE I
RESULTS OF COMBUSTION EXPERIMENTS

Series and no.	m' , g.	ΔT_c , °C.	q_{oil} , cal.	q_{fuse} , cal.	q_{hyd} , cal. eq. V	q_{VI} , cal. eq. VI	q_{Pt} , cal.	q_{HNO_3} , cal.	C , cal.	$-\Delta U_B/M$, cal. g. $^{-1}$
Chlorobenzene, $\text{C}_6\text{H}_5\text{Cl}$ (l); mol. wt. = 112.557, density = 1.106, n in eq. IX = 74										
A1	0.89177	1.99820	497.03	16.05	56.2	11.2	1.98	0.29	27.6	6604.3
A2	.86778	1.99809	656.17	17.11	57.7	7.2	2.08	.29	27.6	6604.4
A3	.86014	1.99260	694.27	16.72	54.7	3.8	2.21	.29	27.6	6606.0
A4	.86466	2.00095	688.33	18.56	55.6	5.3	2.01	.19	27.6	6604.9
A5	.86094	2.00035	717.02	17.23	57.5	3.2	2.28	.25	27.6	6599.5
A6	.86239	2.00183	705.82	16.52	60.0	5.9	1.98	.29	27.6	6602.1
B1	.85033	2.00280	784.04	16.40	59.6	6.6	1.98	.31	27.5	6608.7
B2	.85936	2.01033	746.16	19.39	60.0	7.9	1.78	.51	27.5	6606.2
B3	.86044	1.99855	709.18	17.11	57.3	7.1	1.57	.20	27.5	6603.9
B4	.86691	1.99952	663.14	17.03	66.9	4.8	1.6	.6	27.6	6601.3
B5	.86108	2.00040	704.50	19.19	63.9	5.8	0.8	.5	27.8	6602.3
B6	.84526	2.02298	892.74	15.23	57.1	4.4	1.7	.6	28.2	6603.1
B7	.86134	2.00570	706.61	17.74	71.1	9.4	0.9	.5	28.5	6607.6

Av. 6604.2 \pm 0.7 a

10 ml. of 0.5 N $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ used in bomb Pt 1; Cl^- recovery b = 100.0%; $C_{\text{eff.}}$ (calor.) = 3225.8 $_5$ cal. deg. $^{-1}$ (A series), 3226.6 (B1-B3), 3226.0 (B4-B7).

α -Chloroethylbenzene, $\text{C}_8\text{H}_7\text{Cl}$ (l); mol. wt. = 140.609, density = 1.055, n in eq. IX = 105										
A1	0.75384	1.99533	755.42	15.97	41.2	7.3	0.7	0.5	27.7	7484.7
A2	.76592	2.00141	677.04	16.01	45.6	8.4	.4	.6	28.1	7488.0
A3	.76658	1.99958	673.03	17.31	38.3	7.5	.7	.3	27.7	7487.7
A4	.77573	2.00069	596.87	19.31	46.2	9.5	2.3	.5	28.1	7484.9
A5	.78093	1.99753	559.29	18.37	37.5	7.1	0.5	.4	27.7	7487.6
A6	.78150	1.99967	559.17	18.96	40.4	8.4	.3	.7	28.1	7485.3
A7	.72674	1.99989	968.58	15.38	46.3	9.0	.9	.5	28.5	7483.0
A8	.73035	1.99934	945.34	15.82	40.8	7.6	.6	.4	27.9	7484.1

Av. 7485.7 \pm 0.6 a

10 ml. of 0.5 N $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ used in bomb Pt 1; Cl^- recovery b = 100.0%; $C_{\text{eff.}}$ (calor.) = 3226.0 cal. deg. $^{-1}$

p -Chloroethylbenzene, $\text{C}_8\text{H}_7\text{Cl}$ (l); mol. wt. = 140.609, density = 1.050, n in eq. IX = 105										
A3	0.76114	1.99812	711.39	18.33	36.2	5.2	0.8	0.4	27.7	7488.9
A4	.76532	2.00339	698.61	15.70	33.9	7.9	0.5	.5	28.0	7490.2
A6	.78401	2.00036	546.94	14.44	39.2	6.2	1.3	.4	27.7	7488.6
A7	.78556	2.00151	533.82	19.98	38.7	6.4	1.8	.4	28.0	7488.4
A8	.78737	2.00182	521.59	17.03	39.8	7.5	0.6	.6	27.7	7489.6
A9	.79355	2.00621	473.34	16.92	53.8	10.4	1.1	.5	28.4	7489.3
A10	.79886	1.99278	412.85	16.76	37.6	5.2	0.9	.4	27.9	7487.7

Av. 7489.0 \pm 0.7 a

10 ml. of 0.5 N $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ used in bomb Pt 1; Cl^- recovery b = 100.3%; $C_{\text{eff.}}$ (calor.) = 3226.0 cal. deg. $^{-1}$

o -Dichlorobenzene, $\text{C}_6\text{H}_4\text{Cl}_2$ (l); mol. wt. = 147.006, density = 1.304, n in eq. IX = 35.5										
B1	1.09935	1.90386	629.21	19.39	177.3	16.6	0.3	0.3	26.7	4815.1
B2	1.11768	2.02720	936.33	18.25	175.2	19.9	.3	.4	28.4	4816.9
B3	1.27847	2.01560	91.77	19.31	213.2	17.9	.3	.3	28.2	4813.6
B4	1.26295	2.00437	132.93	19.70	208.6	17.4	.7	.4	28.0	4814.8
B5	1.22603	2.02529	400.66	15.35	192.6	15.6	.6	.3	28.3	4814.6
B6	1.22976	2.00798	323.30	18.68	196.3	12.2	.6	.4	28.1	4814.5
D1	1.22494	2.01495	354.32	19.19	207.6	16.4	.5	.4	28.1	4813.1
D2	1.28900	2.03161	103.77	16.99	207.4	14.4	.5	.4	28.3	4813.4
D3	1.19066	1.99472	473.28	16.95	189.8	13.8	.5	.2	27.7	4816.2
D4	1.20329	2.00567	435.54	17.50	199.6	16.4	.3	.4	27.9	4815.5

Av. 4814.8 \pm 0.3 a

10 ml. of 1.0 N $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ used in bomb Ta 1; Cl^- recovery b = 99.6 and 100.0%; $C_{\text{eff.}}$ (calor.) = 3209.9 (B series), 3209.7 (D series) cal. deg. $^{-1}$

TABLE I (Continued)

Series and no.	m' , g.	ΔT_c , °C.	q_{oil} , cal.	q_{fuse} , cal.	q_{hyd} , cal. eq. V	q_{VI} , cal. eq. VI	q_{Pt} , cal.	q_{HNO_3} , cal.	C , cal.	$-\Delta U_B/M$, cal. g. ⁻¹
<i>m</i> -Dichlorobenzene, C ₆ H ₄ Cl ₂ (l); mol. wt. = 147.006, density = 1.288, n in eq. IX = 35.5										
A2	1.13544	2.00546	789.76	20.05	175.6	16.1	0.4	0.2	28.1	4810.5
A3	1.13393	1.96643	772.04	16.68	171.1	20.6	.3	.3	27.9	4809.7
A4	1.13621	2.00467	769.29	18.48	181.5	24.8	.5	.3	28.1	4811.3
A5	1.09657	1.98914	938.09	17.94	168.7	14.4	.5	.4	27.9	4807.3
A6	1.07840	2.00670	1054.51	16.92	186.1	21.7	.4	.3	28.1	4811.0
A7	1.07865	1.99294	1032.29	18.56	160.8	22.2	.3	.3	27.9	4810.8
										Av. 4810.1 ± 0.6 ₁ ^a

10 ml. of 1.0 N N₂H₄·2HCl used in bomb Ta 1; Cl⁻ recovery^b = 99.7%; C_{eff.}(calor.) = 3209.9 cal. deg.⁻¹

<i>p</i> -Dichlorobenzene, C ₆ H ₄ Cl ₂ (s); mol. wt. = 147.006, density = 1.458, n in eq. IX = 38.5										
A1	0.99246	2.00415	1585.68	15.93	136.1	10.4	3.8	0.3	27.1	4775.0
A3	1.08376	2.00395	1131.91	17.03	150.8	8.4	4.8	.3	27.1	4777.1
A5	1.11346	2.00370	986.70	16.88	156.6	7.0	6.0	.3	27.1	4774.5
A6	1.11540	2.00707	977.80	17.74	161.6	9.9	3.9	.3	27.4	4778.3
A7	1.12262	2.00450	940.11	17.03	160.4	10.8	1.9	.5	27.1	4775.9
A8	1.13713	2.02353	905.53	17.54	182.8	15.2	4.9	.5	27.7	4773.2
A9	1.09584	2.01328	1064.64	16.17	183.3	18.4	4.8	.6	28.1	4776.0
										Av. 4775.7 ± 0.6 ₄ ^a

10 ml. of 1.0 N N₂H₄·2HCl used in bomb Pt 1; Cl⁻ recovery^b = 99.6 and 99.8%; C_{eff.}(calor.) = 3226.0 cal. deg.⁻¹

^a Standard deviation of the mean, $\sqrt{\sum \Delta^2/n(n-1)}$ in which Δ is the deviation of each observation from the mean and n is the number of observations. ^b The quantity of chloride ion found (by precipitation as AgCl) in the bomb solution after a combustion experiment, expressed as per cent. of that calculated from the mass and composition of the sample and the volume and concentration of the reducing solution.

TABLE II

DERIVED DATA AT 25°, KCAL. MOLE⁻¹

Substance	ΔU_B^a	ΔU_R^b	ΔH_R^c	ΔH_f^d
Chlorobenzene (l) 74 ^e	- 743.3 ₅	- 742.4 ₅	- 743.0 ₄	+ 2.5 ₆ ± 0.1 ₃ ^f
<i>o</i> -Chloroethylbenzene (l) 105	-1052.5 ₆	-1051.2 ₁	-1052.4 ₀	-12.8 ₉ ± .3 ₀
<i>p</i> -Chloroethylbenzene (l) 105	-1053.0 ₂	-1051.7 ₇	-1052.9 ₆	-12.3 ₃ ± .3 ₁
<i>o</i> -Dichlorobenzene (l) 35.5	- 707.8 ₀	- 706.8 ₃	- 707.1 ₃	- 4.2 ₀ ± .1 ₇
<i>m</i> -Dichlorobenzene (l) 35.5	- 707.1 ₁	- 706.1 ₄	- 706.4 ₄	- 4.8 ₉ ± .2 ₃
<i>p</i> -Dichlorobenzene (s) 38.5	- 702.0 ₆	- 700.9 ₇	- 701.2 ₇	-10.1 ₂ ± .2 ₆

^a $\Delta U_B = \Delta U_{B/M} \times M$. ^b ΔU_R = the energy change of the idealized combustion reaction IX in which the reactants and products are in their appropriate standard states. ^c ΔH_R = the enthalpy change for reaction IX. ^d ΔH_f = the heat of formation of the compound in the state indicated (l, liquid; s, solid) from graphite and gaseous hydrogen and chlorine in their respective standard states. ^e n in eq. IX. ^f The uncertainty given is equal to twice the final "over-all" standard deviation [see F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, 29, 416 (1939)].

TABLE III

COMPARISON OF DATA OBTAINED BY VARIOUS INVESTIGATORS

Compound	$-\Delta U_R/M$ for Reaction IX at 20°, $n = 600$			
	Chlorobenzene	<i>o</i> -Dichlorobenzene	<i>m</i> -Dichlorobenzene	<i>p</i> -Dichlorobenzene
Investigators and method				
This investigation				
N ₂ H ₄ ·2HCl, glass ampoule static bomb	6599.1 ± 1	4815.9 ± 1	4811.2 ± 1	4775.4 ± 1
Karlsson ^{5c,21}				
As ₂ O ₃ , glass ampoule static bomb	6601.3 ± 3			
Karlsson ^{5c,21}				
As ₂ O ₃ , cellophane static bomb		4808.5 ± 2	4800.1 ± 2	4777.6 ± 1
Bjellerup ²¹				
As ₂ O ₃ , glass ampoule static bomb		4814.1 ± 3.5		
As ₂ O ₃ , glass ampoule moving bomb		4817.3 ± 2.9		
Smith, Sunner ^{20a}				
As ₂ O ₃ , cellophane shaking bomb				4774.6 ± 6
As ₂ O ₃ , cellophane rotating bomb				4776.6
Data of historical interest only				
Thomsen ^{20d}	6751			
Kablukov and Perelman ^{20e}	6535			
Berthelot ^{20f}		4591		
Berthelot ³		4624		

by various investigators^{2,20,21} for chlorobenzene and the dichlorobenzenes. There are no previous data for the chloroethylbenzenes. The column headed "Investigators and Method," gives the following information: the investigators; the reductant used, in all cases As_2O_3 solution except in this investigation in which $N_2H_4 \cdot 2HCl$ was used; the method used for confining the sample, *i.e.*, whether a glass ampoule or a cellophane disk over the crucible was used; and the type of calorimetric system used. The data have all been reduced as far as possible to a common basis for comparison purposes. The values for $-\Delta U_R/M$ refer to reaction IX in which $n = 600$ and the reaction temperature is 20° . As recommended in ref. 21, two corrections have been applied to the data of Karlsson given therein: (a) the revised correction for dissolved noble metals and (b) the estimated Washburn correction of $+0.4 \text{ cal. g.}^{-1}$.

Because of the uncertainties of the Washburn corrections applied and in the purities of the samples used in the various investigations, a precise comparison of the experimental data is not possible. Nevertheless, two general conclusions may be drawn. First, it is apparent that the use of a cellophane-covered crucible to contain a combustion sample resulted in heat of combustion values significantly lower than those obtained when glass ampoules were used. An exception to this was the case of the solid compound, *p*-dichlorobenzene. Second, the results obtained by the quartz-spiral (with glass ampoules), glass-cloth and moving-bomb methods generally agree within the precision uncertainty of the experimental data. Unfortunately, a comparison of all methods is afforded only by the results tabulated for *o*-dichlorobenzene. The data for this compound are in agreement, with the exception of the datum obtained by the quartz-spiral method, with a cellophane-covered crucible and the data of Berthelot.

Discussion of the Method

The problem of determining the heats of combustion of chlorine-containing compounds is that of devising equipment and techniques that will leave a final state in the bomb that is capable of being defined thermodynamically and interpreted thermochemically. The choice of reductant and its mode of support, the chemical examination and identification of the products of the reaction (including corrosion products), and the need for the equilibration of products in a reasonable length of time are all factors to be considered. A discussion of some of these factors follows. It is shown that experiments have been performed to indicate the magnitude of the thermal effects produced by known uncertainties.

Choice of Reductant.—The possibility was considered of reducing free chlorine by a gas phase

(20) (a) Karlsson's²⁰ original data recently have been revised by Smith, *et al.*²¹ The revised data were used here; (b) Bjellerup's measurements were reported in ref. 21; (c) L. Smith and S. Sunner, "The Svedberg Mem. Vol.," Almqvist and Wiksells Boktryckeri, Uppsala, Sweden, 1944, p. 352; (d) J. Thomsen, *Z. physik. Chem.*, **52**, 343 (1905); (e) I. A. Kablukov and F. M. Perelman, *Compt. rend. acad. sci. U.S.S.R.*, **1930A**, 519; and (f) M. P. E. Berthelot, *Ann. chim. phys.*, [6] **28**, 131 (1893).

(21) L. Smith, L. Bjellerup, S. Krook and H. Westermark, *Acta Chem. Scand.*, **7**, 65 (1953).

reaction which would eliminate the question of homogeneity of the reaction products or the necessity of a quartz-wool lining or moving bomb. Experiments to test this possibility included (a) the injection of known amounts of carbon monoxide into the bomb before charging, and (b) the volatilization of pure formic acid during the combustion process. Neither method was successful, and a liquid reductant was used in all later experiments.

Before the choice of the liquid reductant was made, the effects on accuracy caused by the presence of relatively large amounts of solution on the glass cloth in the bomb were studied. This study²² led to the conclusion that the volume of solution should be held to a minimum. Hence, a search was made for a reductant that would be more soluble than As_2O_3 . The Commission of Thermochemistry^{23a} and Roth^{23b,c} have suggested an aqueous solution of hydrazine monohydrochloride as a possible reductant and the latter^{23d} has pointed out that hydrazine dihydrochloride might have suitable properties. Because of the comparative ease of analysis, hydrazine was selected for study, but since hydrochloric acid reacts with the monohydrochloride, hydrazine dihydrochloride was investigated for use as a reductant.

Stability of Reductant.—The stability of hydrazine dihydrochloride was tested by placing a known amount of the solution in a bomb and charging with oxygen to 30 atmospheres pressure. After 24 hours, titration of the hydrazine dihydrochloride indicated oxidation or decomposition of borderline significance. Additional evidence was gained by the combustion of benzoic acid in the bomb in which hydrazine dihydrochloride solution was present on the glass filter cloth lining. The value so obtained for the heat of combustion of benzoic acid was in good agreement with a datum obtained later, in a rotating bomb experiment, in which 10 ml. of water and no glass cloth had been added (see ref. 2) This fact suggests that little oxidation of hydrazine occurred in the initial and final periods.²⁴

(22) The calorimeter was calibrated by the combustion of benzoic acid in the bomb to which 0.1 ml. of water had been added but without filter cloth lining. Then several series of measurements were made of the heat of combustion of benzoic acid with varying amounts of water added initially to the glass cloth in the bomb. The experimental values of $-\Delta U_B/M$ for benzoic acid so obtained were compared with those calculated for the respective conditions from $-\Delta U_R$ by Washburn's method.¹⁸ When 10 ml. of water was added to the bomb, the agreement between the observed and calculated values was within 0.01%. When 20 ml. was added, the observed value was 0.02% lower than computed. Additions of larger amounts of water increased the discrepancy. This might be attributed to incomplete solution of the carbon dioxide.

The amount of water added to the bomb also affected the length of the reaction period. Although the addition of as much as 10 ml. of water did not increase the length of reaction period greatly, the addition of 20 ml. and 50 ml. increased the duration of the reaction period by factors of 1.5 and 2.0, respectively.

(23) (a) Union Internationale de Chimie, Commission Permanente de Thermochemie, "Appendices au Premier Rapport de la Commission," Paris, 1936; (b) W. A. Roth, *Z. Elektrochem.*, **43**, 355 (1937); (c) W. A. Roth, *ibid.*, **45**, 335 (1939); and (d) W. A. Roth, *ibid.*, **50**, 111 (1944).

(24) It should be noted that some of the hydrazine was oxidized during the reaction period. However, oxidation of the reductant during the combustion period causes no error since the chemical analysis and subsequent thermochemical treatment of results takes this into account but oxidation during any other portion of the combustion experiment will result in absolute errors.

As substitutes for the quartz fibers used at the University of Lund, two types of glass cloth were tried in this Laboratory. One was ordinary coarse glass filter cloth (Filter Cloth Type CSS-40, Owens-Corning Fiberglas Corp.), and the other was a special high-silica cloth (Fiberglas High Temperature Cloth). The ordinary glass filter cloth was more satisfactory and was used for all combustion experiments reported here for organic chlorine compounds. The high-silica cloth was unsatisfactory calorimetrically as shown by the following experiment. This cloth, which had been leached with hot hydrochloric acid to bring its SiO_2 content to 99.6% and refired to reduce its porosity, was used in a series of combustion experiments with benzoic acid in which 10 ml. of water was added to the cloth. The average value of the heat of combustion so obtained was 0.05% higher than that calculated for these conditions. An analysis of the initial and final rating periods pointed to a small constant rate of liberation of heat.

Inertness of Glass Cloth.—When the glass cloth is used in the bomb during benzoic acid combustion, the amount of nitric acid formed is less than when no cloth or when quartz cloth is used. Nitrate ion was determined by Devarda's method after two of the combustions, in addition to the usual titration of the acid. The results show 0.058 meq. of nitrate ion and only 0.022 meq. of acid. This fact suggested that when benzoic acid undergoes combustion in the bomb to which glass cloth is added, a reaction occurs between the nitric acid produced and the glass cloth. The error caused by this reaction is probably about 0.5 cal. per combustion. To test whether the presence of hydrazine dihydrochloride or hydrochloric acid on the glass cloth might introduce similar errors, several series of experiments were carried out in which hydrazine dihydrochloride or hydrochloric acid were added to the glass cloth for benzoic acid combustions. The concentrations of the solutions added corresponded to the maximum values that might be present in actual combustions. The results of these investigations yielded in each case a heat of combustion of benzoic acid within 0.01% of a datum obtained later in a rotating bomb to which 10 ml. of water and no glass cloth were added. It seems that the pres-

ence of hydrazine dihydrochloride or hydrochloric acid on the glass cloth has no more thermal effect than the addition of 10 ml. of water alone to the bomb.

Homogeneity.—In combustions of chlorine compounds, inhomogeneity of the combustion products in the final state is a less serious problem than in certain other cases (such as combustions of sulfur compounds) because of the small heat of dilution effect. The practice in this Laboratory of avoiding a pool (see footnote 25) of reductant solution on the bottom of the bomb minimizes inhomogeneity errors.

Equilibrium.—When it is necessary to add an unusually large amount of liquid to a bomb, it is important to know whether or not equilibrium is established with respect to the solution of the combustion gases in the liquid phase.²⁵ Several series of combustions of benzoic acid were carried out using 10 ml. of water. In every series the heat of combustion obtained agreed within the uncertainty of the experiments with the value calculated for these conditions by use of the Washburn equations. This agreement is undoubtedly fortuitous and contains cancelling errors. Nevertheless, it appears that the thermal effect of non-equilibrium of gaseous carbon dioxide with respect to the aqueous solution is not large.

Conclusions.—Some of the uncertainties connected with the glass-cloth method have not been resolved. Nevertheless, the method has been shown to give results of good precision, and it will be satisfactory when accuracy requirements are moderate. It has the advantage that combustion equipment of conventional design can be utilized with only slight modifications.

(25) Roth has informed Jessup [see *J. Research Natl. Bur. Standards*, **29**, 247 (1942)] that when 10 g. of water was added to a static bomb instead of 1 g., the difference in heat of combustion of benzoic acid was 0.064% instead of the 0.10% calculated from the Washburn equations. This discrepancy was attributed to the lack of equilibrium between the gaseous carbon dioxide and the aqueous solution. Also Sunner (see S. Sunner, Thesis, University of Lund, Carl Bloms Boktryckeri, Lund, Sweden, 1949) has shown that the solution of carbon dioxide in 10 ml. of unstirred water, was only 56% complete after 10 minutes under the conditions of his experiment. For these and other reasons the amount of glass cloth used, in this Laboratory, has been made great enough to support all of the reducing solution, i.e., drainage of liquid to the bottom of the bomb was circumvented.

ALKALI CARBONATES OF Np(V), Pu(V) AND Am(V)¹

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The existence of the XO_2^+ ion in crystalline, double alkali carbonates containing Np(V), Pu(V) and Am(V) is established. X-Ray work by F. H. Ellinger and W. H. Zachariassen (reported in detail in the following paper) shows that the RbAm(V), $NH_4Am(V)$, $NH_4Pu(V)$ and $KPu(V)$ (low pH) compounds were hexagonal and had the typical composition: $XAmO_2CO_3$. A phase study of the three-component system $Rb_2CO_3-H_2O-(AmO_2)_2CO_3$ confirmed the existence of the compound $Rb-AmO_2CO_3$. Carbonate compounds containing Np(V), Pu(V) and Am(V) were precipitated from aqueous solutions of sodium, potassium, rubidium or ammonium carbonates. Three crystal phases resulted—hexagonal, orthorhombic and monoclinic—depending upon the radius of the alkali cation and the pH at which the compound was precipitated. These compounds are stable only in contact with carbonate solutions, and undergo alteration when washed with water.

The existence of the pentavalent state has been established for uranium, neptunium, plutonium and americium. The formula of the aqueous (V) ion has been the subject of considerable discussion but has not been completely characterized.

The aqueous U(V) state is the least stable; however, Kraus and co-workers^{2,3} measured its hydrolysis and made predictions concerning its pH stability range. The aqueous pentavalent states of the series are unstable with respect to disproportionation into the (VI) oxidation state and a lower valence state, either (IV) or (III).²⁻⁶ The (VI) states of the series are reduced reversibly to the corresponding (V) state at an electrode.²⁻⁹ Both Np(V) and Am(V) in aqueous perchloric acid have similar infrared absorption peaks of roughly similar shape but are broader and appear at lower energies than the NpO_2^{++} and AmO_2^{++} absorption peaks.¹⁰

Contrary to the behavior of U(V) and Pu(V), both Np(V) and Am(V) are stable over considerable pH ranges.¹¹ For example, Pu(V) disproportionates in both low or high $[H^+]$.¹² However, there have been very few solid compounds prepared containing these states. The principal ones of Np(V) are the hydroxide and the oxalate.¹³

Pentavalent americium was discovered by Werner and Perlman, who oxidized Am(III) in potassium

carbonate solution with sodium hypochlorite to an insoluble compound of unknown composition.¹⁴ Since this Am(V) compound was apparently crystalline, it was decided to determine its composition, *i.e.*, whether it was a salt of the hydroxide such as $KOAmO_2$, or double carbonate, etc. Furthermore, it was of interest to see whether analogous compounds containing Np(V) and Pu(V) could be prepared. Of additional importance would be to show the existence of the ion XO_2^+ in the solid, for determination of its dimensions and linearity by X-ray investigation.

Experimental

Americium(V) Compounds.—The method of Werner and Perlman¹⁴ using potassium carbonate as the solvent for $Am(OH)_3$ and sodium hypochlorite as the oxidant was modified so that there was only a single alkali cation present. Thus, a solution of Am(III) in potassium carbonate was warmed to $\sim 80^\circ$ with potassium hypochlorite, and a solution of Am(III) in sodium carbonate was treated similarly with sodium hypochlorite.

The potassium salt containing Am(V) crystallizes as orthorhombic bisphenoids which are optically biaxial negative with a small optic angle and have refractive indices $\alpha = 1.593 \pm 0.002$, β and $\gamma = 1.596 \pm 0.002$. Washing the product with water resulted in the formation of isotropic alteration rims which had a much higher index of refraction. Eventually whole crystals were altered to this isotropic substance and usually disintegrated. Crystals which were left for some time on the slide in air-dry condition and in ordinary atmosphere gradually altered to a compound which gave the absorption spectrum of trivalent americium and had an index of refraction lower than those of the original crystals. In this case, the external shape of the crystals was well preserved, the alteration being apparent, however, from the irregular, mottled extinction in polarized light.

The sodium salt containing Am(V) crystallizes as six-sided plates which are optically negative with optic angle sensibly zero (later X-ray work indicates the structure is probably monoclinic). The refractive indices are between 1.58 and 1.60. Closer determination of indices was not feasible because of the fine size and unstable nature of the crystals. As in the case of the potassium salt, washing with water resulted in a rise of the apparent index of refraction.

Since the potassium and sodium compounds are crystallographically distinct, well defined species, it was considered highly probable that the Am(V) compounds contain alkali metal ions as an essential constituent; this work alone, however, did not answer the question concerning the carbonate content.

It was later found that the compounds could be washed without alteration using 0.1 M carbonate. Subsequently, additional americium(V) compounds were made from ammonium carbonate and rubidium carbonate using either peroxydisulfate or ozone¹⁵ as the oxidant, resulting in predominantly a hexagonal phase.

Since the Am(V) rubidium carbonate compound cannot

(1) Presented in part by J. P. Nigon at the March, 1953, meeting of the American Chemical Society. This work was sponsored by the AEC.

(2) K. A. Kraus and F. Nelson, *J. Am. Chem. Soc.*, **71**, 2517 (1949).

(3) K. A. Kraus, F. Nelson and G. L. Johnson, *ibid.*, **71**, 2510 (1949).

(4) L. H. Gevantman and K. A. Kraus, "The Chemistry of Plutonium (V). Stability and Spectrophotometry," NNES, IV, 14B, *Transuranium Elements, Part I*, p. 500, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(5) L. B. Asprey, S. E. Stephanou and R. A. Penneman, *J. Am. Chem. Soc.*, **73**, 5715 (1951).

(6) R. Sjoblom and J. C. Hindman, *ibid.*, **73**, 1744 (1951).

(7) L. B. Magnusson, J. C. Hindman and T. J. LaChapelle, "Chemistry of Neptunium(V). Formal Oxidation Potentials of Neptunium Couples," NNES, IV, 14B, *Transuranium Elements*, 1059 (Part II).

(8) W. E. Harris and I. M. Kolthoff, *J. Am. Chem. Soc.*, **67**, 1484 (1945).

(9) R. A. Penneman and L. B. Asprey, "The Formal Potential of the Am(V)-Am(VI) Couple," AECU-936.

(10) L. H. Jones and R. A. Penneman, *J. Chem. Phys.*, **21**, 542 (1953).

(11) J. C. Hindman, L. B. Magnusson and T. J. LaChapelle, *J. Am. Chem. Soc.*, **71**, 687 (1949).

(12) K. A. Kraus, "Oxidation-Reduction Potentials of Plutonium Couples as a Function of pH," "Transuranium Elements," Part I, NNES, IV, 14B, p. 241, McGraw-Hill Book Co., New York, N. Y., 1949.

(13) G. Gibson, D. M. Gruen and J. J. Katz, *J. Am. Chem. Soc.*, **74**, 2103 (1952).

(14) L. B. Werner and I. Perlman, *ibid.*, **73**, 495 (1951).

(15) T. K. Keenan and S. E. Stephanou, unpublished work, referred to in reference 10.

be washed with water to remove excess reagent (but is a pure phase by X-ray), it is necessary to determine the composition of the compound using the residue method of Schreinemakers,¹⁶ by analyzing the wet slurry and clear liquid phase in the three-component system $\text{Rb}_2\text{CO}_3\text{--}(\text{AmO}_2)_2\text{CO}_3\text{--H}_2\text{O}$. Very dilute solutions of americium(III) in 1 *M* rubidium carbonate solution were oxidized to Am(V) with ozone. The resulting precipitate was centrifuged and then slurried with $\frac{1}{10}$ *M* Rb_2CO_3 . Weighed samples of the supernatant liquid and precipitate slurry were removed for analysis. Americium was determined radiometrically to $\pm 1\%$, and CO_2 was determined by evolution into $\text{Ba}(\text{OH})_2$ according to the method of Schroeder and Partridge.¹⁷ For CO_2 analysis, a closed system was used, with a peristaltic pump to circulate the gas and ensure complete absorption of CO_2 .

Plutonium(V) Compounds.—The Pu(V) compounds were made from ammonium, sodium and potassium carbonate solutions. The three crystal phases were isomorphous with the corresponding Am(V) compounds. The Pu(V) compounds were prepared by oxidizing the Pu(IV) to Pu(VI) with hot, dilute nitric acid and reducing to Pu(V) with a stoichiometric amount of iodide according to the method of Kraus and Dam.¹⁸ The iodine was extracted with carbon tetrachloride, and solid alkali carbonate was added immediately to the Pu(V) solution until the pH was brought up to \sim pH 7 and the Pu(V) compound precipitated. Control of pH is important because the Pu(V) disproportionates below pH 2.⁴ Furthermore, using potassium carbonate at pH ca. 7, the hexagonal KPu(V) compound results, and at higher pH the orthorhombic form is obtained.

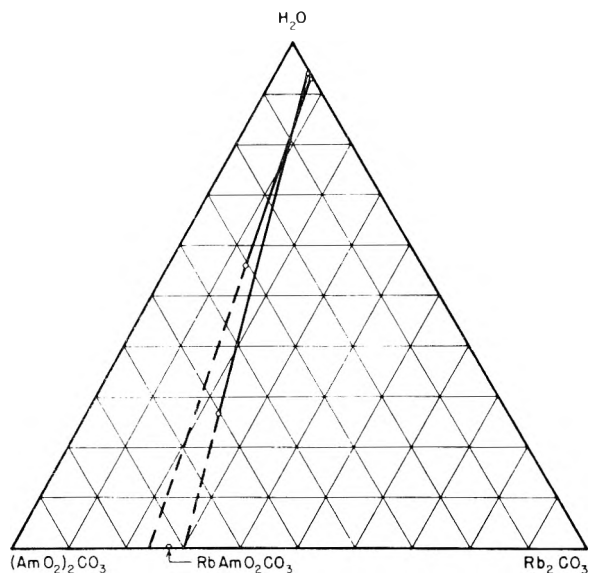


Fig. 1.—The system $(\text{AmO}_2)_2\text{CO}_3\text{--Rb}_2\text{CO}_3\text{--H}_2\text{O}$ at 25° : coordinates in weight per cent; dashed lines extrapolate the analyses of the clear liquid and wet solid by the Schreinemaker method to yield the composition of the anhydrous solid phase.

Neptunium(V) Compounds.—The orthorhombic neptunium(V) compound was made by addition of Np(V) perchlorate solution to potassium carbonate solution, centrifugation of the resulting precipitate and washing with 0.1 *M* carbonate solution. This compound is isomorphous with the orthorhombic KAm(V) and KPu(V) compounds.

Results and Discussion

Samples of each compound were submitted for

(16) S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, Fifth printing, p. 792.

(17) W. C. Schroeder and E. P. Partridge, *Ind. Eng. Chem., Anal. Ed.*, **4**, 262 (1932).

(18) K. A. Kraus and J. R. Dam, "Hydrolytic Behavior of Plutonium(V), The Transuranium Elements," NNES Volume 14B, 1949, p. 478.

X-ray examination as a slurry in a capillary tube. Samples containing < 50 micrograms of americium were necessary to avoid excessive blackening of the X-ray film from the X- and gamma-radiation accompanying americium alpha-emission. W. H. Zachariasen and F. H. Ellinger determined the X-ray constants and structure, reported by them in the following paper. Suffice it to say here that the predominant phase was hexagonal in the case of rubidium and ammonium; orthorhombic or hexagonal with potassium; and monoclinic with sodium. The Am(V) compound prepared from ammonium carbonate consisted of about 50% hexagonal phase, whereas the one from rubidium carbonate was more than 95% hexagonal phase. With the hexagonal phase, they were able to show two rubidium and two americium ions per unit cell and space for ten oxygens, yielding the tentative formula: $\text{RbAmO}_2\text{CO}_3$ or $[\text{Rb}_2(\text{AmO}_2)_2(\text{CO}_3)_2]$ as the content of the unit cell.

The composition $\text{RbAmO}_2\text{CO}_3$, as proposed for the hexagonal compounds by the X-ray work, was confirmed by use of Schreinemakers' method in the system $\text{Rb}_2\text{CO}_3\text{--}(\text{AmO}_2)_2\text{CO}_3\text{--H}_2\text{O}$. Results appear in Table I and are shown in Fig. 1. The extrapolated results for the anhydrous solid phase bracket the composition for the compound $\text{RbAmO}_2\text{CO}_3$, but would not rule out a hydrate. From unit cell volume and symmetry considerations, Ellinger and Zachariasen state the compound is anhydrous.

TABLE I

Grams/100 g. of clear supernatant soln.		Grams/100 g. of slurry	
$(\text{AmO}_2)_2\text{CO}_3$	Rb_2CO_3	$(\text{AmO}_2)_2\text{CO}_3$	Rb_2CO_3
0.376	6.73	30.12	13.84
0.0043	5.64	49.97	23.30

The results of Schreinemakers' method on the orthorhombic potassium-Am(V) compound were inconclusive, giving a range of compositions between $\text{K}_2\text{CO}_3(\text{AmO}_2)_2\text{CO}_3 \sim 1$ to ~ 2 . Consequently, it is not now possible to assign an unambiguous formula to the orthorhombic phase. Furthermore, Zachariasen and Ellinger find evidence of disorder in this phase, indicating possibly that a range of compositions is possible. No work was done with the monoclinic form.

Thus, only the chemical composition of the hexagonal form can be considered established, with the orthorhombic and monoclinic forms remaining unknown. The compounds of Np(V), Pu(V)¹⁹ and Am(V) which have been prepared are listed in Table II.

TABLE II

Hexagonal	Orthorhombic bisphenoids	Monoclinic
$\text{RbAmO}_2\text{CO}_3$	K--Am(V)--CO_3	Na--Am(V)--CO_3
$\text{NH}_4\text{AmO}_2\text{CO}_3$	K--Pu(V)--CO_3	Na--Pu(V)--CO_3
$\text{NH}_4\text{PuO}_2\text{CO}_3$	K--Np(V)--CO_3	
KPuO_2CO_3 (low pH form)		

(19) An uncharacterized compound of Pu(V) was prepared by I. B. Werner by reduction of Pu(VI) in K_2CO_3 solution with Na_2SO_3 (U. S. Patent Appl. 72 754).

THE CRYSTAL STRUCTURE OF $KPuO_2CO_3$, $NH_4PuO_2CO_3$ AND $RbAmO_2CO_3$ ¹

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X-Ray diffraction data and chemical information are used to identify the compounds $KPuO_2CO_3$, $NH_4PuO_2CO_3$ and $RbAmO_2CO_3$. These isostructural compounds are hexagonal with two stoichiometric molecules per unit cell. The unit cell dimensions are listed. The space group is $C6/mmc (D_{6h}^2)$, and the atomic positions are: 2 R in (0,0,0) (0,0,1/2), 2 X in $\pm (1/3, 2/3, 1/4)$, 2C in $\pm (2/3, 1/3, 1/4)$, 6 O_I in $\pm (x, 2x, 1/4)(2\bar{x}, \bar{x}, 1/4)(x, \bar{x}, 1/4)$, 4 O_{II} in $\pm (1/3, 2/3, 1/4 \pm z)$. For the potassium compound, the parameter values are taken to be $x = 0.812$, $z = 0.197$. The structure contains collinear radicals $[O-X-O]^+$ which with the carbonate groups form endless layers of average composition $(XO_2CO_3)^-$. The layers are held together by the alkali ions which lie halfway between layers. Each X atom forms six secondary bonds to carbonate oxygens in addition to the two short oxygen bonds within the radical $[XO_2]^+$. Each alkali ion is bonded to twelve oxygen atoms. The structure gives reasonable values for all interatomic distances.

The preceding article describes the preparation of a number of alkali carbonates of pentavalent neptunium, plutonium or americium. The results of X-ray diffraction studies of some of these carbonate precipitates are presented in the present paper. The preparations to be dealt with are the K-Pu(V) (at low pH), NH_4 -Pu(V) and Rb-Am(V) precipitates which form one isostructural series. In the case of the other preparations discussed in

TABLE II

X-RAY DIFFRACTION DATA FOR THE NH_4 -Pu COMPOUND.
Cu K α

Intensity obsd.	$\sin^2 \theta$ obsd.	$H_1H_2H_3$	$\sin^2 \theta$ calcd.
50	0.0230	002	0.0221
30	.0309	100	.0306
100	.0369	101	.0371
40	.0532	102	.0527
25	.0810	103	.0803
15	.0890	004	.0883
50	.0925	110	.0917
30	.1147	112	.1138
5	.1197	104	.1189
5	.1230	200	.1223
50	.1288	201	.1278
20	.1460	202	.1444
15	.1696	105	.1686
25	.1729	203	.1720
30	.1814	114	.1800
6	.1987	006	.1987
6	.2106	204	.2106
4	.2139	210	.2140
40	.2211	211	.2195
8	.2290	106	.2293
10	.2370	212	.2361
17	.2613	205	.2603
20	.2642	213	.2637
17	.2764	300	.2751
15	.2909	116	.2904
18	.2995	302	.2972
12	.3016	{ 214	.3023
		{ 107	.3011
10	.3220	206	.3210
25	.3512	215	.3520
17	.3650	304	.3634
17	.3671	220	.3669

TABLE I
X-RAY DIFFRACTION DATA FOR THE K-Pu COMPOUND.
Cu K α

Intensity obsd.	$\sin^2 \theta$ obsd.	$H_1H_2H_3$	$\sin^2 \theta$ calcd.
40	0.0244	002	0.0246
15	.0303	100	.0305
100	.0365	101	.0366
40	.0549	102	.0551
15	.0859	103	.0858
40	.0915	110	.0914
12	.0983	004	.0982
17	.1157	112	.1160
4	.1222	200	.1219
45	.1288	{ 201	.1280
		{ 104	.1287
20	.1467	202	.1465
18	.1781	203	.1772
8	.1853	105	.1840
22	.1901	114	.1896
35	.2205	{ 211	.2194
		{ 204	.2201
		{ 006	.2210
10	.2396	212	.2379
6	.2526	106	.2515
14	.2694	213	.2686
22	.2760	{ 300	.2743
		{ 205	.2754
10	.3000	302	.2989
10	.3127	{ 214	.3115
		{ 116	.3124
4	.3319	107	.3314
6	.3460	206	.3429
25	.3687	{ 220	.3657
		{ 215	.3668
12	.3741	304	.3725
14	.3925	{ 222	.3903
		{ 008	.3928
		{ 310	.3962

the preceding article, the X-ray work did not lead to reliable conclusions as to chemical formula and crystal structure.

Interpretation of the X-Ray Diffraction Data.—The X-ray work is based exclusively on the powder method, single crystals not being available. The diffraction data for the three compounds under consideration are given in Tables I–III. The observed diffraction lines correspond to a hexagonal unit cell, the dimensions for the three compounds being

	$a_1, \text{Å.}$	$a_2, \text{Å.}$
K-Pu	5.09 ± 0.01	9.83 ± 0.02
NH_4 -Pu	5.09 ± 0.01	10.39 ± 0.02
Rb-Am	5.12 ± 0.01	10.46 ± 0.04

(1) This work was sponsored by the AEC.
 (2) Consultant to Los Alamos Scientific Laboratory.

TABLE III
X-RAY DIFFRACTION DATA FOR THE Rb-Am COMPOUND.
Cu K α

Intensity obsd.	$\sin^2 \theta$ obsd.	$H_1H_2H_3$	$\sin^2 \theta$ calcd.
30	0.0216	002	0.0216
100	.0358	101	.0356
80	.0520	102	.0518
25	.0789	103	.0788
25	.0863	004	.0864
60	.0910	110	.0905
13	.1127	112	.1121
4	.1214	200	.1207
40	.1269	201	.1261
30	.1430	202	.1423
15	.1651	105	.1652
20	.1703	203	.1693
35	.1776	114	.1769
30	.2175	211	.2166
13	.2248	106	.2246
20	.2336	212	.2328
13	.2561	205	.2557
15	.2615	213	.2598
17	.2727	300	.2716
5	.2852	116	.2849
		302	.2932
9	.2948	107	.2948
		214	.2976
10	.3157	206	.3151
20	.3473	008	.3456
		215	.3462
20	.3594	304	.3580
20	.3641	220	.3621
5	.3771	108	.3758

It is of interest to point out that the K-Pu and NH₄-Pu compounds were observed during the war.³ At the time, they were believed to be double hydroxides of alkali and Pu(VI). On this basis, the interpretation of the X-ray data led to the incorrect formula RPuO₂(OH)₃. G. E. Moore and D. E. Koshland⁴ subsequently showed that the compounds in all probability were alkali hydroxides of Pu(V). This suggestion as to composition was, however, incompatible with the X-ray results. The unit cell dimensions for the plutonium compounds given above and the observations in Tables I and II are those obtained during the war.

In the ammonium compound, plutonium is by far the predominant scatterer, so that the main features of the intensity distribution must be ascribed to the plutonium configuration. It is seen from Table II that the structure factor is zero when $H_1 - H_2 = 3n$ and H_3 odd, large when $H_1 - H_2 = 3n$ and H_3 even, large when $H_1 - H_2 \neq 3n$ and H_3 odd, small when $H_1 - H_2 \neq 3n$ and H_3 even. Accordingly it is necessary to have two heavy atoms per unit cell and in positions 2 X in $\pm (1/3, 2/3, 1/4)$.

The marked increase in the a_3 period with the size of the alkali ion is proof that this ion is a constituent of the structure. Indeed, the effect of the alkali ions on the diffraction intensities is

(3) W. H. Zachariasen, Manhattan Project Reports CN-2610, Jan. 1945, and CN-2742, Feb. 1945.

(4) G. E. Moore and D. E. Koshland, Clinton Laboratories Report CL-P-404, Apr. 1945.

easily seen in Table IV, where observed intensities for the ammonium and rubidium compounds are compared. Elementary structure factor considerations show that the observed intensity variation with the alkali constituent requires two alkali atoms per unit cell and in positions 2 R in (0, 0, 0) (0, 0, 1/2). As described in the preceding article, chemical analysis showed that there is one carbonate group per heavy atom X. Accordingly, the unit cell contains two carbonate radicals.

TABLE IV
THE EFFECT OF ALKALI IONS ON DIFFRACTION INTENSITIES

$H_1H_2H_3$	NH ₄ -Pu	Rb-Am	$H_1H_2H_3$	NH ₄ -Pu	Rb-Am
100	30	Trace	104	5	0
101	100	100	110	50	60
102	40	80	112	30	13
103	25	25	114	30	35

The unit cell content so far deduced, namely, R₂X₂(CO₃)₂, does not account for the observed unit cell volume, nor are the valences balanced. Previous work on compounds of the heavy elements⁵ has shown that the unit cell volume, V , can be represented as the sum $\sum V_i$ of the volume requirements of the individual constituents. Since the heavy ion is so small as to fit into the interstices between the anions, its volume requirement is negligible. The experimental values for the volume requirements of other ions which come into consideration are

Ion	K ⁺	NH ₄ ⁺	Rb ⁺	O ⁻² , OH ⁻ , H ₂ O	CO ₃ ⁻²
$V_i, \text{Å}^3$	21	26	28	18	54

The unit cell volumes are 221 Å³ for the K-Pu compound, 233 Å³ for the NH₄-Pu compound, and 237 Å³ for the Rb-Am compound. The alkali and carbonate ions require a volume of 150, 160 and 164 Å³ for the three compounds, respectively, leaving 71-73 Å³ of the unit cell volume to be accounted for by oxygen and hydroxyl ions and water molecules. The residual volume shows that there are altogether four such constituents. Since the heavy atom is known to be present in the pentapositive state, balancing of valences requires eight anion charges for the additional atoms. Hence, the possibility of some of these four additional constituents being hydroxyl ions or water molecules must be ruled out, *i.e.*, the chemical formula of the compounds is of the form RXO₂CO₃ with two stoichiometric molecules per unit cell.

The chemical compositions having been established, the densities can be calculated, and the result is $\rho = 5.57$ for KPuO₂CO₃, $\rho = 4.99$ for NH₄PuO₂CO₃, and $\rho = 6.06$ for RbAmO₂CO₃. The incorrect formula suggested for the plutonium compounds during the war, RXO₂(OH)₃, corresponds to precisely the same volume as the correct formula, the volume requirement of three hydroxyl groups equaling that of one carbonate group.

Determination of the Structure.—The positions of the heavy atoms and of the alkali atoms have already been deduced from intensity considerations

(5) W. H. Zachariasen, *J. Am. Chem. Soc.*, **70**, 2147 (1948).

as being: 2 R in (0, 0, 0) (0, 0, $1/2$), 2 X in $\pm (1/3, 2/3, 1/4)$. Since there are only two carbonate groups in the unit cell, the carbon atoms must be situated on threefold axes, and the plane of the group must be normal to the threefold axis. However, no carbon atom can lie on the axis (0, 0, z), as then an impossibly small distance K-C \leq 2.46 Å. would result. Thus the positions of the carbon atoms must be $(1/3, 2/3, z_1)$ and $(2/3, 1/3, z_2)$. The observed strength of the reflection 004 in $\text{NH}_4\text{PuO}_2\text{CO}_3$, in spite of the small multiplicity factor, indicates that the structure factor contribution of the CO_3 -group adds to that of plutonium, *i.e.*, $z_1 \approx 3/4$ and $z_2 \approx 1/4$. There is reason to believe that the z -coordinates of the CO_3 -groups are exactly $1/4$ and $3/4$, since each oxygen atom then would be placed equidistantly from two alkali atoms. The positions of the carbon atoms may thus be taken as $\pm (1/3, 2/3, 3/4)$. The value of C-O = 1.28 Å. found in other crystals will be assumed, so that only the orientation of the CO_3 -group about the threefold axis remains undetermined. This orientation may be described by means of the angle ϕ between the C-O bond and the connection line C-X. It suffices to consider the range $0 \leq \phi \leq 30^\circ$. For $\phi = 0^\circ$ the impossibly small distance X-O = 1.66 Å. results, while the K-O bonds in KPuO_2CO_3 become unreasonably long, namely, 3.54 Å. If $\phi = 30^\circ$, X-O = 2.55 Å. and K-O = 2.97 Å., both distances being reasonable. Because of the symmetrical configuration of the cations about the carbon site, there is no apparent reason for ϕ to assume a value between 0 and 30° . With $\phi = 30^\circ$, the positions of the carbonate atoms become 6 O_I in $\pm (x, 2x, 1/4)$ ($2\bar{x}, \bar{x}, 1/4$) ($x, \bar{x}, 1/4$) with $x = 0.81$.

The atomic positions so far deduced correspond to the space group symmetry C 6/m m c, and it is therefore probable that the four remaining oxygen atoms, O_{II} , conform to this symmetry. The positions 4e of C 6/m m c cannot be used for these oxygen atoms, since there is not room for two alkali atoms and four oxygen atoms on the same axis. The only possibility is therefore 4 O_{II} in $\pm (1/3, 2/3, 1/4 \pm z)$. This configuration corresponds to the formation of collinear radicals $[\text{XO}_2]^+$ isostructural with the uranyl radical $[\text{UO}_2]^{+2}$. It is not feasible to determine the parameter z (and hence the size of the $[\text{XO}_2]^+$ group) with any degree of accuracy from the intensity data. The distance U-O in the $[\text{UO}_2]^{+2}$ group in MgUO_2O_2 was found to be 1.93 ± 0.03 Å.⁶ In going from a hexavalent to a pentavalent central atom, one may expect an increase in the X-O distance of 0.03 Å., *i.e.*, U-O = 1.96 Å. in $[\text{UO}_2]^+$. As a consequence of the 5f contraction, a decrease of about 0.01 Å. in the X-O distance may be anticipated every time the atomic number is increased by one unit.⁷ Thus one arrives at the following anticipated values

$[\text{XO}_2]^+$ X-O, Å.	$[\text{UO}_2]^+$	$[\text{NpO}_2]^+$	$[\text{PuO}_2]^+$	$[\text{AmO}_2]^+$
	1.96	1.95	1.94	1.93

(6) Unpublished data, W. H. Zachariasen.

(7) Results obtained by infrared absorption show that the aqueous XO_2^+ and XO_2^{+2} ions may not follow this rule: L. H. Jones and R. A. Penneman, *J. Chem. Phys.*, **21**, 542 (1953).

It is of interest to compare this value of 1.93 Å. deduced for the Am-O distance in the solid carbonate with the value of 1.96 ± 0.05 Å. reported for the Am-O distance in the aqueous AmO_2^+ ion using infrared absorption.⁷

Summarizing the conclusions, the following structure has been deduced for the compounds RXO_2CO_3

Space group C 6/m m c

2 X in $\pm (1/3, 2/3, 1/4)$
2 R in (0,0,0)(0,0,1/2)
2 C in $\pm (2/3, 1/3, 1/4)$
6 O_I in $\pm (x, 2x, 1/4)$ ($2\bar{x}, \bar{x}, 1/4$) ($x, \bar{x}, 1/4$)
4 O_{II} in $\pm (1/3, 2/3, 1/4 \pm z)$

The two parameters are fixed by the requirement C-O_I = 1.28 Å., Pu-O_{II} = 1.94 Å., Am-O_{II} = 1.93 Å., the values being

	x	z
KPuO_2CO_3	0.812	0.197
$\text{NH}_4\text{PuO}_2\text{CO}_3$	0.812	0.187
$\text{RbAmO}_2\text{CO}_3$	0.811	0.185

Tables V and VI show the comparison between observed and calculated intensities. The following intensity formula was used

$$I \propto |F|^2 p \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} A$$

TABLE V

CALCULATED AND OBSERVED INTENSITIES, KPuO_2CO_3

$\text{H}_1\text{H}_2\text{H}_3$	Pu only	All atoms	Obsd.
002	45	43	40
100	22	16	15
101	107	85	100
102	23	39	40
103	41	22	15
110	26	45	40
004	8	17	12
112	38	18	17
200	5	4	4
201	25	35	45
104	8	4	
202	8	16	20
203	17	18	18
105	16	16	8
114	22	31	22
210	5	1	0
211	27	27	35
204	4	2	
006	3	4	
212	8	10	10
106	4	8	6
213	21	15	14
300	7	10	22
205	11	15	
301	0	0.2	0
302	12	6	10
214	6	2	10
116	13	9	
303	0	0.1	0
107	8	5	4
206	3	6	6
220	4	10	25
215	14	16	
304	10	12	

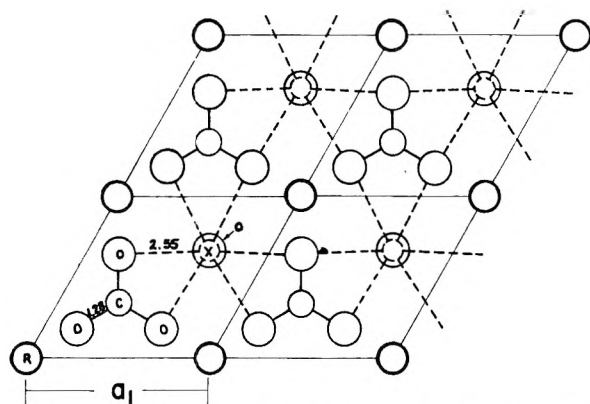


Fig. 1.—Projection of a half-cell of RXO_2CO_3 on the basal plane.

where p is the multiplicity factor, A the absorption factor, and where the other symbols have their usual meaning. The absorption factor was calculated on the basis of a cylindrical sample with $\mu R = 2.0$. The data given in Table V show that the agreement between calculated and observed intensities is greatly improved when account is taken of the light atoms.

Discussion of the Structure.—The two parameters of the deduced structure were fixed by means of reasonable assumptions regarding the C—O_I and X—O_{II} distances. The significant interatomic distances are tabulated below, the assumed values being given in parentheses

	KPuO ₂ CO ₃	NH ₄ PuO ₂ CO ₃	RbAmO ₂ CO ₃
C—3O _I	(1.28 Å.)	(1.28 Å.)	(1.28 Å.)
X—2O _{II}	(1.94 Å.)	(1.94 Å.)	(1.93 Å.)
R—6O _I	2.96	3.08	3.10
R—6O _{II}	2.98	3.01	3.03
X—6O _I	2.55	2.55	2.56

Each atom or group R is bonded to six carbonate oxygens and to six O_{II} atoms, the observed bond lengths being close to those expected from the ionic radii when corrected to coordination number twelve. Each X-atom forms two short bonds to O_{II} atoms, giving collinear $[XO_2]^+$ radicals. In addition, each X-atom forms six secondary bonds to carbonate oxygens with X—O_I = 2.55 Å., these secondary bonds all lying in a plane normal to the primary bonds.

The structure may be described as consisting of layers of average composition $[XO_2CO_3]^-$ held

TABLE VI
CALCULATED AND OBSERVED INTENSITIES

H ₁ H ₂ H ₃	NH ₄ PuO ₂ CO ₃		RbAmO ₂ CO ₃	
	Calcd.	Obsd.	Calcd.	Obsd.
002	36	50	38	30
100	25	30	6	5
101	86	100	112	100
102	29	40	90	80
103	23	25	31	25
004	15	15	18	25
110	38	50	107	60
112	27	30	14	13
104	8	5	1	0
200	7	5	3	4
201	35	50	45	40
202	11	20	31	30
105	18	15	23	15
203	19	25	24	20
114	26	30	55	35
006	5	6	4	0
204	4	6	0.5	0
210	3	4	0.5	0
211	27	40	35	30
106	6	8	17	13
212	6	10	22	20
205	15	17	20	13
213	16	20	21	15
300	8	17	18	17
301	0.2	0	0.3	0
116	12	15	8	5
302	8	18	4	9
107	6	12	8	
214	3		0.3	
206	5	10	12	10
303	0.1	0	0.1	0
215	16	25	21	20
008	2		4	
304	10	17	22	20
220	8	17	16	20

together by the R atoms. Such a layer is shown in Fig. 1. In stacking the layers, the relative horizontal displacement of two layers is $+A$ or $-A$, $A = \frac{1}{3}a_1 + \frac{2}{3}a_2$, positive and negative displacements alternating. The layers $[XO_2CO_3]^-$ are reminiscent of the layers $[UO_2O_2]^{-2}$ of the $CaUO_2O_2$ structure and of the layers in the UO_2F_2 structure. In the $[UO_2O_2]^{-2}$ layers, the secondary U—O bonds are much smaller than in the $[XO_2CO_3]^-$ layer, 2.29 Å. as against 2.55 Å. However, the large value in the latter layer may be due to X—C repulsion, the separation being only 2.94 Å.

THE POTENTIOMETRIC DETERMINATION OF CATIONS AND ANIONS WITH PERMSELECTIVE COLLODION AND PROTAMINE-COLLODION MEMBRANE ELECTRODES¹

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Permselective membranes in concentration chains of numerous electrolytes act electromotively as ideal or nearly ideal reversible electrodes over a fairly wide range of concentrations. Permselective collodion membranes which show an ideal or nearly ideal degree of selective ionic permeability to cations can thus be used as virtually reversible membrane electrodes for cations. The selectively anion permeable, permselective protamine-collodion membranes, notwithstanding a small "leak" of cations, can be used in an analogous manner as membrane electrodes for anions. The determination of ion activities by means of such membrane electrodes can be carried out either by the evaluation of e.m.f. measurements according to the Nernst equation or, better, by the evaluation of e.m.f. data from empirical calibration curves or by the use of a null method involving titration through zero potential. The error of the first exploratory determinations which were made by these methods was on the average considerably less than 1%, in no instance more than 2%. Permselective membrane electrodes thus afford a simple means of determining the activities of numerous cations and anions, including many for which other electrometric methods are not available.

The potentiometric determination of activities of the alkali and alkaline earth metal ions in solution by means of conventional electrodes is beset with experimental difficulties, and so far has been successful for practical purposes only with more concentrated solutions. The potentiometric determination of the activities of anions is at present restricted to a limited number of ionic species, because of the lack of suitable electrodes; the activity of many, even of some of the most common anions cannot be determined electrometrically. Many of these difficulties can be overcome readily by the use of permselective membranes as "membrane electrodes," as was shown in a preliminary note published several years ago.³ Since that time the permselective membrane electrodes have proven themselves as useful tools in the hands of several investigators, particularly in the study of the activities of counter ions in colloidal systems.⁴⁻⁸ This paper presents a description and critical evaluation of the uses of permselective membranes as membrane electrodes in systems which contain only one species of potential determining ions.

The potential usefulness of membrane electrodes was first recognized by Haber,^{9,10} after Nernst and Riesenfeld¹¹ had shown that any interphase (membrane) which in a concentration chain selec-

tively allows the reversible transfer of only a single ion species from the one solution to the other gives rise to a potential and acts electromotively in a manner strictly analogous to a conventional reversible electrode for this ion.

The general theory of membrane electrodes has been discussed in some detail by Haber and collaborators,^{9,10} Horowitz,^{12,13} Tendeloo,¹⁴ Marshall,¹⁵ and most recently by Scatchard.¹⁶ Also pertinent is the work of Meyer and Sievers¹⁷ and the experimental studies on membranes of high ionic selectivity by Michaelis and collaborators,¹⁸ and Sollner and collaborators.¹⁹⁻²⁴

The experimental work on the use of glass membrane electrodes for the determination of hydrogen ions is well known.^{10,25,26} The attempts of Horowitz¹² and Schiller²⁷ to use glasses of various compositions as membrane electrodes for several cations did not meet with success.

Marshall and collaborators^{28,29} and later Wyllie³⁰ have prepared membranes from various zeolitic minerals, and have shown that they can serve as reversible electrodes for alkali and alkaline

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earth cations. These membranes have certain practical drawbacks; they possess high ohmic resistances (1–10 megohms), require several hours or days to attain equilibrium, and are stable for limited periods of time only.

Sollner³ has demonstrated the use of permselective collodion and protamine-collodion membranes as membrane electrodes for numerous cations and anions, respectively, the protamine-collodion membrane being the first anion responsive membrane electrode. The permselective collodion and protamine-collodion membranes are easy to prepare in a reproducible manner, are stable over prolonged periods, show low ohmic resistances, and in a fairly wide range of concentrations rapidly yield stable and highly reproducible potentials in simple concentration chains. These potentials closely approach or coincide with those calculable from known activity data.^{19–21, 31–34}

Membranes were prepared from plastic bonded conventional cation-exchange materials by Wyllie and Patnode³⁵; Juda and McRae,³⁶ Manecke,³⁷ Bonhoeffer, Miller and Schindewolf³⁸ and others have also studied some of the electrochemical properties of ion-exchanger membranes.

Theory and Methods

The determination of the activity of an ionic species in solution by the use of membrane electrodes is based upon the use of a known reference solution containing the same potential determining ions, which in the literature on membranes are frequently referred to as the so-called "critical" ions. Conventionally, chains of the type S.C.E./Sat. KCl//Soln.(2)/Membrane/Soln.(1)//Sat. KCl/S.C.E. are measured, where S.C.E. refers to the saturated calomel electrode connected to the solutions by means of a saturated potassium chloride bridge. Solutions (1) and (2) contain the potential determining ion, the sole ionic species present that can move across the membrane, the "critical" ion being the cation in the case of electronegative, acidic membranes, and the anion with electro-positive, basic membranes. With membranes of ideal ionic selectivity the nature of the non-critical ions in solutions (1) and (2) is of no significance except as far as they co-determine the activity of the critical ions. (With "leaky" membranes a slight error may be introduced if different non-critical ions with a differential tendency to leak are contained in the two solutions.)

When a membrane possesses an ideal degree of ionic selectivity, the e.m.f. is given by the Nernst expression

$$E = - \frac{RT}{nF} \ln \frac{a_1}{a_2}$$

where n is the valence of the critical ion, and a_1 and a_2 its activities in solutions (1) and (2), respectively. Then, if solution (1) is a reference solution where a_1 is known, the determination of E allows the calculation of a_2 in the unknown solution.

The use of the above expression as applied to membrane chains requires that several simplifying assumptions be employed, since measurements of the electromotive forces of cells with or without transference cannot yield thermodynamically defined single ion activities, a topic that has been treated by many authors, notably by Harned and Owen.³⁹ The same limitations exist as for pH measurements.⁴⁰

In the practical determination of such ionic activities, two devices are customarily employed. First, salt bridges are used which reduce the magnitude of the liquid junction potentials, the difference between these two potentials usually being neglected. This practice has been followed in this paper. Second, with regard to ionic activities, some arbitrary assumptions must be made. Conventionally, with uni-univalent electrolytes, single ion activity coefficients are set equal to mean activity coefficients. With bi-univalent and uni-bivalent electrolytes which contain either the potassium or the chloride ion, the ion activities are calculated by assuming that the single ion activity coefficients of these ions are identical with the mean activity coefficient of a potassium chloride solution of the same ionic strength.

The experimental determination of ion activities by means of membrane chains can be carried out by: (1) evaluation of e.m.f. measurements according to the Nernst equation; (2) evaluation of e.m.f. data from empirical calibration curves; and (3) the use of a null method, namely, titration through zero potential.

The Nernst equation can be used in a straightforward manner, without any corrections, only in those cases where the membrane is virtually of an ideal degree of ionic selectivity and where the difference in the magnitude of the two liquid junction potentials is sufficiently small, well within the limits of the desired accuracy. The applicability of this method must be established by the measurement of chains containing solutions of known activity.

Empirical calibration curves can be utilized where membranes do not show ideal behavior due to the "leak" across the membrane of ions other than the critical ions, or where liquid junction potentials are a source of significant error. With this method the use of an unknown solution of approximately the same composition with respect to ions other than the critical ion is indicated.

The null method consists of a potentiometric titration where the membrane separates the solution of unknown activity from a measured quantity of water, to which a standard solution (of higher concentration) of an electrolyte with the same critical ion is added stepwise, until the potential

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passing through the zero point reaches appreciable values of the opposite sign. The same restrictions obtain as in the other cases.

Experimental

Preparation of Membranes.—The details of the preparation of permselective collodion and protamine-collodion membranes have been described elsewhere.^{19,20,31} The negative, cation responsive collodion membranes are prepared from a 4% solution of collodion cotton in 50-50 alcohol-ether; this is poured over 25 × 100 mm. test-tubes rotated in a horizontal position at constant speed. Two successive layers are added at stated intervals, part of the solvent being allowed to evaporate from the films. The latter are coagulated by immersion in water. The resulting membranes of high porosity (80-90% water content by weight) are oxidized (to produce carboxyl groups on the pore surfaces) by immersion in 1 *N* sodium hydroxide for various periods of time. The membranes, still on their casting tubes, are dried at a specified relative humidity. The thickness of these dried membranes is 30-40 μ . Their exact properties depend primarily on the length of the oxidation time and the relative humidity at drying. The classification of these membranes is based on these factors. The abbreviation Ox *X*-Hum *Y* is used to designate a membrane oxidized for *X* minutes in 1.0 *N* NaOH at 25.0°, and dried on its casting tube at the relative humidity, *Y*.

The electropositive, anion responsive protamine-collodion membranes are prepared starting with the same, highly porous membranes described above. These membranes are immersed in a 2% solution of a protamine sulfate at pH 10.5 for several days. After brief washing, and while still on their casting tubes, they are dried at a specified humidity, *Y*. After removal from the tube they are further dried and thereby slightly shrunk at a specified relative humidity, *Z*, without support; accordingly they are designated Hum *Y*-Shr *Z*.

Selection of Membranes.—A membrane for potentiometric determinations should combine a sufficiently high degree of ionic selectivity to approach or attain ideal behavior, with a low ohmic resistance so as to allow rapid and accurate measurements. The type of collodion membrane selected for this study was Ox 12-Hum 43; the protamine-collodion membranes were of the type Hum 58-Shr 58. However, many cases exist where other types of membranes may be more desirable than the ones selected here, e.g., more dense membranes in more concentrated solutions.

In order to make it possible to compare the three different experimental methods, one single membrane specimen each of the negative and the positive membranes, respectively, was used for all the measurements reported herein.

Experimental Procedures.—Previous studies have shown that when the membrane is already saturated with the critical ion species previous to the actual measurement, the rate of attainment of final, stable potentials is quite rapid, in most cases almost instantaneous.³² Therefore all experiments reported herein were carried out with membranes which had been kept immersed in portions of the unknown solutions for several hours prior to the potentiometric determinations proper. The measurements were performed with the chains described previously. A membrane was filled with 20 to 25 ml. of the unknown solution and immersed in a beaker containing the known solution, so that the inside and outside solutions were at approximately the same level. The ends of the potassium chloride-agar bridges which dipped into each of the two solutions were drawn to 0.2-0.3-mm. tips, to minimize contamination of the solution by the salt bridge. When not in actual use, the ends of these bridges were kept in saturated potassium chloride solution. For each potential measurement, they were quickly rinsed with distilled water, wiped dry with filter paper, and then dripped into the appropriate solutions. After each reading, which required less than 15 seconds, they were returned to the saturated salt solution and their symmetry checked. This procedure kept the bridge tips in their original condition, and made for consistent results.

In all experiments both solutions were stirred with a stream of air or nitrogen which had been freed from carbon dioxide. The measurements were carried out at 25.00 ± 0.05°, except the titrations through the null point which were performed at room temperature (24-26°) with the two

calomel half cells side by side so that they were at the same temperature.

Cation Determinations with Collodion Membranes; Evaluation of E.M.F. Measurements According to the Nernst Equation.—A number of chains with the collodion membrane and 0.01 *N* potassium chloride, potassium iodate, potassium sulfate or lithium chloride as solution (1) were set up as described previously. The solutions (2) were varied in concentrations from 0.001 to 0.1 *N*, and contained either the same electrolyte as solution (1) or an electrolyte having the same potential determining ion, as in the chains KCl/Membrane/KNO₃, KCl/Membrane/KIO₃, and KCl/Membrane/K₂SO₄. Constant c.m.f. readings were obtained also in the latter chains within a few minutes after the chains were set up, because the fixed acidic wall groups in the membranes were already saturated with the critical ion.

The experimental e.m.f. data obtained with these chains are shown in Table I; the average experimental error in

TABLE I
EXPERIMENTAL AND CALCULATED MOLAR ACTIVITIES OF
VARIOUS CATIONS IN THE CHAIN: S.C.E.//SOLUTION (2)//
PERMSELECTIVE COLLODION MEMBRANE/SOLUTION (1)//
S.C.F. (*T* = 25.00 ± 0.05°)

Sol. (1) 0.01 <i>N</i> (reference)	Electro- lyte	<i>E</i> _{exp}	Solution (2) <i>a</i> ₂ (found)	<i>a</i> ₂ ' (taken)	Δ <i>a</i> ₂
0.001 <i>N</i>					
KCl	KCl	-57.4	3.016	3.015	+0.001
KCl	KNO ₃	-57.1	3.011	3.015	- .004
KCl	KIO ₃	-57.0	3.009	3.015	- .006
KIO ₃	KIO ₃	-57.0	3.014	3.015	- .001
LiCl	LiCl	-56.5	3.000	3.015	- .015
KCl	K ₂ SO ₄	-58.2	3.029	3.017	+ .012
K ₂ SO ₄	K ₂ SO ₄	-56.0	3.000	3.017	- .017
0.004 <i>N</i>					
KCl	KCl	-34.5 ^a	2.628 ^a	2.623 ^a	+0.005
KCl	KNO ₃	-22.7	2.429	2.427	+ .002
KCl	KIO ₃	-22.9	2.432	2.427	+ .005
KIO ₃	KIO ₃	-22.2	2.425	2.427	- .002
LiCl	LiCl	-22.4	2.424	2.428	- .004
KCl	K ₂ SO ₄	-23.7	2.446	2.432	+ .014
K ₂ SO ₄	K ₂ SO ₄	-22.1	2.427	2.432	- .005
0.01 <i>N</i>					
KCl	KCl	0.0	2.045	2.045	±0.000
KCl	KNO ₃	- .5	2.053	2.038	+ .015
KCl	KIO ₃	- .5	2.053	2.050	+ .003
KIO ₃	KIO ₃	0.0	2.050	2.050	± .000
LiCl	LiCl	0.0	2.045	2.045	± .000
KCl	K ₂ SO ₄	- 1.5	2.070	2.053	+ .017
K ₂ SO ₄	K ₂ SO ₄	0.0	2.053	2.053	± .000
0.04 <i>N</i>					
KCl	KCl	39.2 ^b	1.382 ^b	1.389 ^b	-0.007
KCl	KNO ₃	32.9	1.489	1.496	- .007
KCl	KIO ₃	32.2	1.500	1.496	+ .004
KIO ₃	KIO ₃	33.1	1.490	1.496	- .006
LiCl	LiCl	34.7	1.458	1.479	- .021
KCl	K ₂ SO ₄	31.1	1.519	1.492	+ .027
K ₂ SO ₄	K ₂ SO ₄	32.5	1.503	1.492	+ .011
0.1 <i>N</i>					
KCl	KCl	55.1	1.113	1.113	±0.000
KCl	KNO ₃	53.5	1.140	1.135	+ .005
KCl	KIO ₃	53.1	1.147	1.154	- .007
KIO ₃	KIO ₃	54.1	1.135	1.154	- .019
LiCl	LiCl	55.3	1.110	1.108	+ .002
KCl	K ₂ SO ₄	52.2	1.162	1.131	+ .031
K ₂ SO ₄	K ₂ SO ₄	53.4	1.150	1.131	+ .019

^a Solution (2) 0.0025 *N*. ^b Solution (2) 0.05 *N*.

each reading is ± 0.1 mv. The negative logarithm of the practical (molar) activity of the potential determining ion in solution (2) is shown, pa'_2 , calculated on the basis of the assumptions previously discussed, using molar activity coefficient data calculated from a standard reference.³⁹ The experimentally determined activity, calculated from the Nernst equation, $pa_2 = -E_{\text{exp}}/59.15 - \log_{10} c_1\gamma_1$, is also given, as is the error in pa_2 , $\Delta pa_2 = pa'_2 - pa_2$.

The data of Table I show that with the uni-univalent electrolytes the calculated pa'_2 values virtually coincide with the experimental values, the average deviation being $\pm 0.007 pa_2$ unit. With the chain K_2SO_4 - K_2SO_4 the average error in pa_2 is but slightly larger, being ± 0.01 . With the KCl - K_2SO_4 chain small but significant deviations are observed, with the experimental pa_2 value being in all instances larger than the calculated pa'_2 value by an average of 0.02.

The data of Table I for the chain $LiCl$ - $LiCl$, are plotted in Fig. 1. The points fall on a virtually straight line, the slope of which is very close to the theoretical value of -59.15 millivolts per pa_{Li^+} unit.

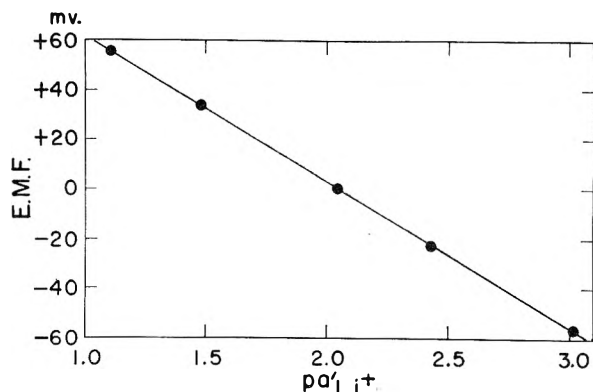


Fig. 1.—Experimental e.m.f. values in millivolts, plotted as a function of pa'_{Li^+} , the negative logarithm of the calculated activity of the lithium ion in solution (2).

In appraising the agreement between the potential values calculated on the basis of the Nernst equation and the experimental data, it must not be forgotten that the apparently excellent agreement is due, at least in part, to a fortuitous factor: the lack of ideality in the ionic selectivity of the membranes and the concomitant lack in ideal electromotive response is in a direction opposite to the error introduced by the asymmetry of the liquid junction potentials at the end of two agar bridges. These two factors thus tend to compensate each other. Thus it appears that the straightforward application of the Nernst equation must be carried out in a judicious manner and in most instances it will be preferable to make use of either of the other two methods on which data are presented in the subsequent paragraphs.

Evaluation of Empirical E.M.F. vs. Activity Curves.—Empirical calibration curves were made by plotting experimental potential values (Table I) as a function of pa'_2 , as shown in Fig. 1. By using large, fine lined drawings it is possible to read off activities in unknown solutions from potential values without a loss in accuracy. The e.m.f. of chains containing solutions of "unknown" activities a_2 is measured, and compared to the true activities a'_2 of the critical ions in these solutions.

Table II summarizes the results of a series of the first, single determinations obtained with this method. The per cent. of error, listed in the last column of Table II, could of course be reduced by taking the average of several determinations. Without this precaution the average error was $\pm 1.0\%$.

Potentiometric Titration through the Zero Potential Point.—For the determination of cations by the titration procedure a membrane bag which had been saturated beforehand with the critical ion species (advantageously by immersion in a portion of the "unknown" solution) is filled with unknown solution, and dipped into a measured volume of water, to which standard solution is added stepwise from a buret, potential measurements being made at

each point. The titration is continued considerably past the point where the potential changes in sign. The end-point (zero potential) is evaluated graphically.

TABLE II

THE POTENTIOMETRIC DETERMINATION OF ACTIVITIES OF VARIOUS CATIONS BY THE USE OF EMPIRICAL CALIBRATION CURVES

Sol. (1) 0.01 N (reference)	Electrolyte in sol. (2) (unknown)	$E_{\text{exp.}}$ mv.	a_2 (found)	a'_2 (taken)	Error, %
KCl	KCl	-46.1	0.00150	0.00151	-0.7
KCl	KCl	-10.0	.00614	.00610	0.7
KCl	KCl	31.0	.0302	.0300	0.7
KCl	KCl	50.8	.651	.0655	-0.6
KCl	KNO ₃	-15.0	.00506	.00490	3.2
KCl	KNO ₃	38.8	.0426	.0424	0.5
KCl	KIO ₃	34.7	.0347	.0347	± 0.0
KIO ₃	KIO ₃	-14.2	.00513	.00501	2.4
KIO ₃	KIO ₃	33.0	.0319	.0315	1.3
LiCl	LiCl	-19.6	.00416	.00415	0.2
LiCl	LiCl	41.5	.0430	.0424	1.4
KCl	K ₂ SO ₄	-16.1	.00497	.00499	-0.4
KCl	K ₂ SO ₄	35.0	.0379	.0379	± 0.0
K ₂ SO ₄	K ₂ SO ₄	-16.3	.00463	.00460	0.7
K ₂ SO ₄	K ₂ SO ₄	35.8	.0361	.0368	-1.0

The temporary contact of the membrane with pure water and very dilute solutions in the early stages of the titration may result in slightly erroneous potentials near the zero point. Therefore, it is advisable in many cases to perform a preliminary titration. In the subsequent accurate titration, the concentration of the outside solution is adjusted to be slightly less than that of the unknown. With this precaution, equilibrium e.m.f. values are ordinarily established with sufficient rapidity to allow most titrations to proceed continuously.

The results of a number of potentiometric titrations of solutions of unknown activities are given in Table III, the data referring to the first, single determination for each unknown. The average error is $\pm 0.4\%$. This error can doubtless be reduced by taking the average for a number of determinations.

TABLE III

THE POTENTIOMETRIC TITRATION OF VARIOUS MONOVALENT CATIONS WITH PERMSELECTIVE COLLODION MEMBRANES

Electrolyte	a_2 (found)	a'_2 (taken)	Error, %
KCl	0.00423	0.00425	-0.5
KCl	.0390	.0390	.0
KIO ₃	.00515	.00517	-.4
KIO ₃	.0379	.0378	.5
K ₂ SO ₄	.00423	.00423	.0
K ₂ SO ₄	.0450	.0448	.4
NH ₄ Cl	.00399	.00400	-.2
NH ₄ Cl	.0465	.04635	.3
NaCl	.00495	.00490	1.0
NaCl	.0366	.0362	1.1
LiCl	.00414	.00413	0.3
LiCl	.0459	.0463	-0.8

Anion Determinations with Protamine-Collodion Membranes; Evaluation of E.M.F. Measurements According to the Nernst Equation.—The protamine-collodion membranes used in these experiments were known to deviate significantly from the postulated ideal ionic selectivity and the concomitant virtually ideal electromotive behavior in concentration chains, being at all concentrations slightly "leaky," i.e., permeable also to the non-critical ions (cat-

ions) to a significant extent.⁴¹ In addition, the error caused by the asymmetry of the liquid junction potential (contrary to the situation existing with the electronegative membranes) lies in the same direction as that due to the leak. Thus, the use of the Nernst equation is likely to result in a significant error.

The reference solutions used in these experiments were 0.01 *N* potassium chloride, measured against solutions of potassium, sodium, lithium and magnesium chloride, and 0.01 *N* potassium iodate solution measured against potassium iodate solutions. Table IV presents the activity values found in these chains, pa_2 , together with the corresponding calculated pa_2' values.

TABLE IV

EXPERIMENTAL AND CALCULATED MOLAR ACTIVITIES OF VARIOUS ANIONS IN THE CHAIN: S.C.E./SOLUTION (2)/PERMSELECTIVE PROTAMINE-COLLODION MEMBRANE/SOLUTION (1)/S.C.E. ($T = 25.00 \pm 0.05^\circ$)

Sol. (1) (reference)	Electrolyte	E_{exp}	Solution (2) pa_2 (found)	pa_2' (taken)	Δpa_2
0.001 <i>N</i>					
KCl	KCl	55.4	2.982	3.015	-0.033
KCl	NaCl	55.1	2.977	3.015	- .038
KCl	LiCl	55.1	2.977	3.015	- .038
KCl	MgCl ₂	56.4	2.999	3.017	- .018
KIO ₃	KIO ₃	55.4	2.987	3.015	- .028
0.004 <i>N</i>					
KCl	KCl	33.5 ^a	2.611 ^a	2.623 ^a	-0.012
KCl	NaCl	21.2	2.403	2.425	- .022
KCl	LiCl	21.2	2.403	2.428	- .025
KCl	MgCl ₂	22.5	2.425	2.432	- .007
KIO ₃	KIO ₃	22.0	2.422	2.427	- .005
0.01 <i>N</i>					
KCl	KCl	0.0	2.045	2.045	± 0.000
KCl	NaCl	0.3	2.050	2.044	+ .006
KCl	LiCl	- 0.4	2.038	2.045	- .007
KCl	MgCl ₂	1.1	2.064	2.053	+ .011
KIO ₃	KIO ₃	0.0	2.050	2.050	$\pm .000$
0.04 <i>N</i>					
KCl	KCl	-37.5 ^b	1.411 ^b	1.388 ^b	+0.023
KCl	NaCl	-31.2	1.519	1.479	+ .040
KCl	LiCl	-32.5	1.495	1.479	+ .016
KCl	MgCl ₂	-30.5	1.529	1.492	+ .037
KIO ₃	KIO ₃	-33.5	1.484	1.496	+ .012
0.1 <i>N</i>					
KCl	KCl	-53.0	1.149	1.113	+0.036
KCl	NaCl	-52.1	1.164	1.109	+ .055
KCl	LiCl	-53.1	1.147	1.108	+ .039
KCl	MgCl ₂	-50.8	1.186	1.131	+ .055
KIO ₃	KIO ₃	-50.5	1.196	1.153	+ .043

^a Solution (2) 0.0025 *N*. ^b Solution (2) 0.05 *N*.

In agreement with expectation the experimental pa_2 values are consistently smaller than the calculated pa_2' values in solutions which are more dilute than the reference solution. In the more concentrated solutions the values of pa_2 are consistently too high, the errors amounting to several hundredths of a pa_2 unit. Unless membranes of superior selectivity are used (see below) this method must be considered to be of but restricted interest, particularly in view of the satisfactory results obtainable with the two methods presented in subsequent paragraphs.

(41) The membranes used for the experiments described here are not as "leaky" as might be concluded from the e.m.f. data with potassium chloride concentration chains which were presented in some earlier papers^{23,24} without correction for the asymmetry of the liquid junction potentials at the tips of the potassium chloride agar bridges. The data given previously for 2:1 and 10:1 concentration ratio chains are too low by 0.3 and 1.1 mv., respectively.

Evaluation of Empirical E.M.F. vs. Activity Curves.—Using calibration curves prepared from the data of Table IV, some direct potentiometric determinations were made of the activities of the anions in various chains. The results of the first, single determination by this method are shown in Table V. The average error is $\pm 0.9\%$.

TABLE V

THE POTENTIOMETRIC DETERMINATION OF VARIOUS ANIONS BY THE USE OF EMPIRICAL CALIBRATION CURVES

Sol. (1) 0.01 <i>N</i> (reference)	Electrolyte in sol. (2) (unknown)	E_{exp} , mv.	a_2 (found)	a_2' (taken)	Error, %
KCl	KCl	50.2	0.00120	0.00122	-1.7
KCl	KCl	7.7	.00667	.00663	+0.6
KCl	KCl	-27.6	.0273	.0274	-0.4
KCl	KCl	-47.6	.0614	.0626	-2.0
KCl	NaCl	22.0	.00360	.00363	-0.8
KCl	NaCl	-36.5	.0413	.0417	-1.0
KCl	LiCl	17.9	.00447	.00448	-0.2
KCl	LiCl	-27.5	.0285	.0282	-1.0
KCl	MgCl ₂	28.0	.00293	.00299	-2.0
KCl	MgCl ₂	-39.5	.0462	.0465	-0.6
KIO ₃	KIO ₃	17.4	.00454	.00448	+1.3
KIO ₃	KIO ₃	-41.5	.0387	.0387	± 0.0

Potentiometric Titration through the Zero Potential Point.—The results of the first single determination of various anions in concentration chains by means of the titration procedure are given in Table VI; the average error is $\pm 0.5\%$.

TABLE VI

THE POTENTIOMETRIC TITRATION OF VARIOUS MONOVALENT ANIONS WITH PERMSELECTIVE PROTAMINE-COLLODION MEMBRANES

Electrolyte	a_2 (found)	a_2' (taken)	Error, %
KCl	0.00447	0.00447	0.0
KCl	.0396	.0398	- .5
NaCl	.00433	.00431	.5
NaCl	.0414	.0415	- .2
LiCl	.00475	.00474	.2
LiCl	.0461	.0458	.7
MgCl ₂	.00482	.00478	.8
MgCl ₂	.0399	.0402	- .7
KNO ₃	.00473	.00472	.2
KNO ₃	.0398	.0397	.3
KClO ₃	.00534	.00537	- .6
KClO ₃	.0444	.0443	.2
KClO ₄	.00506	.00506	$\pm .0$
KClO ₄	.0331	.0333	- .6
KF	.00496	.00499	- .6
KF	.0355	.0351	1.1
KIO ₃	.00485	.00481	0.8
KIO ₃	.0386	.0382	1.1
KAc	.00389	.00392	-0.8
KAc	.0372	.0374	-0.5

It might be added here that with all three methods similarly accurate results were obtained when working on a semimicro scale, with 2 to 3 ml. of unknown solution, provided the diffusion of potassium chloride from the agar bridges was kept to a minimum. There is little doubt that the use of a more sensitive galvanometer in combination with agar bridges with capillary tips will permit the application of this method on a truly microchemical scale.

Discussion

The foregoing experimental results require little comment. The general methods of determining

activities of ions in systems containing a single "critical" potential determining ion which were used here are, of course, applicable equally to any other type of permselective membranes, provided their electromotive response with a given critical ion, at the concentration under investigation, follows the Nernst equation reasonably closely.

Specifically, it has been shown that the permselective collodion membrane Ox 12-Hum 43 which was used in this work acts electromotively as a virtually reversible membrane electrode for the alkali metal cations in solutions which are 0.1 *N* or less. For uni-univalent electrolytes the experimentally determined activities agree with calculated values to within ± 0.01 *pa* unit; the average deviation is but slightly larger with univalent electrolytes, where the calculated values may be in error due to an inexactness in the assumptions employed in making the calculations. When empirical calibration curves are employed, the determination of cationic activities is accurate to $\pm 1\%$. With the titration procedure the average error in single determinations is $\pm 0.4\%$.

Because of the accuracy of the results they yield and the ease and convenience of their preparation and use, the permselective collodion membrane electrodes have been used by various authors.⁴⁻⁸

The permselective protamine-collodion membranes used in the experiments described in this paper did not possess quite the same, nearly ideal degree of ionic selectivity as the permselective collodion membranes, and the error due to the asymmetry of the liquid junction potentials lies in the unfavorable direction (see above). Thus, a small but significant deviation exists between the experimentally determined activities and those calculated by the Nernst equation. When an empirical calibration curve was used the activities of a great variety of anions were determined in the concentration range of 0.1 *N* or less with an average accuracy of $\pm 0.9\%$. With the titration procedure the average error in single determinations is $\pm 0.5\%$. One might add that membranes with a considerable "leak" of non-critical ions, far inferior in selectivity to the membranes used here, can be used as membrane electrodes with a considerable degree of accuracy.

The permselective protamine-collodion membranes are the first membrane electrodes which can be used for the electrometric determination of the activities of numerous anions, including many for the determination of which other electrodes do not exist.

The concentration range within which the membranes described in this paper can be used as membrane electrodes has not been explored fully; it depends considerably upon the accuracy which is desired. At higher concentrations where the membranes are significantly leaky, the nature of the non-critical ion in the two solutions becomes gradually more significant. However, it can be stated that the methods of empirical calibration curves and titration through zero, judiciously applied, permit the performance of fairly

accurate determinations up to concentrations of several tenths normal, where other factors such as the asymmetry of the liquid junction potentials begin to play a significant role.⁴²

The variety of ions, the activity of which can be determined by means of the permselective collodion-base and other membranes, has likewise not been fully explored; the examples presented in this paper by no means circumscribe the range of their usefulness. Generally speaking, the determination of the activities of all critical ions which form highly dissociated surface compounds with the fixed wall groups can be expected to fall within the reach of the method. Nevertheless, it is necessary with each new species of ion to test whether or not the membrane under investigation responds electromotively in an adequate manner, as well as the effective concentration range which obtains. In certain instances, particularly with di- and polyvalent ions and with all somewhat larger organic ions, it will be advantageous to use membranes of somewhat higher porosity than those referred to in this paper, as described previously.³¹⁻³⁴

Bivalent and polyvalent ions as yet have not been studied in a systematic manner.

Permselective oxidized collodion membranes are not suitable for the electrometric determination of the activities of calcium, barium and strontium ions, because of the specific interaction of the latter with polymeric carboxyl compounds.⁴³ In this respect they are inferior to the clay membranes prepared by Marshall and collaborators. This, however, does not hold true with the recently described strong acid type sulfonated polystyrene collodion-base membranes⁴⁴ which respond rapidly and accurately when used as membrane electrodes for the determination of the activities of the alkali earth metal ions.⁴⁴⁻⁴⁶ These membranes also show a higher degree of selectivity in neutral solutions of uniunivalent electrolytes up to higher concentrations than do the permselective oxidized collodion membranes; in addition they respond electromotively to hydrogen ions in an excellent manner.

The behavior of bivalent anions in chains with protamine-collodion membranes has not been investigated in detail. However, on the basis of the chemical nature of the protamine alone, one might anticipate that the determination of the sulfate and similar ions can readily be carried out. In this connection, it seems worthwhile to remark that the preparation of strong base type permselective membranes which are essentially free of the "leak" of non-critical ions was accomplished recently.⁴⁷

(42) In establishing experimental calibration curves with membranes of the before-mentioned type it will be helpful in many instances to remember that the range of concentrations within which a membrane is of ideal or nearly ideal ionic selectivity is a function of the concentration of the solutions on both sides of the membrane²¹; thus, the use of a fairly dilute reference solution may be indicated in certain instances.

(43) H. P. Gregor and L. Luttinger, in preparation.

(44) K. Sollner and R. Neihof, *Arch. Biochem. and Biophys.*, **33**, 166 (1951); R. Neihof, in press.

(45) C. W. Carr, *Arch. Biochem. and Biophys.*, **43**, 147 (1953); **46**, 424 (1953).

(46) R. Neihof, in preparation.

(47) M. Gottlieb, R. Neihof and K. Sollner, in preparation.

The nature of the non-critical ion present in the unknown solution is of little consequence since it does not affect significantly the behavior of systems with membranes of ideal or nearly ideal ionic selectivity. This means that the "unknown" solution need not be the same with regard to non-critical ions as the reference solution.

There is one severe limitation on the use of membrane electrodes by the methods described here, namely, that, in general, they are applicable only in chains with a single species of critical (potential-determining) ions. In comparing different types of membranes for their usefulness as membrane electrodes, a variety of factors must be considered: whether or not the membrane shows an ideal or nearly ideal degree of ionic selectivity and thus gives an adequate electromotive response with a given electrolyte within a specific concentration range; the ohmic resistance per unit area and the speed with which well-defined and stable potentials are obtained; the ease of preparation of the membranes and their stability. In addition, with membranes to be used in systems with two or more potential-determining species of ions, the specific, differential selectivity of the membranes to these ions, to be discussed shortly, becomes of paramount importance.

In most of these respects, the permselective collodion membranes compare favorably with the clay membranes of Marshall^{28,29} and of Wyllie,³⁰ the only type of membranes concerning which an adequate amount of accurate experimental material has been published. The permselective collodion membranes are much easier to prepare and much more stable over prolonged periods of time than the synthetic clay membranes, and respond electromotively more accurately (except at the fairly high concentrations) and much more rapidly than do the latter membranes. Their resistance is several orders of magnitude lower and permits the use of simple, low resistance potentiometer circuits.

The exchange resin type membranes³⁵⁻³⁸ which heretofore have been described do not seem to offer as yet any advantages over the permselective collodion and collodion-base membranes, particularly the recently improved types.^{44,47} Two outstanding shortcomings of the commercial resin type membranes for the purpose on hand seem to be their considerably higher water content and water permeability, and their much higher exchange capacity per unit area.

In concluding, it seems appropriate to discuss briefly systems which contain more than one species of potential-determining ions. Here, the electrical situation is much more involved than in the systems with only one such ion, as was pointed out in detail in a discussion of the bi-ionic potential.⁴⁸

In membrane chains with more than one "critical" (potential-determining) species of ion, each species makes a contribution to the measurable potential which is a function of its activity in the two solution phases and its nature, and also of

the nature of the membrane which in turn determines the relative concentration and mobility of the different critical species of ions in the membrane.

Three methods are known which allow the determination of the activities of several co-existing species of ions by means of permselective membranes. First, membranes may be used which show a high degree of specific selectivity for one of the critical ions present. If, for instance, certain critical ions are virtually excluded from the membrane because of their size and therefore do not contribute significantly to the membrane potential, the membrane system acts as a concentration chain with respect to the permeable ion. Clay membranes of this nature were prepared by Marshall for the determination of potassium ion in the presence of calcium ion.^{28,29} Permselective collodion base membranes in general show a rather high degree of preferential selectivity for univalent over divalent ions and therefore should be adaptable to the determination of univalent cations as well as anions in the presence of bi- and polyvalent ions of the same sign.⁴⁸

Another approach worked out by Marshall and applied with considerable success to cations using clay membranes is based on the fact that different membranes may have a differential selectivity for two co-existing species of critical ions in the system under consideration. This selective specificity can be based on a steric factor, the differential exclusion of the larger ions from the membranes, or on chemical specificity which makes for the preferred presence in the membrane of the one or the other species of ions. By combining the data of two sets of measurements with two different membranes it is possible to evaluate the activities in solution of two species of ions. This method is, of course, applicable to any kind of membrane of high ionic selectivity, and will become a more general and useful tool as different membranes of higher specific ionic selectivity become available.

A third approach not tested thus far experimentally is based on the ionic Donnan equilibrium and the concomitant membrane potentials which are established between an unknown solution and a completely analyzable, known reference solution.⁴⁹ This method would be applicable and particularly useful with systems containing more than two species of critical ions, or ions which are very similar in character such as the ions of sodium, potassium and ammonia. An experimental test of this method is anticipated in the near future.

The accumulation of evidence on specific ionic selectivity which is gradually emerging from numerous studies of ion exchangers, together with the rapidly growing knowledge of the chemistry of the chelate compounds seems to point the way toward the preparation of membranes having a high degree of ionic selectivity which ultimately should make it possible in many instances to use membranes as specific electrodes for the direct determination of the various ionic species in mixed systems.

(48) K. Sollner, *This Journal*, **53**, 1211, 1226 (1949).

(49) K. Sollner, *J. Am. Chem. Soc.*, **68**, 156 (1946).

EQUILIBRIA BETWEEN 18 AND 100° IN THE AQUEOUS TERNARY SYSTEM CONTAINING Sr^{2+} , Mg^{2+} AND Cl^-

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The ternary system strontium chloride–magnesium chloride–water has been investigated between 18 and 100°. No double salt occurs within this temperature range. The lowest formation temperature of strontium chloride dihydrate is at 19.4°, that of strontium chloride monohydrate is at 80.5°.

In two earlier papers the present authors¹ reported the results from the investigations on the equilibria in the system calcium chloride–strontium chloride–water and this system combined with potassium and sodium chlorides. As these components also occur together with magnesium chloride, there are good reasons for extending the investigations to include this component.

Earlier Royer² assumed the occurrence of a double salt between strontium and magnesium chlorides with composition similar to that of tachydrite. This assumption was based upon the ebullioscopic properties of the solutions at 100°. Recently Dodonov, Eferova and Kolosova³ evaporated samples from some brines in the Saratovsk oil district at about 30°. They obtained the compounds tachydrite, carnallite and $2\text{CaCl}_2 \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Moreover, they assumed the presence of double salts of hydrates of calcium and strontium chloride, but no compound containing strontium and magnesium chloride. The supposed double salts might have been the solid solution of the hexahydrates of calcium and strontium chloride, described by the present authors.¹ It seemed therefore to be necessary to investigate the

aqueous system of magnesium and strontium chloride more systematically.

Experimental.—The experiments were performed as earlier described.¹

Magnesium and strontium were determined in the solutions and the solids in the following manner. The weighed sample, contained in a platinum crucible, was transformed into sulfates and weighed. From the mixed sulfates magnesium sulfate was extracted by a solution containing 50 vol. water, 50 vol. ethyl alcohol and 1 vol. sulfuric acid. The strontium sulfate was filtered off, washed with the extraction solution and with pure ethyl alcohol, ignited gently and weighed. The magnesium chloride content was calculated by difference. The analyses of solutions of known composition showed an agreement within 0.2–0.4% between the found and calculated values for the total weight of chlorides present.

Results.—The results will be given briefly here. There is no double salt in the system between 18 and 100°. It is noteworthy, that the saturated magnesium chloride solutions contain only small amounts of strontium chloride and that they have a very strong dehydrating influence on the strontium chloride hydrates, similar to that of the corresponding calcium chloride solutions¹ (Table I). No isotherms will be given here. A synopsis of isothermally invariant equilibria is given in Fig. 1. There it is presumed, that the solubility of strontium chloride in the magnesium chloride solutions is insignificant below 0°. At higher temperatures the anhydrous chlorides of the two components form melts; the composition at their eutectic point at 535° is 62% strontium chloride and 38% magnesium chloride.⁴

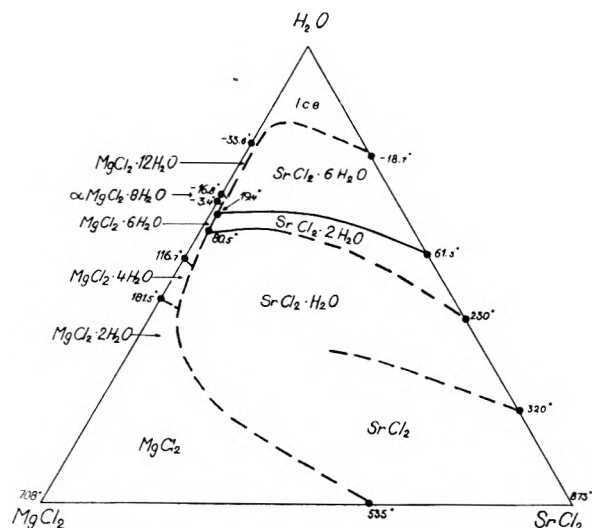


Fig. 1.—Synopsis of the composition of the solutions at the invariant and univariant equilibria of the ternary system $\text{SrCl}_2\text{--MgCl}_2\text{--H}_2\text{O}$.

(1) G. O. Assarsson and A. Balder, *THIS JOURNAL*, **57**, 717 (1953); **58**, 253 (1954).

(2) E. Royer, *Ann. chim.* [10] **13**, 451 (1930).

(3) Y. Y. Dodonov, L. V. Eferova and V. S. Kolosova, *Doklady Akad. Nauk. S.S.S.R.*, **63**, 301 (1948).

TABLE I

THE TERNARY SYSTEM $\text{SrCl}_2\text{--MgCl}_2\text{--H}_2\text{O}$; SOME EQUILIBRIA BETWEEN 18 AND 100°

Temp., °C.	Solution		Wet residue		Solid phase
	SrCl_2	MgCl_2	SrCl_2	MgCl_2	
18.9	1.2	34.8	36.2	15.3	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$
19.4	1.3	34.7	33.8	16.6	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O} + \text{SrCl}_2 \cdot 2\text{H}_2\text{O}$
19.9	1.3	34.8	57.5	10.5	$\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$
80	1.7	39.0	51.4	15.3	$\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$
81	1.7	39.2	36.4	23.8	$\text{SrCl}_2 \cdot \text{H}_2\text{O}$
100	1.7	41.2	57.2	15.6	$\text{SrCl}_2 \cdot \text{H}_2\text{O}$
	1.5	42.0	0.6	45.5	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

THE INVARIANT POINTS

Temp., °C.	Solution		Solid phase
	SrCl_2	MgCl_2	
19.4 ± 0.2	1.3	34.7	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O} + \text{SrCl}_2 \cdot 2\text{H}_2\text{O}$
80.5 ± 0.5	1.7	39.1	$\text{SrCl}_2 \cdot 2\text{H}_2\text{O} + \text{SrCl}_2 \cdot \text{H}_2\text{O}$

(4) C. Sandonnini, *Gazz. chim. ital.*, **44**, I, 343 (1914).

STUDIES ON COSOLVENCY. V. LEWIS ACID CHARACTER OF IODO COMPOUNDS IN ENHANCING THE SOLUBILITY OF ANTHRACENE IN HYDROCARBON SOLVENTS

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Anthracene shows cosolvency in binary mixtures (A, iodobenzene or iodoethane; B, benzene, cyclohexane and cyclohexane). Since the δ -value of anthracene is higher than that of either iodobenzene or benzene, the explanation offered by Gordon and Scott¹ of analogous cosolvency of phenanthrene in cyclohexane-methylene iodide mixtures as due to the δ -value of the solute being intermediate between those of the two cosolvents being a corollary of the regular solution theory of Hildebrand,² seems to be inapplicable. It is suggested that the strong complex-forming tendency of iodine is carried over in iodides like RI where R is a sink of electrons, and this power of complex formation by iodine atoms is responsible for the codissolving power of the iodides.

Introduction

Hildebrand² assumed that a sufficiently correct approximation to the actual behavior of mixtures could be obtained by assuming them to be "regular," *i.e.*, their entropy of mixing is that of an ideal solution whereas the energy of mixing is not zero. From this assumption and some further approximations, he derived the solubility equation in the case of a solid non-electrolyte

$$RT \ln \frac{a_1}{x_1} = V_1 \Phi_0 (\delta_1 - \delta_0)^2$$

where x_1 the mole fraction, a_1 the activity, V_1 the molal volume and δ_1 the solubility parameter of the solute considered as supercooled liquid and Φ_0 the volume fraction and δ_0 the solubility parameter of the solvent. The δ is characteristic of the pure substance and its square is often called cohesive energy density (CED) and is given by

$$\delta^2 = \text{CED} = (\Delta E/V_1)$$

where ΔE is the internal energy change for the vaporization process and V_1 is the molal volume of

TABLE I
SOLUBILITY OF ANTHRACENE IN MIX-SOLVENTS

Mole % hydrocarbon in the mix- solvent	Temperature, °K.							
	300	305	310	315	320	325	330	340
Benzene-Iodobenzene (Fig. 1)								
0	...	1.462	1.728	2.014	2.344	2.738	3.145	...
6.39	...	1.622	1.916	2.213	2.570	3.002	3.447	...
19.17	...	1.622	1.916	2.213	2.570	3.002	3.447	...
34.59	...	1.549	1.820	2.113	2.469	2.867	3.293	...
56.15	...	1.365	1.594	1.862	2.175	2.526	2.900	...
100	...	0.912	1.059	1.245	1.437	1.698	1.934	...
Benzene-Iodoethane (Fig. 2)								
0	1.189	...	1.612	...	2.175	2.867
33.06	1.303	...	1.778	...	2.385	3.141
47.80	1.342	...	1.820	...	2.435	3.219
57.21	1.303	...	1.778	...	2.385	3.141
70.83	1.216	...	1.660	...	2.226	2.951
100	1.059	...	1.437	...	1.934	2.558
Cyclohexane-Iodoethane (Fig. 3)								
0	0.8414	...	1.1890	...	1.6120	...	2.1750	...
11.17	.7989	...	1.1610	...	1.7080	...	2.4550	...
21.28	.7780	...	1.1170	...	1.6410	...	2.3440	...
47.65	.5888	...	0.8590	...	1.2590	...	1.8200	...
54.51	.5041	...	0.7586	...	1.1430	...	1.6600	...
100	.2985	...	0.4571	...	0.6683	...	0.9772	...
Cyclohexane-Iodoethane (Fig. 4)								
0	0.8414	...	1.1890	...	1.6120
12.67	.8318	...	1.2160	...	1.6980
43.01	.5309	...	0.7586	...	1.1090
100	.1641	...	0.2512	...	0.3715

(1) L. J. Gordon and R. L. Scott, *J. Am. Chem. Soc.*, **74**, 4138 (1952).

(2) J. H. Hildebrand and R. L. Scott, "Solubility of Non-electrolytes," A.C.S. Monograph, 3rd edition, Reinhold Publ. Corp., New York, N. Y., 1950.

the liquid. Evidently, the highest solubility would be observed if $\delta_1 - \delta_0 = 0$.

It is immediately apparent that if the same theory is applicable to solvent mixtures the phenomenon of

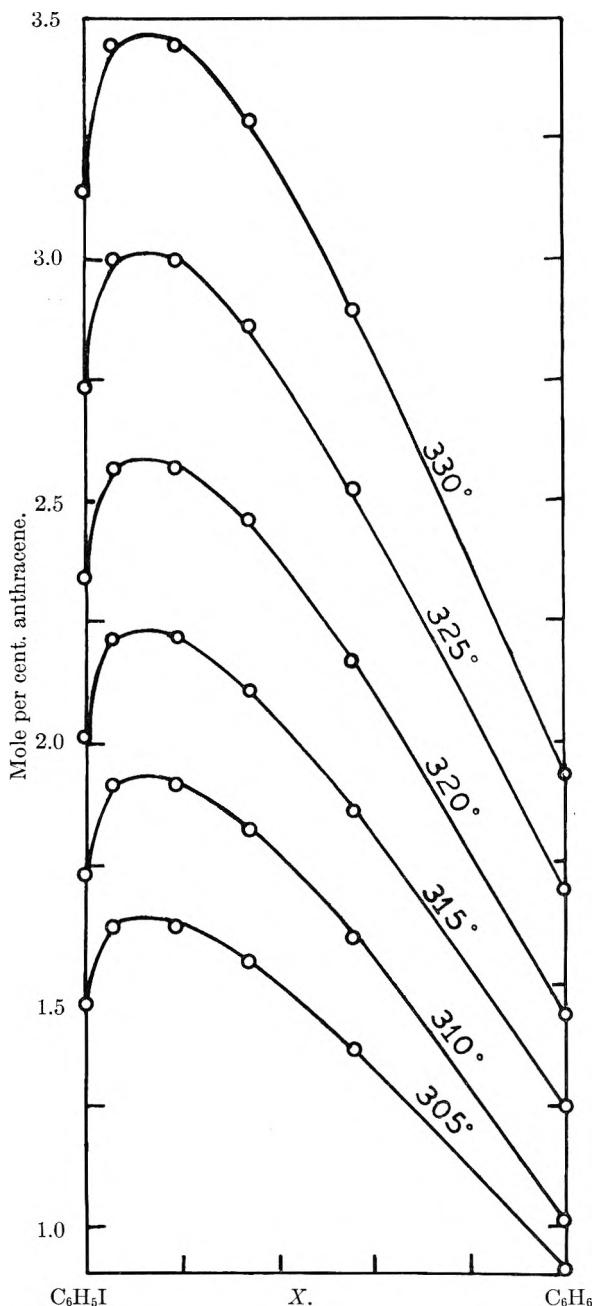


Fig. 1.—Solubility of anthracene as a function of composition of the mix-solvent: iodobenzene and benzene at selected temperatures.

cosolvency would be observable with any two solvents provided the δ of the solute lies in between the δ -values of the two pure solvents. Gordon and Scott¹ provided confirmation of the above concept by demonstrating strong cosolvency for phenanthrene ($\delta = 9.8$), by a mixture of methylene iodide ($\delta = 11.8$) and cyclohexane ($\delta = 8.2$). We report here some observations of enhanced solubility of anthracene in several more or less analogous solvent mixtures, which do not follow the regular solution theory. These anomalous findings throw doubt on the applicability of the regular solution concept to the results obtained by Gordon and Scott and it is suggested that the behavior has its origin to an electron donor-acceptor mechanism on which

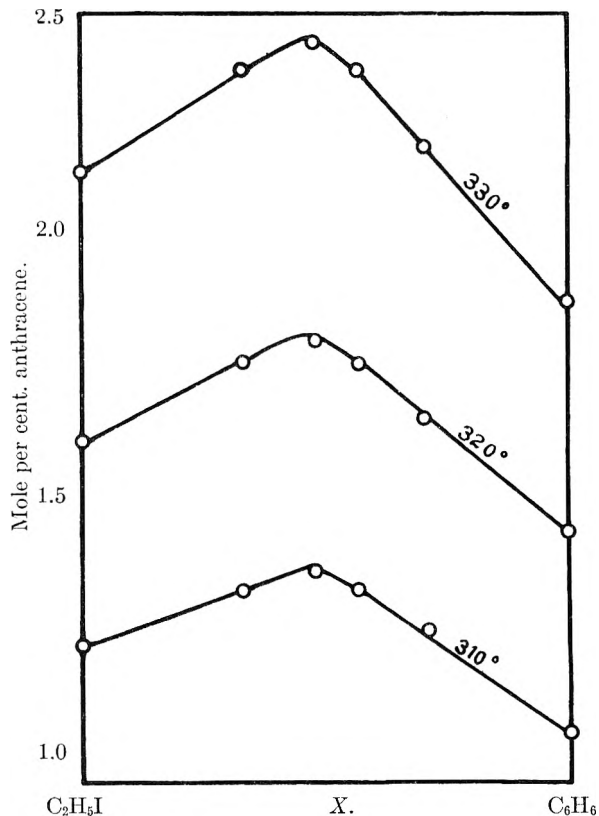


Fig. 2.—Solubility of anthracene as a function of composition of the mix-solvent: iodoethane and benzene at selected temperatures.

a vast literature³⁻⁷ has recently grown and which is consistent with our previous explanation⁸ of highly pronounced cosolvency of soaps in glycolic mixtures, and polymers in organic solvents.⁹

Experimental

Materials.—Anthracene (J. T. Baker Co., U. S. A.) was purified either by sublimation or by repeated crystallization from alcohol followed by final crystallization from ethyl acetate, m.p. 216–217°. Thiophene-free benzene (A.R.) was dried over anhydrous calcium chloride and distilled. The middle fraction was then allowed to stand over sodium and distilled from it, b.p. 80.1°. Cyclohexane of the Eastman Kodak Co., was dried over anhydrous calcium chloride and distilled, b.p. 83°. Cyclohexene (Eastman Kodak Co.) was also purified as cyclohexane, b.p. 81.4°. Iodobenzene (Columbia Organic Chemicals Co.) was freshly distilled before use and the middle fraction boiling at 188.6° was used. Iodoethane was prepared in our laboratory by way of Beilstein and Hunt.¹⁰ It was finally dehydrated over anhydrous calcium chloride and distilled, b.p. 72.4°.

Method.—The "synthetic" method was adopted for studying the solubility of anthracene in the binary mixtures, (1) iodobenzene + benzene, (2) iodoethane + benzene, (3) iodoethane + cyclohexene, (4) iodoethane + cyclohex-

(3) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950); **74**, 811 (1952); *J. Chem. Phys.*, **19**, 514 (1951); *This Journal*, **56**, 801 (1952).

(4) F. Fairbrother, *Nature*, **160**, 87 (1947); *J. Chem. Soc.*, 1051 (1948).

(5) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **70**, 2832 (1948); **71**, 2703 (1949).

(6) N. S. Bayliss, *Ann. Revs. Phys. Chem.*, **3**, 229 (1952).

(7) J. Kleinberg and A. W. Davidson, *Chem. Revs.*, **42**, 601 (1948).

(8) S. R. Palit, *J. Ind. Chem. Soc.*, **19**, 271 (1942); *J. Am. Chem. Soc.*, **69**, 3120 (1947).

(9) H. Daoust and M. Rinfret, *J. Colloid Sci.*, **7**, 11 (1952).

(10) Beilstein and Hunt, see Cohen, "Practical Organic Chemistry," Macmillan and Co., Ltd., London, 3rd edition, 1946, p. 64.

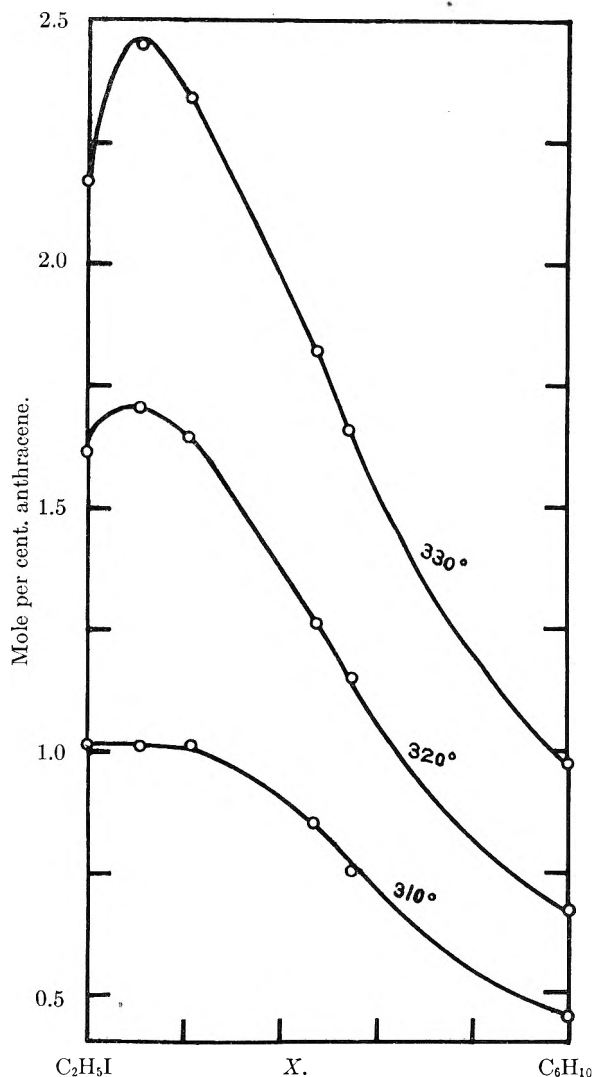


Fig. 3.—Solubility of anthracene as a function of composition of the mix-solvent: iodoethane and cyclohexene at selected temperatures.

anc. Known amounts of solute and solvent were taken in a glass ampule. The ampule was then immersed in liquid air (so as to solidify the solvent), evacuated and sealed. For noting the critical solution temperature, the sealed ampule was first warmed until the solute evanesces and then cooled rapidly to bring the solute into a state of final crystals. The ampule was again warmed this time at a rate not exceeding one-half degree per minute and the critical solution temperature was noted with a precision of $\pm 0.3^\circ$. Thus the solubility of anthracene was studied at various temperatures ranging from $20\text{--}80^\circ$.

Solubility curves were drawn plotting the logarithm of mole fraction of anthracene in solution against $1/T$. From such curves the solubility at selected temperatures was read and recorded in Table I. Figures 1-4 represent the solubility of anthracene at various temperatures as a function of the composition of the mix-solvent. The ideal solubility of anthracene was calculated from the equation

$$RT \ln x^i = -\Delta H^F(1 - T/T_m)$$

where, ΔH^F , its heat of fusion is taken as 6890 cal./mole¹¹ and T_m , its melting point as 489.5°K. The

(11) G. S. Parks and H. M. Huffman, *Ind. Eng. Chem.*, **23**, 1138 (1931).

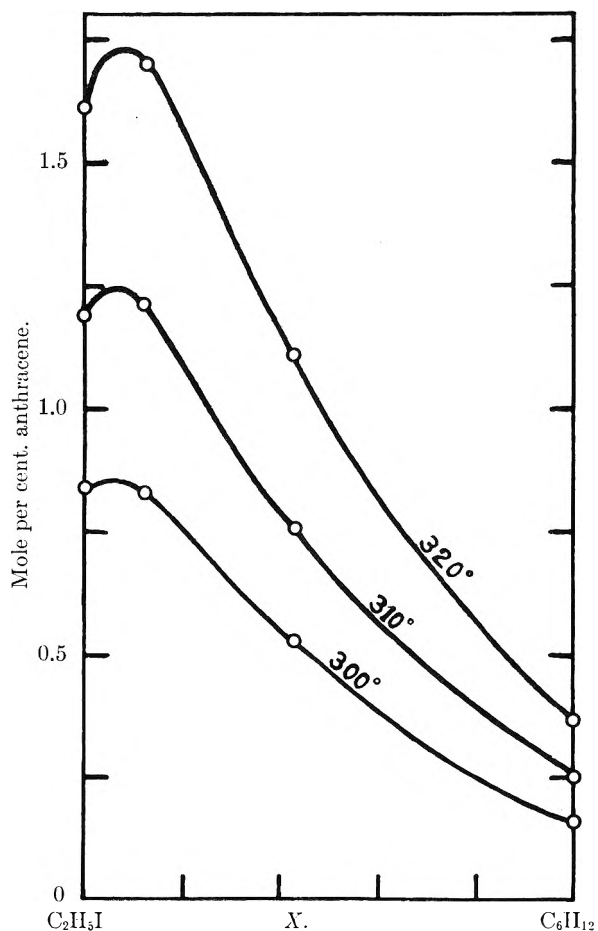


Fig. 4.—Solubility of anthracene as a function of composition of the mix-solvent: iodoethane and cyclohexane at selected temperatures.

solubility of anthracene in pure solvents along with that in an ideal solvent is furnished in Table II. A graphical representation of the results in Table II is made in Fig. 5.

TABLE II

SOLUBILITY OF ANTHRACENE IN SEVERAL ORGANIC SOLVENTS
Expressed in 100 mole fraction $C_{14}H_{10}$ (cf. Fig. 5).

T, °K.	Solvent					Ideal solvent
	Cyclo- hexane	Cyclo- hexene	Bcnzene	Iodo- ethane	Iodo- benzene	
300	0.1641	0.2985	0.7586	0.8414	1.230	1.143
305	.1855	.3715	0.9120	1.012	1.462	1.380
310	.2512	.4571	1.059	1.189	1.728	1.660
315	.3038	.5559	1.245	1.389	2.014	1.982
320	.3715	.6683	1.437	1.612	2.344	2.350
325	.4467	.8128	1.698	1.995	2.738	2.805
330	.5309	.9772	1.934	2.175	3.145	3.266
335	.6346	...	2.226	2.483	3.610	3.819
340	.7586	...	2.558	2.867	...	4.446

Results and Discussion

It is seen from Figs. 1-4 and Table I that iodoethane or iodobenzene shows cosolvency for anthracene in admixture with hydrocarbons, *e.g.*, benzene, cyclohexene or cyclohexane. The family of curves presented in Fig. 5 reveals that the solubility of anthracene in the solvents decreases in the order: iodobenzene \approx ideal solvent $>$ iodoethane $>$ benzene $>$ cyclohexene $>$ cyclohexane. Thus it is seen

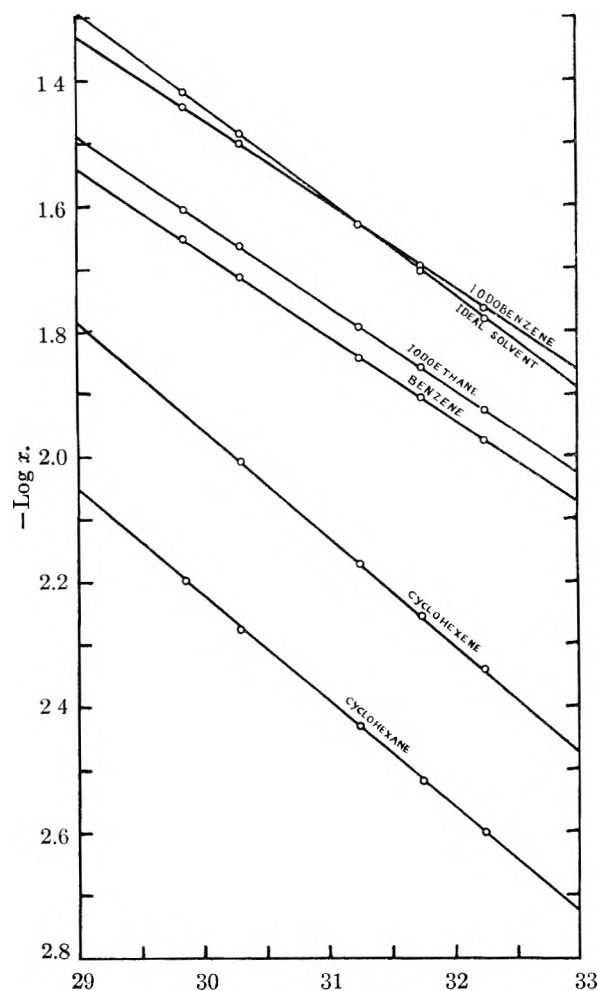


Fig. 5.—Plot of logarithm of solubility of anthracene versus $1/T$ in various organic liquids.

that iodo compounds are powerful solvents for anthracene; in fact, the behavior of iodobenzene is practically that of an ideal solvent. The point of interest here is that iodobenzene with its $\delta = 9.41$ is an ideal solvent of anthracene; an ideal solvent would have its $\delta = 9.9^{12}$ that of anthracene, according to the regular solution theory. This points to the fact that in the case of iodobenzene and anthracene there is strong interaction which ultimately results in the formation of a loose molecular complex. Solvation in this case is clearly not a matter of simple electrostatic solvation by polar molecules (for in that case iodoethane with an electric moment of 1.66 would have been a better solvent than iodobenzene with an electric moment of 1.3) but rather does it seem to depend mainly upon the Lewis acid–base interaction between solvent and solute.

Molecular complex formation between aromatics and other substances such as halogens, interhalogens, hydrogen halides, etc., through donor–acceptor mechanism has been recently well established.^{3–7} The most typical of such cases is com-

(12) J. H. Hildebrand, "Solubility," A.C.S. Monograph, 2nd edition, Reinhold Publ. Corp., New York, N. Y., 1936, p. 160; δ -value for iodobenzene comes to be only 8.35 if we calculate from the equation $\delta = 1.25P_e^{1/2}$ using $P_e = 44.6$ atm. (K. A. Kobe and R. E. Lynn, *Chem. Revs.*, **52**, 117 (1953).

plex formation between aromatics and iodine. Iodine behaves as an amphoteric substance and takes part in complex formation with many solvents through donor–acceptor mechanism. It may be assumed that this tendency of iodine to form complexes is retained in iodides, particularly, in any compound RI, where R can serve as a sink of electrons. In such compounds the iodine atom will become electrophilic and tend to make complexes with basic or aromatic solutes. Mulliken³ from various physical and chemical evidences is of the opinion that the halogens in organic halides may serve both as donors and also as acceptors of electrons. Aromatic hydrocarbons can also serve as donors through their diffuse π -electrons and also as the acceptors through their weakly acid hydrogen atoms. We therefore consider that a complex formation between anthracene and the halides used by us takes place, no matter in what way anthracene acts since the iodo compounds can act in the counterway and this lies at the root of the observed cosolvency. Mathieu's¹³ results on cosolvency of anthracene in binary mixtures, *viz.*, (a) nitrobenzene and hexane, and (b) aniline and cyclohexane are in accord with our supposition. In reaction with nitrobenzene an acceptor, anthracene, functions as a donor and with aniline, a donor, it functions as an acceptor.

That iodobenzene or iodoethane shows cosolvency for anthracene in admixture with hydrocarbons, *e.g.*, benzene, cyclohexene or cyclohexane, suggests that the behavior of these solutions is not "regular." As a matter of fact, no such mix-solvents for anthracene should be formed out of the solvents mentioned above from considerations of δ -values only (see Table III). Therefore we have attempted to explain the mechanism of cosolvency by taking into account the Lewis acid–base interaction forces and van der Waals forces.

TABLE III

SOLUBILITY PARAMETERS AT 25° ¹	
Compound	
Methylene iodide	11.8
Anthracene	9.9
Phenanthrene	9.8
Iodobenzene	9.41 ¹²
Iodoethane	9.4
Benzene	9.15
Cyclohexene	...
Cyclohexane	8.2

Mechanism of Cosolvency.—We may roughly formulate our ideas by borrowing a somewhat similar concept put forth by Winsor¹⁴ to explain solubilization. For systems as we are concerned with at present where dipole–dipole (present or induced) interaction is absent or negligible, any solute requires a balanced attraction by the solvent through the operation of van der Waals (dispersion) forces and Lewis acid–base interaction forces involving both p- and π -electrons. If we call van der Waals attraction for the solvated solute

(13) J. Mathieu, *Bull. soc. chim. belg.*, **45**, 667 (1936), through A. Seidell, "Solubilities of Organic Compounds," D. Van Nostrand Co., Inc., New York, N. Y., 3rd edition, 1941.

(14) P. A. Winsor, *Trans. Faraday Soc.*, **44**, 376 (1948).

is by the first solvent A_1 as $A_{V\bar{S}A_1}$, and the Lewis attraction as $A_{L\bar{S}A_1}$, and similarly for the second solvent A_2 , we can define the affinity ratio

$$R = \frac{A_{V\bar{S}A_1} + A_{V\bar{S}A_2}}{A_{L\bar{S}A_1} + A_{L\bar{S}A_2}} \quad (1)$$

so that R must have a definite value for any solute which when reached for any mixture of A_1 and A_2 would produce the maximum solubility under the conditions and the more the actual R departs from the ideal value (either higher or lower) the further the mixture will be from maximum solubilization. For iodobenzene, van der Waals attraction $A_{V\bar{S}A}$ is weaker in comparison with Lewis attraction $A_{L\bar{S}A}$ whereas for benzene it is just the other way round and so, a suitable mixture makes R attain the optimum value for maximum solubility. It is realized that this rough formulation is not much helpful except for qualitative understanding of cosolvency but has the merit of making it possible to express our ideas briefly.

It is clear from equation 1 that if for two solvents A_1 and A_2 , A_1 has a higher value for $R_1 = A_{V\bar{S}A_1}/A_{L\bar{S}A_1}$, i.e., $R_1 > R_2$ we have to add the cosolvent

benzene (whose van der Waals attraction for anthracene is presumably quite high) to a larger extent for A_1 than for A_2 to produce the maximum solubility. This is the explanation of why the maximum occurs at a higher proportion of benzene for iodoethane than for iodobenzene.

The other observations on cosolvency recorded in this paper are in general accord with the ideas developed above. Thus, the cosolvent power decreases in the order: benzene > cyclohexene > cyclohexane, is due to the fact as is well known from the color of iodine solutions that they form complexes with iodine in the above order, and that the van der Waals attraction for anthracene is expected to be in the above order. But the point we want to make is that though the δ -values may have their place in understanding the phenomenon of solubility in pure solvents, their applicability to mixtures will be on quite a limited field only, because in most cases solvation phenomena arising out of donor-acceptor interaction between solute and solvent would introduce complications not envisaged in the regular solution theory.

RADIATION CHEMISTRY OF MIXTURES: CYCLOHEXANE AND BENZENE-*d*₆^{1,2}

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Radiolysis of a mixture of cyclohexane and benzene-*d*₆ by 1.5 Mv. electrons yields among other gaseous products H₂, HD and D₂. The yield of HD is used to estimate the number of H atoms which disappear by a reaction associated with formation of benzene-*d*₆ polymer. It is shown that the results are consistent with an interpretation that benzene-*d*₆ actually protects excited cyclohexane from decomposition, the mechanism of protection being energy transfer. Some slight decomposition of cyclohexane by a rearrangement mechanism to yield H₂ in an elementary process appears to be sensitized by benzene-*d*₆ which has been excited to a low-lying state.

1. Introduction

In radiolysis of mixtures of benzene and aliphatic hydrocarbons under electron bombardment, decrease of gas yield below that indicated by a law of averages has been attributed to a protective effect³ of the "sponge" type⁴ by the benzene. Since only gases were measured there is a possibility, considered also by Manion and Burton,³ that what may occur in the mixture is a preferential reaction of a free atom or radical with the benzene.⁵ The functional relationship which expresses the yield $G(\text{H}_2)$ in a mixture in terms of electron fractions and mole fractions of the components may be transcribed from the form of Manion and Burton into the equally correct but more general expression

(1) A contribution from the Radiation Project operated by the University of Notre Dame and supported in part by the Atomic Energy Commission under Contract AT (11-1)-38.

(2) Abstracted from a thesis presented to the Department of Chemistry of the University of Notre Dame by W. N. Patrick in partial fulfillment of requirements for the degree of Doctor of Philosophy.

(3) J. P. Manion and M. Burton, *THIS JOURNAL*, **56**, 560 (1952).

(4) M. Burton, S. Gordon and R. R. Hentz, *J. chim. phys.*, **48**, 190 (1951).

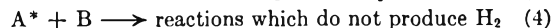
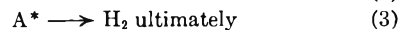
(5) One of us (M. B.) is particularly indebted to Doctors E. J. Y. Scott, J. C. Devins and M. Magat for discussions of this point.

$$G(\text{H}_2) = \frac{\epsilon(\text{A}) \cdot G(\text{H}_2, \text{A})}{1 + b_{\text{NB}}} + \epsilon(\text{B}) \cdot G(\text{H}_2, \text{B}) \quad 1$$

where

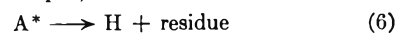
$G(\text{H}_2)$ is 100 e.v. yield of H₂ in a soln. of any composition
 $G(\text{H}_2, \text{A})$ and $G(\text{H}_2, \text{B})$ are 100 e.v. yields of H₂ in pure A and pure B, resp.

$\epsilon(\text{A})$ and $\epsilon(\text{B})$ are the corresponding electron fractions
 n_{B} is the mole fraction of B, and b is a constant resultant from the scheme

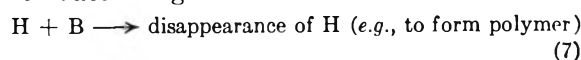


For this scheme $b = k_4/k_3$ and reaction 4 should be (over-all) one order higher in B than reaction 3.

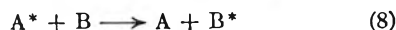
Reaction 4 includes the possibility that H atoms produced, for example, from the reaction



react according to



as well as the possibility of the simple energy transfer reaction



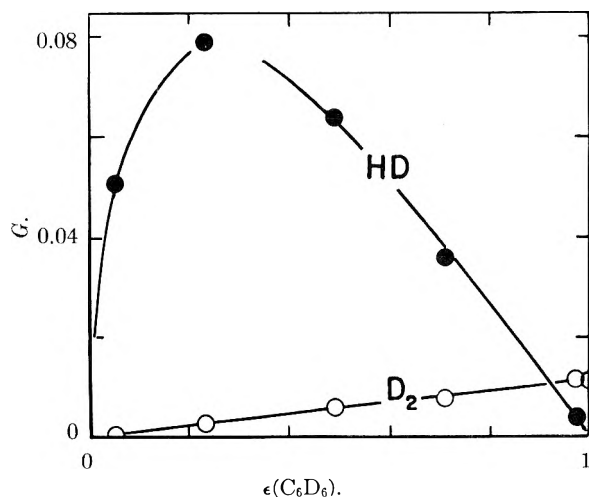
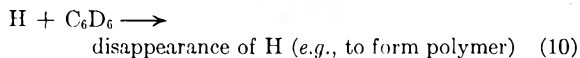
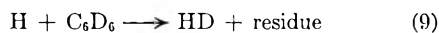


Fig. 1.—Variation of 100 e.v. yields of HD and D₂ with electron fraction of benzene-d₆ in a mixture with cyclohexane.

For reaction 8 to occur it is required according to the simple excited-molecule theory of liquids^{3,6,7} that $E_A > E_B$ where the reference is to the lowest excitation levels (not necessarily optically attainable) of A and B, respectively.

Although Manion and Burton⁵ established by logical argument that reaction 8 was in reality responsible for the apparent protection of aliphatic hydrocarbons by benzene, there has been no direct experimental verification of the conclusion. Recently, however, studies of the radiolysis of a liquid mixture of propionaldehyde and benzene-d₆ have indicated that for the reactions



the ratio $k_{10}/k_9 \gg 7.3$.

In this paper the value of k_{10}/k_9 is employed in a study of the 1.5 Mv. electron-induced radiolysis of a mixture of cyclohexane and benzene-d₆ to estimate the portion of the general H₂ disappearance process 4 which is in reality a contribution of reaction 7 (the equivalent of 10) to reaction 4 and, thus, further to demonstrate the reality of protection in radiolysis of liquid mixtures. Such a test was not possible in the previous work,³ where hydrogen contribution from the benzene was unlabeled.

2. Experimental

2.1. Chemicals.—Benzene-d₆ employed in this work was a portion of the same sample used in the propionaldehyde study.⁸ It had a deuterium content of 98.5% corresponding to 8.4 mole per cent. of C₆D₆H impurity.

A 500-g. sample of Fisher Scientific Co. cyclohexane, C.P., was distilled in a 50-theoretical-plate column and the middle one-third boiling at 80.4° at a pressure of 74.54 cm. was retained; n_D^{25} 1.4231; "I.C.T.," n_D^{25} 1.4266.

2.2. Cells and Cell Filling.—The irradiation cells were the same as those used in previous work.⁸ The windows were ground glass, 5 mils thick and 0.9 cm. in diameter.

Reagents were well dried before introduction into the cells. Cyclohexane was stored over sodium wire. Ben-

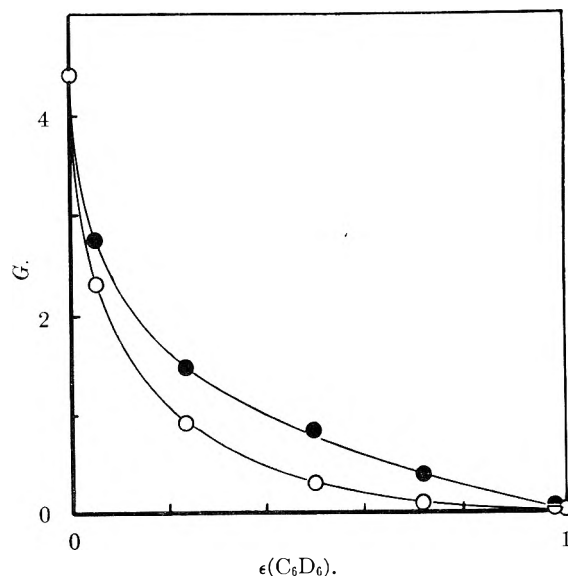


Fig. 2.—Variation of 100 e.v. yield of hydrogen with electron fraction of benzene-d₆ in mixtures with cyclohexane: O, H₂ yield actually observed; ●, calculated maximum primary yield of hydrogen.

zene-d₆ was treated as described for the propionaldehyde mixtures.⁹

Individual components of the mixtures were introduced into the cells by syringe-operated pipets. Micropipets were used for the accurate measurements required with mixtures. A check, made by filling the cells under vacuum and distilling the contents through a plug of P₂O₅ to remove all water, showed no noticeable change in the results upon irradiation.

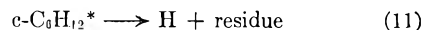
2.3. Electron Bombardments.—Electron bombardments were made with 1.5 Mv. electrons from an HVEC Van de Graaff generator precisely as described for the work with propionaldehyde mixtures.⁸ Corrections and errors were as previously described.

2.4. Product Analyses.—Analyses of the product gases were also as previously described except that the separation was into gases non-condensable at -196° and -120° (the latter instead of -95°). The former consisted of hydrogen and methane, the latter of ethane, ethylene and acetylene. Analysis was by mass spectrometry.⁹

2.5. Reliability of Data.—For reasons already given,⁸ determinations of $G(\text{H}_2)$ and $G(\text{HD})$ were accurate to better than 5% while measurements of $G(\text{D}_2)$ had much lower accuracy. The hydrocarbons including ethane, ethylene and acetylene were determined with accuracy less than 5% and, in some cases, with accuracy, no better than the D₂ values. Individual values for the hydrocarbons are not reported since they are not germane to the purposes of the present work. Results were consistent with the findings of Manion and Burton.³

3. Results and Discussion

Results on H₂, HD and D₂ are summarized in Figs. 1 and 2. Figure 1 shows that as the concentration of C₆D₆ is increased the 100 e.v. yield of HD first increases and then falls. Free H atoms result from the reaction



the contribution of which decreases with increasing electron fraction of C₆D₆. Yield of HD comes essentially from reaction 9. Since $G(\text{D}_2)$ from pure C₆D₆ is only 0.0113,¹⁰ contribution of a reaction of D atoms on cyclohexane can be neglected. Consump-

(6) M. Burton, C. L. Magee and A. W. Samuel, *J. Chem. Phys.*, **20**, 760 (1952).

(7) A. H. Samuel and J. L. Magee, *ibid.*, **21**, 1080 (1953).

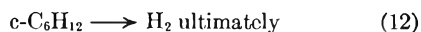
(8) W. N. Patrick and M. Burton, *This Journal*, **58**, 424 (1954).

(9) The authors are indebted to Prof. R. R. Williams and Mr. H. S. Weisbecker for their cooperation in these analyses.

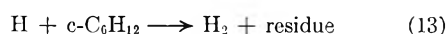
(10) S. Gordon and M. Burton, *Discs. Faraday Soc.*, No. 12, **88** (1952).

tion of H atoms in reaction 10 has been shown by previous work not to exceed 7.3 times HD production. Thus, if $8.3 \times G(\text{HD})$ is added to $G(\text{H}_2)$ as in Fig. 2, we obtain a curve which would appear to represent the maximum possible 100 e.v. yield of primary reaction giving either H_2 or H atom. Obviously, this curve departs markedly from a law of averages result (*i.e.*, a straight line) in a manner clearly explicable on the basis of a sponge-type protection mechanism⁴ in which benzene- d_6 protects cyclohexane by an energy transfer process such as reaction 8.

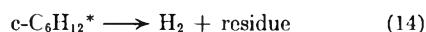
The equivalent in this case of the general reaction 3 is the over-all reaction



A portion of the H_2 yield so shown may be produced *via* the reaction



The remainder of the H_2 may be formed by a rearrangement mechanism in a single elementary process



The total $G(\text{H}_2)$ may be represented as $G(\text{H}_2, 12)$, *i.e.*, $G(\text{H}_2) \equiv G(\text{H}_2, 12) = G(\text{H}_2, 13) + G(\text{H}_2, 14)$. If the ratio $G(\text{H}_2, 13)/G(\text{H}_2, 14)$ is constant one would expect that, with $N(c\text{-C}_6\text{H}_{12})$ and $N(\text{C}_6\text{D}_6)$ as the mole fractions, the ratio

$$\frac{G(\text{H}_2)/N(c\text{-C}_6\text{H}_{12})}{G(\text{HD})/N(\text{C}_6\text{D}_6)} = \rho \quad 2$$

would be a constant since it seems to have the form of a ratio of rate constants. The values of ρ for various mole fractions of C_6D_6 are shown in Table II.

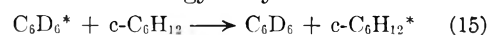
TABLE II

VALUES OF ρ (DEFINED AS IN EQUATION 2 AS A FUNCTION OF MOLE FRACTION OF BENZENE- d_6 IN MIXTURES WITH CYCLOHEXANE)

$N(\text{C}_6\text{D}_6)$	0.051	0.234	0.492	0.711	0.978
ρ	2.6	4.1	5.0	6.3	39

There is a suggestion in the regular increase of ρ with benzene- d_6 concentration that at such higher concentrations the yield of H_2 is favored by a reaction not involving H atoms for it would be unlikely that reaction 13 is catalyzed by C_6D_6 . The simplest alternative explanation is that reaction 14 becomes increasingly important at high C_6D_6 concentrations. This unexpected, but not astonishing, conclusion may be understood in terms of energy transfer from C_6D_6 to $c\text{-C}_6\text{H}_{12}$.

According to the views heretofore expressed on the resistance of benzene to high-energy radiation, stabilization occurs by a series of internal-conversion and collisional-deactivation processes until the benzene is finally at an energy level too low for decomposition. While this level can be at 4.8 e.v., it appears likely that excited benzene will degrade to an even lower state, *e.g.*, at 3.6 e.v.¹¹ Excited C_6D_6^* in such a low triplet state is very persistent. It may transfer its energy to cyclohexane



and produce a (triplet) state which possesses insufficient energy for a free-radical split but may decompose by rearrangement into H_2 plus a triplet residue, as by reaction 14. This radiosensitization reaction is similar to one offered in explanation of the variation of $G(\text{C}_2\text{H}_6)$ in propionaldehyde-benzene- d_6 mixtures.⁸

The linear relationship between $G(\text{D}_2)$ and $\epsilon(\text{C}_6\text{D}_6)$ in Fig. 1 would tempt speculation as to the mechanism of D_2 formation. This is quite unlike the results of Gordon and Burton on mixtures of benzene and benzene- d_6 .¹⁰ In the latter case, unlike the present work, the absolute reliability of D_2 determinations was of the same order as that of HD and H_2 determinations. In spite of the clearly shown straight line we hesitate to draw conclusions regarding the mechanism of D_2 formation in radiolysis of benzene- d_6 : if the reality of the straight line were accepted it would be consistent with an exclusive rearrangement mechanism for production of D_2 but inconsistent with other work.¹⁰

(11) *Cf.* H. Stull, *J. Chem. Phys.*, **17**, 295 (1949).

RADIATION CHEMISTRY OF MIXTURES: PROPIONALDEHYDE AND BENZENE- d_6 ^{1,2}

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Received January 15, 1954

In liquid propionaldehyde bombarded with 1.5 Mv. electrons 100 e.v. yields of gaseous products are H₂, 1.26; CO, 1.60; C₂H₄, 1.12; CH₄, 0.114; C₂H₆, 0.34; C₃'s, traces. In liquid benzene- d_6 100 e.v. yields are C₂D₂, 0.014; D₂, 0.0114. In liquid mixtures protection of C₂H₅CHO by C₆D₆ is not expected (and not found) because the lowest excited state (presumably triplet) of the former lies lower than that of the latter. Yields of CH₄ and C₂H₄ are linear functions of electron fraction of propionaldehyde. Yields of H₂ and HD are used for approximate calculation of relative rates of H + C₂H₅CHO → H₂ + residue (8), H + C₆D₆ → HD + residue (9) and, H + C₆D₆ → polymer (10): $k_{10}/k_9 > 7.3$; $k_8/k_9 \sim 2.7$ at room temperature. The k_{10}/k_9 data are consistent with an interpretation involving "hot" H atom reactions. The C₂H₆ yields are interpreted as evidence of a rearrangement decomposition of C₂H₅CHO sensitized by excited benzene- d_6 .

1. Introduction

In radiolysis of liquid mixtures of benzene and aliphatic hydrocarbons benzene appears to afford a protective effect, at least so far as the appearance of gaseous product is concerned.³ It has been shown that this protection is consistent with a mechanism which involves energy transfer to the benzene molecules and energy dissipation in the benzene itself.⁴ The latter process may involve a rapid degradation of energy into thermal energy in successive transfers between adjacent benzene molecules. The high efficiency of such successive "down-hill" transfers is attributed to the relatively small distance between successive vibrational states of excited benzene.⁵ In spite of the formally very attractive features of this picture,⁶ it has been apparent from the very beginning that other processes, perhaps entirely chemical in their nature,⁴ may be responsible for the seeming protection in these cases.⁷ A great difficulty in consideration of the previous cases studied has been an essential inability to establish unequivocally the sources of the gaseous products observed. In the work here reported on mixtures of propionaldehyde and benzene- d_6 , the source of any H atoms or H₂ molecules must be propionaldehyde. Furthermore, it appears (as was expected on theoretical grounds) that H atom production in radiolysis of such a mixture is a linear function of the electron fraction⁴ of propionaldehyde. Thus, the origins of H₂, HD and D₂ in the gaseous mixtures may be examined and their relative yields can be subjected to reasonable interpretation.

2. Experimental

The methods employed were similar to those described in previous studies of the radiation chemistry of mixtures.^{4,5}

(1) A contribution from the Radiation Project operated by the University of Notre Dame and supported in part by the Atomic Energy Commission under Contract AT(11-1)-38.

(2) Abstract from a thesis presented to the Department of Chemistry of the University of Notre Dame by W. N. Patrick in partial fulfillment of requirements for the degree of Doctor of Philosophy.

(3) Cf. C. S. Schoepfle and C. H. Fellows, *Ind. Eng. Chem.*, **23**, 1396 (1931); M. Burton, *Proc. Conf. Nuclear Chem., Chem. Inst. Canada*, 179 (1947).

(4) J. P. Manion and M. Burton, *THIS JOURNAL*, **56**, 560 (1952).

(5) S. Gordon and M. Burton, *Discs. Faraday Soc.*, No. 12, 88 (1952).

(6) Cf. J. L. Magee, *THIS JOURNAL*, **56**, 555 (1952).

(7) At this time, one of us (M. B.) wishes to acknowledge stimulating discussions on this point, with Dr. E. J. Y. Scott, with Dr. J. C. Devins, and most recently with Dr. M. Magat at the Faraday Society Radiation Chemistry Conference at Leeds, England, in April, 1952.

2.1. Chemicals.—Two liters of Merck C.P. benzene, thiophene-free, was purified in three successive recrystallizations, with rejection of approximately one-quarter at each freezing. The residue, distilled at atmospheric pressure in a 50-theoretical-plate column, yielded a middle third with b.p. 80.0° at 74.88 cm., retained for subsequent use; n_D^{25} 1.4976, d_{25} 0.8733; Soffer and De Vries,⁸ n_D^{25} 1.49748, d_{25} 0.8734 ± 0.0002.

Benzene so purified and subsequently kept dry over sodium was employed in synthesis of benzene- d_6 according to the method of Ingold, Raisin and Wilson⁹ using five successive equilibrations in 51 mole per cent. D₂SO₄ in heavy water.¹⁰ The product had a deuterium content of 98.5% corresponding to 8.4 mole per cent. C₆D₅H impurity.

A 500-g. sample of Eastman Kodak propionaldehyde, boiling range 47.8–50.5°, distilled in a 50-theoretical plate column in an atmosphere of nitrogen, yielded a middle fraction with b.p. 48.1° at ~769 mm. pressure.

2.2. Cell Filling.—Reagents were carefully dried before introduction into irradiation cells. Benzene- d_6 was dried over barium oxide overnight and then vacuum distilled into a flask containing phosphorus pentoxide. There it was shaken and permitted to stand 15 minutes and then vacuum distilled and sealed into small storage flasks of 1.5–3 ml. capacity. Propionaldehyde collected under a nitrogen atmosphere was thoroughly degassed on a vacuum line, distilled into a tube containing Drierite, and sealed off.

Since propionaldehyde is oxidized on exposure to air, it cannot be transferred into cells by syringe-operated pipets, as previously described.⁴

Instead, it was vacuum distilled and sealed in a variety of amounts into small vessels made of 2, 4 and 6 mm. tubing, equipped with break-off seals. The level of the liquid in each tube was marked with a file, so that when emptied the exact volume of the liquid previously contained in the tube could be determined by simple mercury-weighting technique. A single such tube was sealed onto the vacuum line together with an irradiation cell. Benzene- d_6 was measured out with a micropipet into a tube joined to the vacuum line by means of a ground glass joint⁴ and vacuum-distilled into the irradiation cell through a plug of phosphorus pentoxide, which was then sealed off. The benzene- d_6 was thoroughly degassed. Then, the break-off seal on the propionaldehyde tube was broken and the propionaldehyde was distilled into the cell. Thus, mixtures of known composition were introduced into irradiation cells without atmospheric contamination.

2.3. Electron Bombardments.—All irradiations were made at 1.5 Mv. and currents ranging from 1.0 to 2.1 μ amp. on a type A, model S HVEC Van de Graaff generator. The cells were the identical ones used by Gordon and Burton.⁵ The windows were ground glass, 5 mils thick and 0.8 cm. in diameter. Techniques of irradiation, current measurement and calculation of energy expenditure in the window have been described by Hentz and Burton.¹¹ At the volt-

(8) H. Soffer and T. De Vries, *J. Am. Chem. Soc.*, **73**, 5817 (1951).

(9) C. K. Ingold, C. G. Raisin and C. L. Wilson, *J. Chem. Soc.*, 915 (1936); A. P. Best and C. L. Wilson, *ibid.*, 242 (1946).

(10) The heavy water, furnished by the Atomic Energy Commission, had a deuterium content of 98.5%.

(11) R. R. Hentz and M. Burton, *J. Am. Chem. Soc.*, **73**, 532 (1951).

age employed the correction for energy loss in the window was 3%. The accuracy of determination of the number of coulombs flowing into the cell is estimated at $\pm 2\%$.

During irradiation, cells were kept at approximately room temperature by an air stream directed so that both window and walls were cooled.

Data on yield are reported in the usual G units; *i.e.*, number of molecules produced or converted per 100 e.v. of energy expended in the irradiated material.

2.4. Product Analyses.—After irradiation, the gaseous contents of each cell were divided into fractions by conventional methods: a first fraction non-condensable at -196° (hydrogen, methane, carbon monoxide) and a second depending on the liquid examined. For pure benzene-*d*₆, the second fraction included non-condensables at -120° (ethylene, acetylene); if propionaldehyde were present, the second fraction was taken at -95° and also included ethane and C₂ hydrocarbons, of the latter of which there was a small amount. The pressure of each fraction was determined in a calibrated volume on a Saunders-Taylor apparatus.¹²

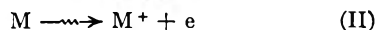
The first fraction was collected in a bulb with stopcock closure, the second in a tube equipped with a break-off seal. Both fractions were analyzed on a Consolidated Model 21-103A Mass Spectrometer.¹³

2.5. Reliability of Data.—Determinations of G for CO, CH₄, H₂ and HD, as well as gases collected at -95° , were accurate within 5%. Because of the large volume of gases produced in the irradiation of propionaldehyde and of its mixtures, irradiations were only for short periods, 75 to 181 sec. In such intervals, the amount of D₂ production is less than 0.3% of the gas collected over liquid nitrogen. Therefore, values of $G(D_2)$ in the mixtures have low accuracy. However, this fact does not decrease the significance of the other results.

The mass spectrometer indicated the presence of C₂ hydrocarbons in the -95° fraction from irradiated mixtures, by peaks 0.5–10 divisions in height in the 39 to 43 mass range. Such peak heights are to be compared with a 2,176 division height for mass 28. A reported yield of C₂ hydrocarbons represents the difference between a calculated value for C₂ hydrocarbons and the total gas collected at -95° . Strictly speaking, it merely represents a trace of C₂ hydrocarbons in the fraction; the values have little absolute reliability.

3. Results and Discussion

3.1. Theory of Radiolysis of Liquids.—In previous discussions of the behavior of mixtures,^{4,5} the mechanism of the decomposition has included consideration of the chemical consequences of two separate primary steps.



Thus, it has been necessary to discuss excitation and ionization transfer as well as possible chemical decomposition¹⁴ of ionic species. Recently, however, consideration of the phenomena involved in the radiolysis of water has led Samuel and Magee¹⁵ to the conclusion that in that case the back reaction $H_2O^+ + e \rightarrow H_2O^\dagger$ takes place in a time short in comparison with 10^{-13} sec. The excited species H₂O[†] so produced is in a higher state than the excited species produced as in reaction I and may consequently enter into characteristically different reactions.

It is an important feature of the Samuel-Magee picture that their model is more likely to be correct

(12) K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, **9**, 618 (1941).

(13) The authors express their grateful appreciation to Prof. R. R. Williams and Mr. H. L. Weisbacker for their cooperation in these analyses.

(14) Cf. M. Burton, *Ann. Rev. Phys. Chem.*, **1**, 113 (1950); *J. Chem. Educ.*, **28**, 404 (1951).

(15) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

if the liquid has low dielectric constant.¹⁶ Thus, for organic liquids especially, instead of reaction II, one should write the operationally more correct equation



where M[†] represents a highly excited state which may differ in chemical activity from M*. Arguments against such theory have been presented particularly by Platzman.¹⁷ However, it is unlikely that there will be any definitive settlement of the question for some time to come. As a matter of convenience we shall use the I-II' (rather than the I-II) picture. It will be seen to contribute features of simplicity to interpretation of the results.

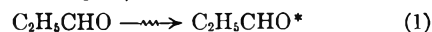
3.2. Propionaldehyde.—Table I summarizes some results of experiments on bombardment of pure liquid propionaldehyde. It was not convenient to separate either such gaseous products as were non-volatile above -95° or possible liquid products. However, one sample of the irradiated liquid, distilled from the exposure vessel under vacuum, left an extremely small residue of white needle-like crystals inadequate for identification.

TABLE I
GAS YIELDS IN RADIOLYSIS OF LIQUID PROPIONALDEHYDE
WITH 1.5 MV. ELECTRONS AT $\sim 1 \mu$ AMP.

Energy input, 10 ²⁰ e.v.	4.79	7.41
G (total gas)	4.53	4.61
G (H ₂)	1.24	1.28
G (CH ₄)	0.113	0.116
G (CO)	1.61	1.58
G (C ₂ H ₄)	0.330	0.356
G (C ₂ H ₆)	1.08	1.15
G (C ₂ 's) approx.	0.052	0.051
G (CO ₂)	0.110	0.077

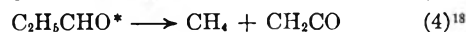
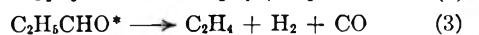
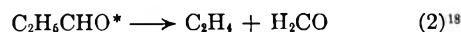
The 100 e.v. yield of carbon monoxide is greater than those either of ethane or of hydrogen, which are not greatly different. It is much less than the sum of the two. Evidently, some decomposition products do not involve carbon monoxide as an ultimate product.

For understanding of the radiolytic behavior of liquid propionaldehyde, we write



where, generally, C₂H₅CHO* refers to a whole spectrum of excited species which may react differently and which may proceed by internal conversion from high excited states to lower ones.

Production of ethylene and methane may be by reactions of the type



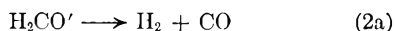
Some of these reactions (specifically indicated by reference) and others not here included have been considered by Blacet and Pitts¹⁸ in their study of

(16) Cf. M. Burton, J. L. Magee and A. H. Samuel, *ibid.*, **20**, 760 (1952).

(17) R. L. Platzman, Report of Highland Park Conference on Basic Mechanisms in Radiobiology, National Research Council, 1953, Publication 305, p. 1.

(18) F. E. Blacet and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **74**, 3382 (1952).

the photolysis of propionaldehyde vapor. Reaction 3 is of a type ordinarily discounted on the basis of the principle of microscopic reversibility. However, in this connection we may extend an idea employed by Blacet and Pitts in their consideration of the behavior of the free HCO radical formed from propionaldehyde. If the H₂CO of reaction 2 is formed with sufficient excess energy (a very probable event in radiation chemistry) it may dissociate immediately subsequent to its formation by the reaction



substantially as if reaction 3 had occurred in a single elementary process. If all the H₂CO were to decompose this way, the appearance would be as if reaction 2 had not occurred at all and as if reaction 3 were the only process for production of ethylene. Evidence for just such a situation is given in section 3.5.2.

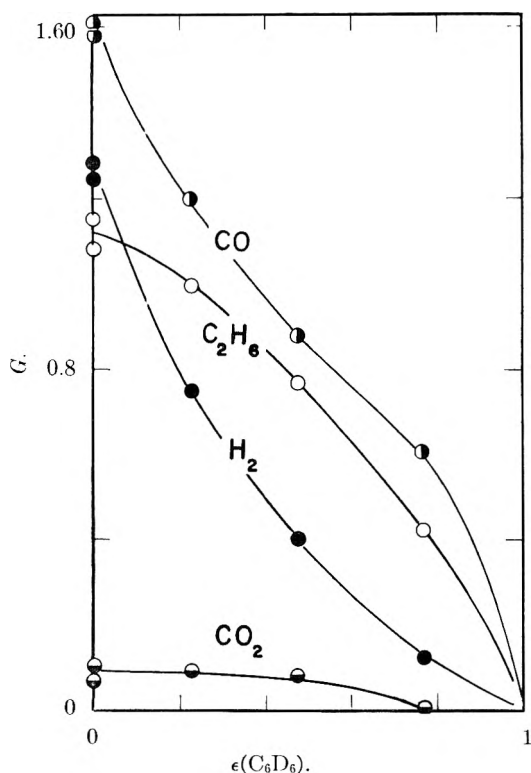
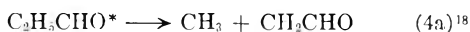


Fig. 1.—Variation of 100 e.v. yields of some gaseous products with electron fraction of C₆D₆ in a mixture with propionaldehyde.

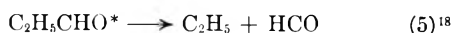
Reaction 4 may also have its free radical counterpart which can be written partially as



followed by



Contrary to the analytical results of Garrison and Burton¹⁹ which indicate that in photolysis of the vapor the only significant free-radical decomposition of the excited species is by the reaction

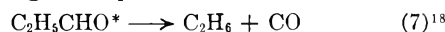


recent results of Dodd²⁰ on the effect of temperature in the photolysis (in addition to those of Blacet and Pitts¹⁸) indicate that there are two simultaneous modes of decomposition of approximately the same kinetics and magnitude. Thus, reactions 4a and 4b are not ruled out. However, choice between ultimate-molecule and free-radical mechanisms for radiolytic production of methane is not an objective of this paper.

Reaction 5 is offered as a feature of the radiolysis because it is very probably the precursor of H atoms via the reaction



In sections 3.5.1. and 3.5.2 it is concluded that there are two sources of hydrogen production: reaction 3 and a reaction in which atomic H seems to be produced in a primary chemical act. It will be seen that ethylene is produced exclusively by reaction 3 or an equivalent sequence and that, in mixtures at least, ethane is probably also produced by a low-energy rearrangement process



In this case the C₂H₅CHO* is probably in an optically unattainable state too low for free-radical decomposition.²¹ Decomposition of aldehyde into alkane plus carbon monoxide is almost thermo-neutral.

Carbon dioxide production was unexpected. It has not been reported in photolysis. The small yield here reported and also found in the mixtures, may represent either some complicated reaction, which is doubtful, or a trace of CO₂ impurity present in the propionaldehyde originally. Mass spectrometric analysis of the original sample showed a barely discernible 44 peak. No analysis was performed on the vapor above the original sample.

3.3. Benzene-d₆.—Radiolysis of liquid benzene-d₆ at room temperature gave results substantially the same as those hitherto found.⁵ The earlier values for benzene-d₆ of slightly greater deuterium content were $G(\text{H}_2) = 0$, $G(\text{HD}) = 0.0004$, $G(\text{D}_2) = 0.0113$; in this work the values were $G(\text{H}_2) = 0.0001$, $G(\text{HD}) = 0.0006$, $G(\text{D}_2) = 0.0114$.

3.4. Mixtures of Propionaldehyde and Benzene-d₆.—All the results of the investigation of mixtures are shown in Figs. 1–3 inclusive. While the yields of methane and of ethylene are very nearly a linear function of the electron-fraction⁴ of propionaldehyde, the situation is different for the other products. Yields of ethane and of hydrogen (Fig. 1) depart regularly from a linear relationship and in opposite directions. Yield of carbon monoxide is not a simple function of propionaldehyde concentration. Attempts to obtain a material balance on the basis of gas analyses alone (which is all that was studied) proved futile. Among the several conclusions, the most obvious speculation is that non-volatile products, undetected by our methods, have been formed.

On the other hand, the linear nature of the methane and ethylene yields (Fig. 2) suggests that they

(20) R. E. Dodd, *J. Chem. Soc.*, 1878 (1952).

(21) For discussion of the contribution of low-lying states in electric discharge processes cf. H. Wiener and M. Burton, *J. Am. Chem. Soc.*, **75**, 5815 (1953), and also J. C. Devins and M. Burton, *ibid.*, **76**, 2618 (1954).

(19) W. M. Garrison and M. Burton, *J. Chem. Phys.*, **10**, 730 (1942).

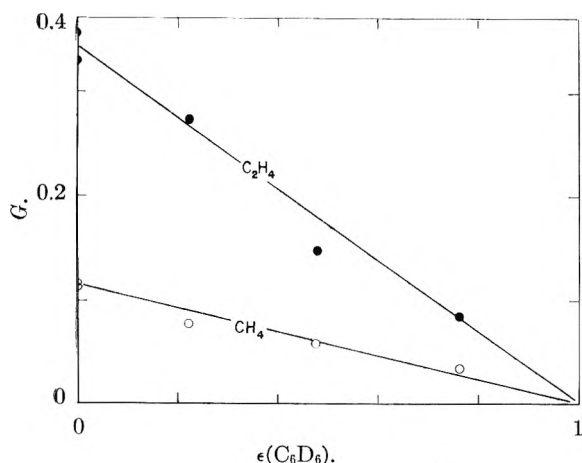
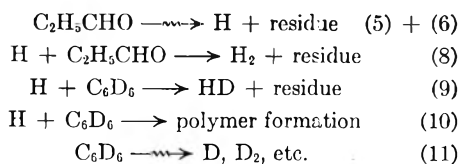


Fig. 2.—Variation of 100 e.v. yields of methane and ethylene with electron fraction of benzene- d_6 in mixture with propionaldehyde.

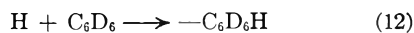
truly reveal a rather simple aspect of these results, namely that the probability of electronic excitation and of consequent primary chemical processes in the propionaldehyde is proportional to its electron fraction.

3.5. Mechanism in Mixtures.—This system is too complicated for real analysis of mechanism. Nevertheless, interpretation of the HD yields in relation to D_2 , H_2 and polymer formation^{4,22} requires consideration of the following (purely formal) reaction scheme, its consequences and some of its details.



Reaction 10 is introduced in a formal sense to represent the class of reaction in which free H atom disappears without formation of gaseous product. There is evidence in the case of liquid benzene^{4,22} that the disappearance is accompanied by polymer formation. It is not necessary to the argument that the same polymer be formed in a propionaldehyde mixture but it is a reasonable presumption that the first step in the disappearance reaction is the same in the mixture as in pure benzene.

According to Melville and Robb,²³ reaction of H atom with benzene in the vapor state has low activation energy. Their method (*i.e.*, test for survival of H atoms with a molybdenum oxide mirror) did not distinguish between addition and H-atom extraction as the modes of reaction. However, earlier work of Forbes and Cline²⁴ supports the interpretation that addition occurs as a first step. One interpretation of our results is that the reaction



is a common step in the path of over-all reactions 9

(22) For polymer formation in radiolysis of benzene, *cf.* W. N. Patrick and M. Burton, *J. Am. Chem. Soc.*, **76**, 2626 (1954).

(23) H. W. Melville and J. C. Robb, *Proc. Roy. Soc. (London)*, **A202**, 181 (1950).

(24) G. S. Forbes and J. E. Cline, *J. Am. Chem. Soc.*, **63**, 1713 (1941).

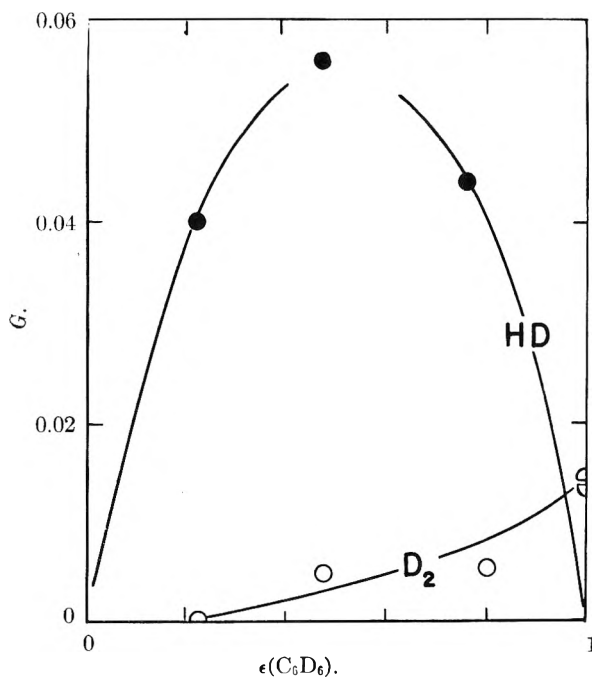
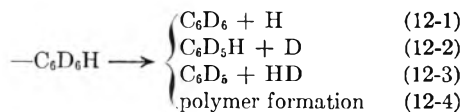
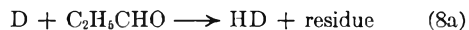


Fig. 3.—Variation of 100 e.v. yields of D_2 and HD with electron fraction of benzene- d_6 in a mixture with propionaldehyde.

and 10. The fate of the $-C_6D_6H$ radical may be written variously as



According to Schiff and Steacie²⁵ the exchange reaction of D atoms (produced in a Wood-Bonhoeffer tube) with benzene occurs with collision yield somewhat greater than the disappearance of H atoms in the analogous reaction between H and C_6D_6 (*cf.* Melville and Robb²⁸). We must accordingly consider the possibility that HD may result not only from reaction 9 but also from the reaction



In sections 3.5.1–3.5.3 we shall examine the extreme possibilities that (i) all HD is formed *via* reaction 9 and (ii) all HD is formed *via* reaction 8a.

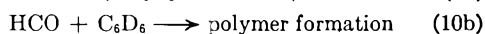
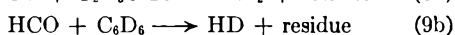
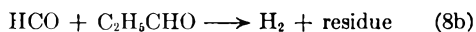
Assumption ii of the previous paragraph is equivalent to acceptance of the statement that reaction 12-2 occurs with high probability compared with reaction 12-1. The work of Schiff and Steacie²⁵ does not inherently support such an interpretation. Exchange of D with C_6H_6 *via* $-C_6H_6D$ is more probable than exchange of H with C_6D_6 *via* $-C_6D_6H$, for the former process involves a split of a C–H bond, which has a higher zero-point energy than the C–D bond, whose split is involved in the second process. Thus, it is altogether possible, even in view of the results of Schiff and Steacie, that reaction 12-2 does not occur to an important extent in this work. In such event practically exclusive occurrence of (12-1), as

(25) H. I. Schiff and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1 (1951). The exchange reaction is measured in this work in terms of D atoms introduced into the benzene. The mechanism is not indicated and may even involve an extraction reaction (*cf.* reaction (12-3)) as an intermediate step.

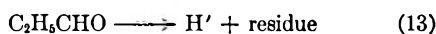
compared with (12-2), would have the appearance of mere scattering of H atoms by C_6D_6 .

The other fates left open to the $-C_6D_6H$ radicals are represented by reactions 12-3 and 12-4. Reaction 9 is thus the combination of processes 12 and 12-3 while reaction 10 includes (12) and (12-4). The fact that production of H_2 departs negatively from a linear relationship to electron-fraction of propionaldehyde is consistent with such reactions.

Most of the previous discussion in this section is without bearing on this work if H atoms are not formed in radiolysis of propionaldehyde and if the important free radical reactions, similar in their consequences to (8), (9) and (10), are



However, the results of Blacet and Pitts¹⁸ on photolysis of propionaldehyde vapor support the interpretation that reaction 6 is of increasing importance with increase of energy supplied to the propionaldehyde (*i.e.*, with decreasing wave length in their case) and that reaction 8 occurs. If reaction 6 occurs, as suggested by Blacet and Pitts, it must be as a "hot" radical process before the first collision; *i.e.*, 10^{-9} sec. in their work. They offer no evidence for reaction 8b; *i.e.*, according to their work in the gaseous state $r_6 > r_{8b}$, where the r 's are rates. Under the more energetic conditions of radiation chemistry, it consequently appears proper to write



as an important process, which may be primary or may include reactions 5 and 6, with the H atom actually formed with excess energy. Reaction 8b would not occur in the presence of benzene if it does not occur in its absence. According to (9b) and (10b) the function of the benzene is to remove HCO before it decomposes by (6); *i.e.*, in the liquid state r_{9b} and $r_{10b} > r_6$. However, a necessary corollary assumption would be that under such circumstances HCO could react with propionaldehyde by (8b); *i.e.*, in the liquid state $r_{8b} > r_6$. This conclusion is not necessarily inconsistent with the contrary one regarding the relative rates in gases. However, it may be emphasized that reaction 13 probably occurs with such rapidity that reaction 6 need not be considered at all as an intermediate. Thus, while the possibility of reactions 8b, 9b and 10b must be considered, the probability is that they are not responsible for the effects observed. However, the possibility that they do occur in the liquid state does require experimental test.

Other assumptions of reaction mechanisms of increasing complexity may be considered. In general, they depart more and more from our knowledge of these cases. In sections 3.5.1 and 3.5.2 it will appear that the facts are consistently and adequately interpreted without inclusion of (8a), (8b), (9b), (10b) or more complicated mechanisms.

This study is primarily concerned with the establishment of the rate of reaction 10 relative to the rates of other easily measurable reactions of H atom. In particular, we should like to determine the ratio k_{10}/k_9 and come to some conclusions re-

garding the relative importance of reactions 8 and 8a.

3.5.1. Ratio k_{10}/k_9 .—The ratio k_{10}/k_9 is calculated according to the following argument, in which r has the general significance of rate and Y is a yield.

$$\frac{k_{10}}{k_9} = \frac{r_{10}}{r_9} = \frac{Y(\text{polymer from (10)})}{Y(\text{HD from (9)})} \quad 1$$

The term $Y(\text{polymer from (10)})$ is vague and is better equated to the H atoms which react according to (10). As for $Y(\text{HD from (9)})$, we shall adopt assumption (1) in section 3.5, namely, that 12-2 does not occur to any important extent. Furthermore, the D atoms coming directly from radiolysis of benzene itself, *via* reaction 11, can make only a negligible contribution to HD yield in reaction 8a because $G(D_2)$, which includes D_2 formed both *via* free-atom and ultimate-molecule processes, in pure benzene- d_6 totals only 0.0114. We write

$$\frac{k_{10}}{k_9} = \frac{G(H_2 \text{ unaccounted for})}{G(HD)} \quad 2$$

where $G(H_2 \text{ unaccounted for})$ is simply the decrease in H_2 yield below that expected on the law of averages after provision is made for such H atoms as may have reacted to give HD. Thus

$$\frac{k_{10}}{k_9} = \frac{G(H_2)_{\text{pure}} \times \epsilon(\text{prop}) - G(H_2) - G(HD)}{G(HD)} \quad 3$$

where $G(H_2)_{\text{pure}}$ is the 100 e.v. yield of H_2 from pure propionaldehyde. The values for the three concentrations studied are

$\epsilon(C_6H_6)$	0.222	0.477	0.762
k_{10}/k_9	4.8	3.6	3.0

The calculated curve taken from the H_2 and HD curves of Figs. 1 and 3, respectively, extrapolates to $k_{10}/k_9 > 7.3$ at $\epsilon(C_6D_6) = 0$. A simple interpretation of this result is that the smaller values of k_{10}/k_9 at higher concentrations of benzene- d_6 reflect a small effect of hot hydrogen atoms favorable to reaction 12-3 as contrasted with 12-4 and thus favorable to the over-all reaction 9.

3.5.2. Ratio k_8/k_9 .—We continue for the moment with the assumption that (8a) makes no contribution to the HD yield. Furthermore, we make the reasonable assumption that the ratio r_2/r_{13} remains constant at all concentrations of the mixture. As written, reactions 2 and 13 imply that the propionaldehyde receives its energy in a primary excitation process. It is very unlikely that primarily excited $C_6D_6^*$ retains a large amount of energy a long time; rather, the evidence⁹ is that internal conversion and collisional deactivation cause rapid energy degradation in $C_6D_6^*$. Thus, if $C_6D_6^*$, after such energy depletion, transmits energy to C_2H_5CHO in a radio-sensitization process, it is improbable that the $C_2H_5CHO^*$ produced contains sufficient energy for decomposition by bond rupture to give H atoms in a process analogous to (13). Consequently, it is required by the assumption of the constancy of the ratio r_2/r_{13} that the atomic hydrogen yield is a linear function of $\epsilon(\text{prop})$; *i.e.*, $G(H_2) \propto \epsilon(\text{prop})$.

For the calculation, we note that the statements of the previous paragraph entail the relationships

$$G(H_2, \text{rearr}) = \epsilon(\text{prop}) \times G(H_2, \text{rearr})_{\text{pure}} \quad 4$$

where the two G values refer to H_2 production by rearrangement in mixture and in pure propionaldehyde, respectively, and

$$G(H_2, 8) = G(H_2) - G(H_2, \text{rearr}) \quad 5$$

The ratio of interest is then

$$\frac{k_8}{k_9} = \frac{[G(H_2) - \epsilon(\text{prop}) \times G(H_2, \text{rearr})_{\text{pure}}]/N(\text{prop})}{G(\text{HD})/N(\text{C}_6\text{D}_6)} \quad 6$$

where $N(\text{prop})$ and $N(\text{C}_6\text{D}_6)$ are respective mole fractions.

Table II lists values of k_8/k_9 calculated on the basis of various possible assumptions, for the three mixtures studied. None of the assumptions gives perfect concordance for all the mixtures; indeed, errors of measurement introduce so much inaccuracy in the low-propionaldehyde-concentration mixtures

TABLE II

TESTS OF POSSIBLE MECHANISM OF HYDROGEN PRODUCTION AS REFLECTED IN CALCULATED RATIO OF RATE CONSTANTS k_8/k_9

Assumption: $G(H_2, \text{rearr}) =$		$\epsilon \cdot \text{prop}) \times$				$G(\text{C}_2\text{H}_4)_{\text{obs}}^a$
$\epsilon(\text{C}_6\text{D}_6)$	$N(\text{C}_6\text{D}_6)$	0	0.3	0.34	0.4	
0.222	0.186	4.3	2.8	2.8	2.5	2.7
.477	.410	5.0	4.3	2.8	2.4	3.1
.762	.708	6.9	3.0	2.4	1.7	2.2

^a $G(\text{C}_2\text{H}_4)_{\text{obs}}$ is the yield actually observed (see Fig. 2). Because of experimental error of analysis, which becomes important at small yields, it is not exactly the same as the calculated value $\epsilon(\text{prop}) \times G(\text{C}_2\text{H}_4)_{\text{pure}}$.

that perfect concordance is not to be expected. However, the assumption that the frequency of occurrence of the primary process in propionaldehyde is a linear function of its electron fraction and that $G(H_2, \text{rearr})_{\text{pure}}$ is ~ 0.34 gives a reasonably small spread of values. Thus, $k_{10}/k_9 \gg 7.3$, and $k_8/k_9 = 2.7 \pm 0.1$ (at room temperature). Correspondingly, $k_8/(k_9 + k_{10}) \ll 0.33$.

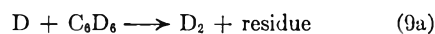
The value $G(H_2, \text{rearr})_{\text{pure}} \sim 0.34$ is to be compared with $G(\text{C}_2\text{H}_4)$ in pure propionaldehyde ~ 0.34 . A scheme in which reaction 3 plays a straightforward and simple role is consequently consistent with the results obtained.

An interesting and significant conclusion of this section is that, even in the presence of benzene- d_6 , an important path for production of H_2 is by H-atom reaction on $\text{C}_2\text{H}_5\text{CHO}$; *i.e.*, by reaction 8. The corollary conclusion is that neither H atoms nor D atoms can disappear entirely by reaction with benzene- d_6 .

3.5.3. Consideration of Reaction 8a.—In this section we consider the extreme possibility that reaction 12-2 occurs to the exclusion of reaction 12-1, that reaction 12-3, and consequently 9, does not occur at all, and that reaction 8a is the sole source of HD. Elimination of 9 is flatly contradictory to the results of Gordon and Burton,⁵ who find HD in radiolysis of mixtures of benzene and benzene- d_6 . In this latter case HD can be formed only by reaction 9 and the analogous reaction of atomic D with C_6H_6 . Furthermore, in their work about 75% of the total H_2 , D_2 and HD seems to result from atom reactions on C_6H_6 and C_6D_6 .

Figure 3 shows that $G(D_2)$ departs negatively from a linear relationship to $\epsilon(\text{C}_6\text{D}_6)$ over the entire

range. The conclusion must consequently be that at least some of the D atoms disappear in a reaction other than

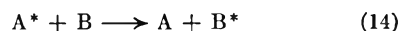


The obvious reaction for such disappearance is (8a). Furthermore, the nature of the $G(D_2)$ data suggests that there are approximately twice as many D atoms available for reaction 9a at $\epsilon(\text{C}_6\text{D}_6) = 0.477$ as at $\epsilon(\text{C}_6\text{D}_6) = 0.762$. Thus, it would appear that reaction 12-2 makes a real, if perhaps small, contribution to the various possible fates of $-\text{C}_6\text{D}_6\text{H}$. On the other hand, this contribution cannot be large at $\epsilon(\text{C}_6\text{D}_6) = 0.222$, for at that value $G(D_2)$ goes precipitously almost to zero.

We conclude that, although reactions 12-2 and 8a are not to be ignored, they do not enter importantly into the over-all effect. Consequently, the conclusion $k_{10}/k_9 \gg 7.3$ is probably very closely correct. Similarly, the value $k_8/k_9 \sim 2.7$ is probably also rather reliable.

The best justification for the omission of consideration of (12-2) and (8a) from the calculations of sections 3.5.1 and 3.5.2 is that the values thus obtained are nevertheless internally consistent.

3.6. Protection and Radiosensitization.—The results signify that benzene- d_6 exerts no protective effect in radiolysis of propionaldehyde. In order to understand the mechanism of protection^{4,5,26} we can fasten our attention on the excited molecule (*cf.* section 3.1). The substance B can effectively protect A



only when $E_B < E_A$, where the references are to respective lowest excitation potentials of the two species. These are probably not optically observable excited states. Benzene is known to have a low-lying triplet state at ~ 3.6 e.v.²⁷ The triplet states of propionaldehyde have not been described but we may expect that they will lie lower than those of benzene, much like the relationship between the lowest singlet states.

Thus, according to the energy-transfer picture, benzene should not protect propionaldehyde. Any protection should be in just the opposite direction. The 100 e.v. yield of ethane in the various mixtures has been established with sufficient accuracy so that one may have considerable confidence in the shape of the curve. The positive departure from the relationship $G(\text{C}_2\text{H}_6) = [G(\text{C}_2\text{H}_6) \text{ of pure liquid}] \times \epsilon(\text{prop})$ is clearly indicative of sensitization of propionaldehyde decomposition by benzene. Since, as shown in section 3.5.1, $G(\text{H})$ appears to be a linear function of $\epsilon(\text{prop})$, it follows that H atom production is not radiosensitized. Thus, if ethane production is sensitized, it cannot be *via* reaction 5. An alternative, rather satisfactory conclusion from the present point of view regarding the radiation chemistry of liquid mixtures is that the process here effective



involves very low excited states C_6D_6^* and $\text{C}_2\text{H}_5\text{CHO}^*$ incapable of entrance into reactions 11 or 5,

(26) M. Burton, S. Gordon and R. R. Hentz, *J. chim. phys.*, **48**, 190 (1951).

(27) H. Shull, *J. Chem. Phys.*, **17**, 295 (1949).

respectively, but quite capable of yielding reaction 7. The $C_6D_6^*$ involved in reaction 15 may result from stepwise energy degradation.⁵ Such a molecule does not have enough energy for decomposition by any process, for its state of excitation is probably no higher than that of the known triplet state of benzene at 3.6 e.v.^{27,28}

(28) Benzene vapor excited with λ 2537 Å. (~4.8 e.v.) does not have enough energy to decompose to gaseous product. Cf. J. E. Wilson and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **63**, 3025 (1941).

Speculation regarding the details of the excited states of reactants and products in reactions 15 and 7 is tempting, particularly in view of the curious variation of $G(CO)$ with $\epsilon(C_6D_6)$, but is hardly justified by the limited data at hand.

The authors wish to express their appreciation to Dr. J. Chanmugam and Dr. R. W. Hummel for stimulating criticisms and discussions during the preparation of this paper.

VISCOSITIES OF BENZENE- d_6 AND CYCLOHEXANE- d_{12} ¹

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The viscosities of benzene- d_6 and cyclohexane- d_{12} have been determined for the temperature range 293.18 to 333.18°K., and the data are expressed by the linear equation $\ln \eta = A + B/T$. Viscosity-temperature coefficients and fractional change of viscosity with temperature are reported. The effect of mass upon viscosity is briefly discussed and the "energy of viscous flow" and the "free energy of activation for viscous flow" are shown to increase with increasing mass. The infrared spectra are included.

Introduction

No viscosity theory that can be applied in the laboratory without appreciable assumptions and approximations has been synthesized from first principles. The opposite mode of attack, analysis, is extremely hazardous because of the difficulty of isolating or changing any one of the parameters without affecting the others. Replacement by deuterium of the hydrogens in a hydrocarbon may approach this latter course. The only perdeuterated hydrocarbon which has been examined carefully by previous workers is benzene- d_6 . The work of Ingold, Wilson and co-workers² indicates that the molecular refraction, molecular volume, melting point, heat of fusion, boiling point and heat of vaporization do not undergo gross changes on deuteration. The flow properties were not reported. To the authors' knowledge,³ the only viscosities on non-polar liquid compounds containing deuterium were reported by Bresler and Landerman⁴ on heavy methane.

In the present paper the viscosities of benzene- d_6 and cyclohexane- d_{12} are reported at several temperatures. The influence of mass on the viscosity and on the viscosity-temperature function are discussed.

Experimental

The preparations of the benzene- d_6 and cyclohexane- d_{12} have been reported in detail elsewhere.⁵

Following the procedure of Ingold, *et al.*,² benzene- d_6 was prepared by successive equilibrations of benzene with 51% D_2SO_4 until the desired deuterium content was reached.

(1) Part of investigation by American Petroleum Institute Research Project 42.

(2) C. K. Ingold, C. S. Raisin, C. L. Wilson, C. R. Bailey and B. Topley, *J. Chem. Soc.*, 915 (1936); see also L. H. P. Weldon and C. L. Wilson, *ibid.*, 235 (1946).

(3) A. H. Kimball, "Bibliography of Research on Heavy Hydrogen Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(4) S. E. Bresler and A. Landerman, *J. Exptl. Theoret. Phys. (U.S.S.R.)*, **10**, 250 (1940); *C. A.*, **34**, 7679 (1940).

(5) J. A. Dixon and R. W. Schiessler, *J. Am. Chem. Soc.*, **76**, 2197 (1954).

The cyclohexane- d_{12} was obtained by treatment of the benzene- d_6 with deuterium at elevated pressure at 100–125° over a kieselguhr-supported nickel. Analyses by density and mass spectra⁶ indicate the benzene has 99.3% of the hydrogens replaced by deuterium, and the cyclohexane 98.8%. Assuming a statistical distribution of isotopes the benzene should be a mixture of 95.8% C_6D_6 and 4.2% C_6D_5H while the composition of the deuterated cyclohexane should be 86.5% C_6D_{12} , 12.6% $C_6D_{11}H$ and 0.8% $C_6D_{10}H_2$.

Viscosities were determined at 293.18, 310.96 and 333.18°K. in Cannon-Fenske-Ostwald viscometers. The bath temperatures were regulated to $\pm 0.025^\circ$; the efflux times measured with calibrated stopwatches; the viscosity checks with known standards indicate a precision of $\pm 0.2\%$.

Refractive indices and densities have already been reported.⁵

The infrared spectra (Figs. 1 and 2) were determined by Professor D. H. Rank and Mr. P. E. Biemiller⁷ using a Perkin and Elmer Model 12-C spectrophotometer.

Discussion

In Table I are given the viscosity data for the pure compounds and four mixtures of partially deuterated benzenes. Analyses of the mass spectrometer patterns of these materials by Dr. John Y. Beach of the California Research Corporation, Richmond, California, established that the mixtures had the composition required by a statistical distribution of the hydrogen isotopes. The viscosities of the benzenes can be expressed as a linear function of the per cent. hydrogen replaced by deuterium. It was previously shown⁵ that in line with the small change in molecular volume the density of the benzene was a linear function of per cent. isotope replacement. The viscosities of the completely deuterated compounds were calculated on the assumption that cyclohexane would behave similarly. It should be noted that these corrections to 100% isotope replacement are, in all cases, less than the estimated deviations of the measurements.

(6) We are indebted to Dr. John Y. Beach of the California Research Corporation for determination and interpretation of the mass spectra.

(7) Department of Physics, College of Chemistry and Physics, The Pennsylvania State University.

TABLE I
VISCOSITIES^a OF DEUTERATED BENZENE AND CYCLOHEXANE

Hydrogen replaced by deuterium, ^b %	Kinematic viscosities (cs.)			Absolute viscosities (cp.)		
	293.18°K.	310.96°K.	333.18°K.	293.18°K.	310.96°K.	333.18°K.
	Benzene					
0.0	0.7417	0.5910	0.4676	0.6519	0.5082	0.3908
29.0	.7390	.5885	.4653	.6646	.5177	.3980
45.4	.7378	.5863	.4651	.6719	.5224	.4029
69.5	.7359	.5842	.4606	.6826	.5301	.4062
97.0	.7312	.5814	.4581	.6923	.5385	.4125
99.3	.7314	.5810	.4581	.6939	.5393	.4134
100.0 (calcd.)	.7313	.5809	.4580	.6942	.5395	.4136
	Cyclohexane					
0.0	1.261	0.9591	0.7184	0.9821	0.7307	0.5321
98.8	1.171	.8896	.6658	1.0441	.7756	.5639
100.0 (calcd.)	1.170	.8887	.6652	1.045	.7760	.5643

^a Based on 1.0038 cp. for viscosity of water at 20°. ^b In partially deuterated fractions the isotopes are statistically distributed. See reference 5.

TABLE II
RATE OF CHANGE OF VISCOSITY WITH TEMPERATURE AND RELATED QUANTITIES AT 293.18°K.

Compound ^c	$\frac{d\eta/dT}{\text{cp. deg.}^{-1}} \times 10^2$	$1/\eta^{d\eta/dT} \times 10^{-2}$	ln A	$B \times 10^{-3}$	$\Delta E_{\text{vis.}}$, cal./mole	$\Delta F_{\text{vis.}}^{\pm}$, cal./mole	$\Delta H_{\text{vap.}}^a$, cal./mole
Benzene	9.47	1.45	-4.6984	1.2514	2486	2899	8151
Benzene- <i>d</i> ₆	10.37	1.49	-4.7259	1.2794	2542	2934	8160
Cyclohexane	16.93	1.72	-5.0993	1.4884	2957	3252	7970
Cyclohexane- <i>d</i> ₁₂	18.30	1.75	-5.0894	1.5050	2990	3287	7901

^a At 298.1°K. and one atmosphere. See reference 10.

In Table II appear the values of rate of change of viscosity with temperature and the fractional change of viscosity with temperature⁸ at 293.18°K. Over the temperature range examined $\ln \eta$ varies linearly with the reciprocal of absolute temperature with a maximum deviation less than one per cent. The constants for the equation

$$\ln \eta = \ln A + B/T \quad (1)$$

are also recorded in Table II. Differentiation of (1) and substitution of the experimentally obtained values of A and B led to $d\eta/dT$. Apparently the viscosity-temperature coefficient is significantly sensitive to isotope replacement.

Following Eyring,⁹ the "energy of viscous flow,

$E_{\text{vis.}}$ " has been calculated from equation 1 and " $\Delta F_{\text{vis.}}^{\pm}$, the free energy of activation for viscous flow," calculated from equation

$$\Delta F_{\text{vis.}}^{\pm} = RT \ln \frac{V\eta}{hN} \quad (2)$$

where V is the molar volume, η the viscosity in poises and N Avogadro's number. The heats of vaporization¹⁰ at 298.1°K. appear in Table II.

If it is assumed that the difference in the heats of vaporization of benzene and benzene-*d*₆ is essentially equal to the difference in the energies of vaporization, there appears to be little correlation between the change of free energy of activation for viscous flow, and the change of energy of vaporization when

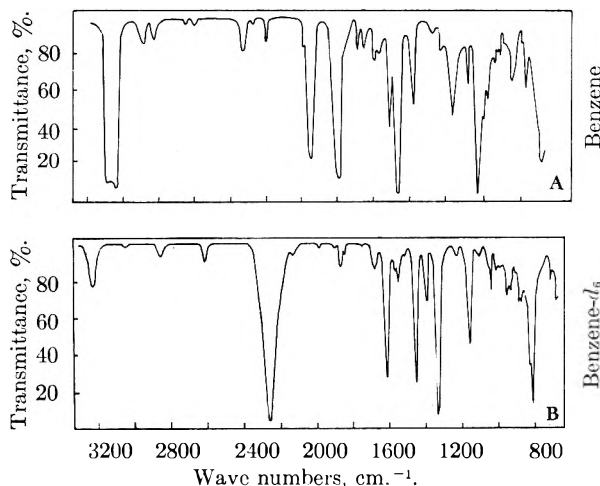


Fig. 1.—Infrared spectra of: A, benzene; B, benzene-*d*₆.

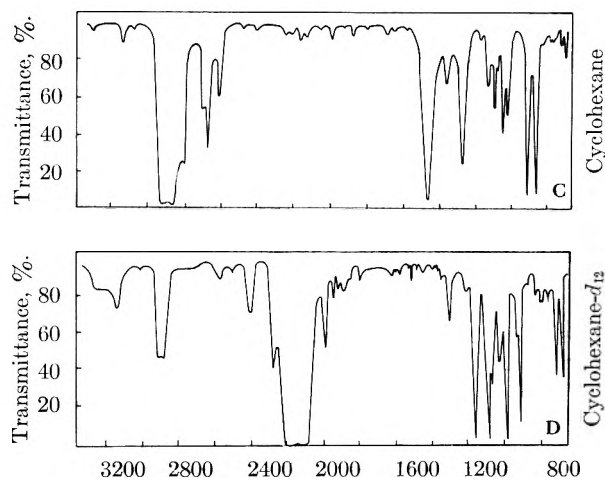


Fig. 2.—Infrared spectra of: cyclohexane and cyclohexane-*d*₁₂

(8) J. H. Ramser, *Ind. Eng. Chem.*, **41**, 2053 (1949).

(9) S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

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the hydrocarbon is converted to the deuterocarbon. A like statement may be made for the cyclohexane. The relationship⁹ is apparently due to a fortunate

$$\Delta F_{\text{vis}}^{\ddagger} \approx 2.45 \Delta E_{\text{vap}} \quad (3)$$

cancellation of a number of opposing effects.

The ratios of viscosity of deuterocarbon to viscosity of precursor hydrocarbon, at three temperatures, appear in Table III. It is surprising that, for a given temperature, the ratios are the same for two very different structures, benzene and cyclohexane. Before embarking on a speculative flight it would be most desirable to see whether this relationship would hold for other hydrocarbon structures.

TABLE III
RATIOS OF VISCOSITIES OF
DEUTEROCARBONS AND HYDROCARBONS

Compounds	Temp., °K.	η_D/η_H	$M_D/M_H^{1/2}$
C_6D_6/C_6H_6	293.18	1.065	1.038
	310.96	1.062	
	333.18	1.058	
C_6D_{12}/C_6H_{12}	293.18	1.064	1.070
	310.96	1.062	
	333.18	1.060	
C_6H_{12}/C_6H_6	293.18	1.506	
C_6H_{12}/C_6H_{14}	293.18	3.192	

Although the decrease with temperature of the ratio of the viscosities is small it exceeds the devia-

tion of the measurements and is believed to be real.

Due to the number of simplifying assumptions involved in deriving presently available viscosity equations^{9,11,12} and also because two important parameters of most such equations energy of vaporization^{10,13} and "energy of activation for viscous flow"¹⁴ appear to be sensitive to isotope replacement it is felt that comparison of the data here reported with predictions of the equations may not be meaningful. However, as predicted by most of the theories the viscosity does appear to be a function of a fractional power of the molecular weight.

Included in Table III are the ratios of the viscosities of cyclohexane to benzene, and of cyclohexane to *n*-hexane. These data point up an observation previously reported,¹⁵ that the effect of molecular weight on viscosity is very small in comparison with the effects of other structural parameters.

The infrared spectra of cyclohexane-*d*₁₂ has been included because the only previously published spectrogram was obtained¹⁶ on material whose purity and isotopic composition is not obvious.

Acknowledgment.—The authors express their appreciation to the American Petroleum Institute for the grant which made this research possible.

(11) J. Frenkel, "Kinetic Theory of Liquids," Clarendon Press, Oxford, 1946.

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(14) See values of E_{vis} in Table II.

(15) R. W. Schiessler, *et al.*, *Proc. A.P.I.*, **24**, III, 49 (1943); **26** III, 254 (1946).

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THE ELECTRON TUNNELLING HYPOTHESIS FOR ELECTRON EXCHANGE REACTIONS¹

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The available data pertaining to electron-exchange reactions in aqueous solutions are collected and classified on the basis of the entropy of activation. An electron tunnelling mechanism is developed and discussed in relation to the Franck-Condon principle. The extremal value for the specific rate constant as a function of the distance of approach is used to determine the most stable activated complex. This maximization is necessary to find the best distance of approach for the interacting ions, leading to largest values for the probability of electron penetration consistent with the smallest energy of activation. An approximate expression for the closest distance of approach is derived and related to variables such as temperature, dielectric constant, and also to the nature of the reacting ionic species. Calculated values agree satisfactorily with the available experimental data.

Introduction

Whereas any oxidation-reduction reaction may be termed an electron-exchange reaction, this name is more usually applied to a group of ionic reactions for which the standard free energy change is zero, *i.e.*, the reacting species are identical with the products. In such systems, radioactive tracers are usually employed to follow the course of the reaction. It appears that this technique was first in-

troduced by Hevesy and Zechmeister³ in 1920. The availability of radioactive tracer materials in recent years has greatly expanded work in this field. This particular class of reactions can be given a more quantitative formulation at the present time.

The pertinent experimental data are presented in Tables I and II, based on recently published information on electron-exchange reactions. The tabulated data refer only to the *rate-determining step* in each case except for reactions 1, 3 and 4 of Table II, for which the mechanism of the over-all reaction is less certain. All of these rate studies were carried out in perchlorate salt media where the

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(2) This material is taken in part from a thesis submitted by Rudolph J. Marcus to the faculty of the Graduate School, University of Utah, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) G. Hevesy and L. Zechmeister, *Z. Elektrochem.*, **26**, 151 (1920).

TABLE I
 SUMMARY OF DATA

Rate constants measured at 25° for all reactions except the ones involving Fe⁺², where the temperature was 20°. All reactions are first order in each of the two reactants. The electronic transmission coefficient (κ_e) was evaluated from the relation $\Delta S^\ddagger = R \ln \kappa_e$.

Reaction	ΔE_{exp} , kcal./mole	ΔS^\ddagger , e.u.	ΔF^\ddagger , kcal./mole	κ_e	Reference
Co(En) ₃ ⁺² -Co(En) ₃ ⁺³	14.3	-33	23.5	7×10^{-8}	9
Tl ⁺¹ -TlOH ⁺²	14.7	-33	23.9	7×10^{-8}	10
VOH ⁺² -VO ⁺²	10.7	-24	17.2	6×10^{-6}	11
Fe ⁺² -Fe ⁺³	9.9	-25	16.7	4×10^{-6}	12
Fe ⁺² -FeOH ⁺²	7.4	-18	12.2	1×10^{-4}	12
Fe ⁺² -FeCl ⁺²	8.8	-24	15.3	6×10^{-6}	12
Fe ⁺² -FeCl ₂ ⁺¹	9.7	-20	15.1	5×10^{-5}	12

 TABLE II
 SUMMARY OF DATA

Rate constants measured at 25° for all reactions except the ones involving Ce⁺³ where the temperature was 0°. All reactions are first order in each of the two reactants except U⁺⁴-U⁺⁶, which is second order in U⁺⁴.

Reaction	ΔE_{exp} , kcal./mole	ΔS^\ddagger , e.u.	ΔF^\ddagger , kcal./mole	Other orders	κ_e	Reference
Fe ⁺³ -Np ⁺⁴	35.0	+51	19.2	[H ⁺] ⁻³		13
Fe ⁺³ -hydroquinone ion	20.2	+53	3.8			14
U ⁺⁴ -U ⁺⁶	33.4	+31	23.6	[H ⁺] ⁻³		15
Sn ⁺² -Sn ⁺⁴ (abs. alc.)	23.7	+16	18.3			16
Ce ⁺³ -Ce ⁺⁴ (1)	7.7	-40	18.0		2×10^{-9}	17
(2)	24.0	+25	16.6	[H ⁺] ⁻²		17

effects of complexing are negligible. This question of participation of foreign anions in these reactions has been examined thoroughly and the results are available elsewhere.⁴

Among inorganic systems only positive ions have been observed to react with measurable rates. Some preliminary studies have been made by Adamson⁵ and co-workers on electron-exchange reactions involving negative ions; in general, these proceed with immeasurably fast rates. Other workers⁶⁻⁸ have obtained similar results with negative ion reactions. The reason for this is that the reorganization free energy of activation, ΔF^\ddagger , of the hydration shell is so small for negative ions that the electron transfer becomes immeasurably fast.

An examination of the data in Tables I and II indicates that there are two possible reaction paths for electron-exchange reactions: one with a low energy of activation and a negative entropy of activation (*i.e.*, low frequency constant), and the other with a higher energy of activation and a positive entropy of activation (*i.e.*, high frequency constant). It is interesting to see that the cerium re-

action may proceed by either path; for all other reactions, one or the other of these possible paths is definitely favored. A consideration of the current theories and models based on media effects such as dielectric constant, ionic strength, electrostatic charge effects, the effects of solvation and desolvation of the activated complex, fail to yield a consistent explanation of the above facts.⁴ An approach including, in addition, the hypothesis of electron tunnelling explains these anomalous experimental results satisfactorily.

Application of the Franck-Condon Principle

In the oxidation-reduction reactions under consideration, the polyatomic ions modify their structure in such a way that transfer of the electron leaves the total energy unchanged. During the approach of the reactive ionic species leading to the transition state, ionic repulsion forces are overcome and the coordination and hydration shells of both ions rearranged until their electronic states are symmetrical, thus permitting a rapid transition to take place. Those configurations which give the fastest reaction will be the ones measured.

Such configurations will be the best compromise giving frequent electronic transitions without too high a free energy of activation. Thus any measurable rate for an oxidation-reduction reaction necessarily involves a transmission coefficient less than unity since it is arrived at as this best compromise. To a first approximation, its magnitude will be determined by the height and thickness of the electronic barrier for this transition. The variation in the thickness of the electronic barrier with the relative distance of approach of the two ions is shown schematically in Fig. 1b and is related to the total molecular electronic energy of the reaction system in Fig. 1a for three values of the atomic reaction coordinate.

It is to be expected that cases will exist where

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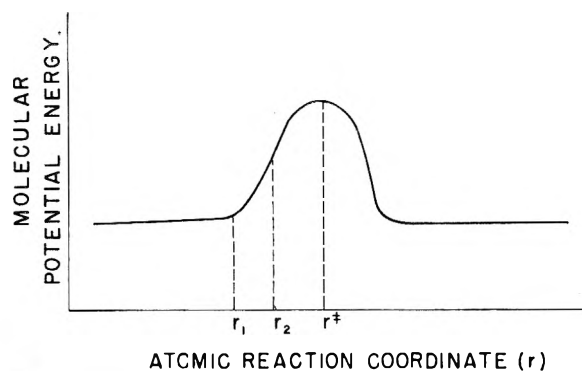


Fig. 1a.

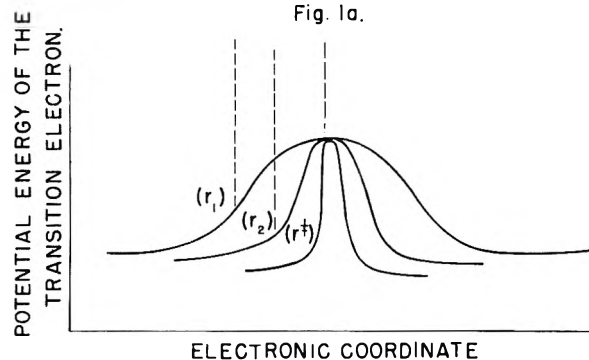


Fig. 1b.

the electronic barrier is quite thin at the transition point with the probability of transition, *i.e.*, the transmission coefficient, being near unity. This extreme case is demonstrated by the class of reactions with positive entropies of activation and large energies of activation, the latter being due to the closeness of approach of the reacting cations. The positive entropies of activation can, in turn, be ascribed to dehydration and change in coordination in the activated states. The entropy of fusion for water is 5.3 e.u. per mole. The number of water molecules lost in the dehydration process is actually greater than that indicated by the apparent positive entropy of activation by the amount necessary to compensate for the transmission coefficient being less than unity.

The reactions characterized by apparent negative entropies of activation (calculated by taking $\kappa = 1$), according to the proposed model, are those with appreciable electron barrier widths at the activated state, consistent with smaller energies of activation at larger critical distances of ion approach. Thus, as previously stated, a reaction occurs at a maximum velocity for the particular activated state defined in terms of the maximum value for the product of the electronic transmission coefficient and the factor $\exp(-\Delta F^\ddagger/RT)$. Qualitatively, somewhat similar considerations have been discussed by Franck and more recently by Libby.^{18,19}

Theoretical Analysis

In a complete solution to the problem of an electron-exchanging positions between two polyatomic cations, it is necessary to calculate the probability of electronic transitions from the known eigenfunc-

tions for the two cations. The approximations that have to be made with respect to the nuclear coordinates of complex systems to make these calculations possible have been pointed out recently in a paper by Melvin Lax.²⁰ In our particular approach to the problem, the probability of an electronic transition is considered as a transmission coefficient (κ_e) in the expression for the specific rate constant and, in addition, the free energy of activation for the electron exchange reaction is considered to be made up of the free energy for rearrangement of the hydration and coordination shells of the two cations plus the electrostatic repulsive energy. The exchange repulsions of inner shells have been assumed to make a negligible contribution because of the comparatively large interionic distances of electron transfer. Similarly, the free energy change due to coordination and hydration changes seem largely unaffected by the approach of the ions toward each other at the large distance at which electron transfer occurs. The contributions considered will be discussed in turn.

For convenience, the electronic transmission coefficient is assumed to be represented by the approximate expression which can be derived for the case of a triangular potential barrier.²¹ This can be expressed in the following form

$$\kappa_e = \exp \left[-\frac{8\pi}{3\hbar} r_{ab}(2m(V-W))^{1/2} \right] \quad (1)$$

where

- V = height of the electron barrier
- W = kinetic energy of the tunnelling electron
- r_{ab} = tunnelling distance
- m = electron mass
- h = Planck's constant

The choice of the expression for a triangular barrier was dictated by the ease of algebraic manipulation in the analysis which follows. It is recognized that the characteristics of the actual barrier will be intermediate between the two extremes of triangular and rectangular barriers. At a point where $V = -2W$ and $V_m = 0$, where the electron tunnelling distances through the two kinds of barriers are equal, the ratio of transmission coefficients is found to be

$$\kappa_{\text{rect.}}/\kappa_{\text{tri.}} = 4 \exp \left[-\frac{4\pi}{3\hbar} (mV)^{1/2} r_{ab} \right] \quad (2)$$

For values of r_{ab} of 3, 6 and 9 Å., the ratio in equation 2 has the values 0.63, 0.10 and 0.025, respectively, when a value of $V = 6.7$ e.v., corresponding to the $\text{Fe}^{+2}-\text{Fe}^{+3}$ system is used.

In estimating the height of the electronic barrier, however, a smoothed potential function is actually used, based on the simple one-dimensional electrostatic model that is diagrammed in Fig. 2. The height of the potential barrier is then given by

$$V = V_m - V_0 \quad (3)$$

where V_0 is the zero-point energy of the electron and V_m is the maximum potential energy for the system consisting of the exchanging electron interacting with the two cations of charges n_a and n_b , respectively.

(20) M. Lax, *J. Chem. Phys.*, **20**, 1752 (1952).

(21) N. F. Mott and I. N. Sneddon, "Wave Mechanics and Its Applications," Clarendon Press, Oxford, 1948.

(18) W. F. Libby, *This Journal*, **56**, 863 (1952).

(19) R. J. Marcus, B. J. Zwolinski and H. Eyring, to be published.

Using Coulomb's law for point charges, and assuming the cations to be fixed at some distance r_{ab} , the potential energy is expressed by

$$V' = \frac{e^2 n_a n_b}{Dr_{ab}} - \frac{e^2 n_a}{Dx} - \frac{e^2 n_b}{D(r_{ab} - x)} \quad (4)$$

where D is the dielectric constant of the medium and x is the distance of the interacting electron from the cation of smaller ionization potential (n_a). Maximizing with respect to x , one obtains

$$x^* = \frac{r_{ab}}{1 + \gamma} \quad (5)$$

where $\gamma^2 = n_b/n_a$ and in turn

$$V_m = -\frac{e^2}{Dr_{ab}} f(n) \quad (6)$$

where

$$f(n) = n_a[(1 + \gamma)^2 - n_b]$$

An expression is needed for the zero-point energy of the exchanging electron to permit one to calculate the height of the barrier by use of equation 3. It is assumed that the zero-point energy is given by

$$V_0 = -\frac{e^2 Z^*}{r_0} \quad (7)$$

where Z^* is the positive charge on the central atom of the complex ion and r_0 is the radius of the classical orbit for the exchanging electron. Equation 7 applies to the complex cation whose central coordinated atom or ion has the smallest ionization potential. When all the coordinating groups about the central ion are neutral, then $Z^* = n_a$. The radius of the electronic orbit is assumed to be given by

$$r_0 = n^{*2} a_0 \quad (8)$$

Here n^* is the effective principal quantum number as given by Rice,²² and a_0 is the Bohr radius. Other expressions for this radius have also been considered, such as those derived from Slater atomic eigenfunctions; however, there seems to be considerable uncertainty about the proper expression for r_0 for the case of hydrated ions in solution. There seems little to choose between the different possible estimates of r_0 except that the present choice leads to a more reasonable distance of approach of the ions.

From equations 3, 6 and 7, the height of the electronic barrier is given by

$$V = \frac{e^2 Z^*}{r_0} - \frac{e^2 f(n)}{Dr_{ab}} \quad (9)$$

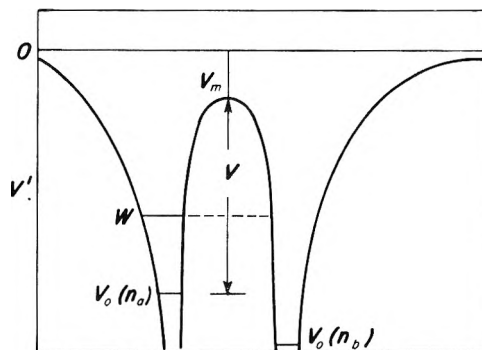
To the same approximation as for the potential energy of the electron given by equation 7, the kinetic energy W is, according to the virial theorem

$$W = \frac{e^2 Z^*}{2r_0} \quad (10)$$

The expression for the transmission coefficient, based on the above approximations is now

$$\kappa_e = \exp \left\{ -\frac{8\pi}{3h} r_{ab} \left[2me^2 \left(\frac{Z^*}{2r_0} - \frac{f(n)}{Dr_{ab}} \right) \right]^{1/2} \right\} \quad (11)$$

The free energy of activation is assumed to be made up of the electrostatic repulsion energy contribution and of the energy ΔF_{r^\ddagger} arising from the re-



ELECTRON COORDINATE.

Fig. 2.

organization of the coordination and hydration shells of the two reacting ions. The specific rate constant for the electron-exchange reaction is, therefore

$$k' = \frac{kT}{h} \exp \left\{ -\frac{8\pi}{3h} r_{ab} \left[2me^2 \left(\frac{Z^*}{2r_0} - \frac{f(n)}{Dr_{ab}} \right) \right]^{1/2} - \frac{\Delta F_{r^\ddagger}}{RT} - \frac{e^2 n_a n_b}{RTDr_{ab}} \right\} \quad (12)$$

where ΔF_{r^\ddagger} is the activation free energy for rearrangement of the hydration and coordination shells and D is the dielectric constant. The best distance for electron transfer is usually at a sufficiently large distance that the two reacting ions interfere negligibly with each other's hydration shell. In this case $\alpha = \partial \Delta F_{r^\ddagger} / \partial r_{ab} \approx 0$. The ordinary atomic or nuclear transmission coefficient is assumed to be unity.

Expression 12 for the rate constant includes in the exponent the contribution to the apparent entropy of activation ($-R \ln \kappa_e$) made by the electronic transmission coefficient. There is also a positive activation entropy of rearrangement (ΔS_{r^\ddagger}) as part of the free energy of rearrangement. This formulation of the rate constant expresses the competition between the two mechanisms that have been indicated: namely, the "easy" path of low repulsive energy leading to the larger tunnelling distances for the electron, and the "hard" path of close approach where κ_e has an increased value approaching unity. At some definite value of r_{ab} these two tendencies will balance each other, and there will be a critical or "best" intercationic distance at which the rate of reaction will have its maximum value. If this resistance to electron exchange did not exist, electron tunnelling would occur at large distances.

To find the critical value of the intercationic distance in the activated state, it is necessary to find the extremal value for the specific rate constant with respect to r_{ab} . By defining the following dimensionless parameters

$$a \equiv \frac{64\pi^2 m e^2 r_0 Z^*}{9h^2}$$

$$b \equiv \frac{128\pi^2 m e^2 r_0 f(n)}{9h^2 D}$$

$$c \equiv \frac{e^2 n_a n_b}{kTDr_0}$$

$$\alpha \equiv \frac{1}{r_0 kT} \times \frac{d\Delta F_{r^\ddagger}}{dx} \approx 0$$

(22) C. K. Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Co., Inc., New York, N. Y., 1940. p. 96.

and the normalized variables

$$y = \frac{k'h}{kT}$$

$$x = \frac{r_{ab}}{r_0}$$

equation 12 in logarithmic form can then be expressed as

$$-\ln y = (ax^2 - bx)^{1/2} + \int \alpha dx + c/x \quad (13)$$

Maximizing with respect to x , one obtains

$$-d \ln y/dx = (2ax - b)/2(ax^2 - bx)^{1/2} - c/x^2 \quad (14)$$

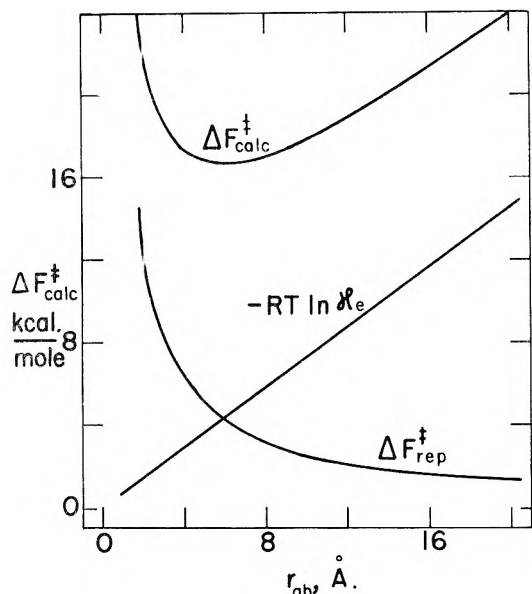


Fig. 3.

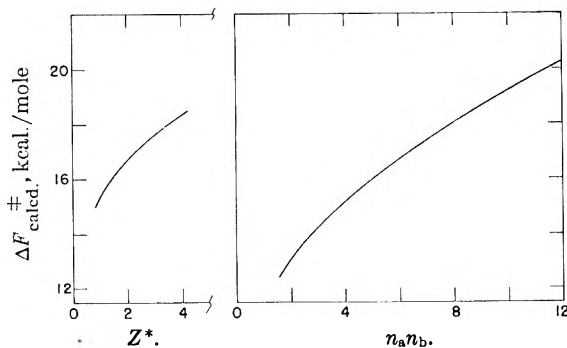


Fig. 4.

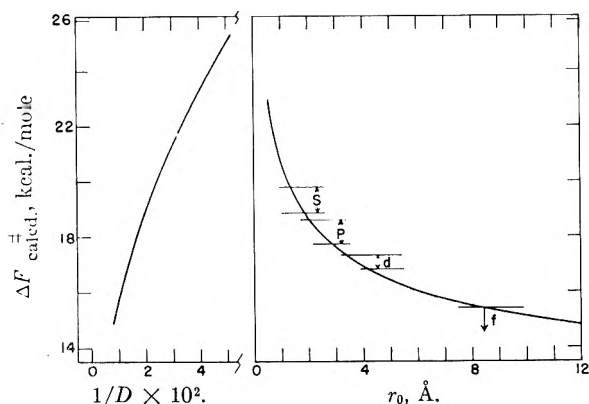


Fig. 5.

which expression is set equal to zero and on proper factoring reduces to

$$a^{1/2}(1 - b/2ax)/(1 - b/ax)^{1/2} = c/x^2 \quad (15)$$

Using the binomial expansion on the square root term and retaining only the first two terms of the expansion, (15) simplifies to

$$x^2 = c/a^{1/2} \quad (16a)$$

The critical parameter in this expansion is the dielectric constant of the medium. If D is set equal to 8 and the values $f(n) = 6.5$, $r_0 = 4.3 \times 10^{-8}$ cm., $Z^* = 2$ and $r_{ab} = 6.5 \times 10^{-8}$ cm. are used for all the other parameters, the error is found to be about 7% if the quadratic term is neglected in the expansion. For $D \geq 70$, this error is reduced to less than 0.1%. Substituting the parameters defined above, the explicit expression for the critical intercationic distance in the activated state is, in this approximation

$$r_{ab}^{*2} = \frac{3e^2 n_a n_b h r_0^{1/2}}{8\pi \epsilon k D T (m Z^*)^{1/2}} \quad (16b)$$

Discussion

On the basis of the equations developed in the preceding section, values of the free energies of activation of electron-exchange reactions can be calculated provided values of ΔF_r^\ddagger are known. If ΔF_r^\ddagger is taken equal to 8.1 kcal. for all these reactions, one finds the calculated values given in the next to the last column of Table III. In reactions where the coordination is different for the two reacting ions it is not surprising to find ΔF_r^\ddagger different from 8.1 kcal. The critical values of r_{ab}^* , the tunnelling distance for the exchanging electron, were found to vary from 3.4 Å. for the $\text{Fe}^{+2}-\text{FeCl}_2^{+1}$ system to 9.3 Å. for the $\text{Ce}^{+3}-\text{Ce}^{+4}$ system. These distances appear to be of the right order of magnitude and so provide some justification of the proposed model for the electron-exchange process.

TABLE III
COMPARISON OF ELECTROSTATIC MODEL WITH EXPERIMENTAL DATA^a

Reaction	r_{ab}^* (Å.)	$-RT \ln \kappa_e$	ΔF_{rep}^\ddagger	ΔF^\ddagger Calcd.	Total Obs.
$\text{Co}(\text{en})_3^{+2}-\text{Co}(\text{en})_3^{+3}$	5.9	4.38	4.32	16.8	23.5
$\text{Tl}^{+1}-\text{TlOH}^{+2}$	3.3	2.63	2.57	13.3	23.9
$\text{VOH}^{+2}-\text{VO}^{+2}$	4.4	4.00	3.86	16.0	17.2
$\text{Fe}^{+2}-\text{Fe}^{+3}$	6.0	4.37	4.25	16.7 ^b	16.7
$\text{Fe}^{+2}-\text{FeOH}^{+2}$	4.9	3.57	3.47	15.1	12.2
$\text{Fe}^{+2}-\text{FeCl}^{+2}$	4.9	3.57	3.47	15.1	15.3
$\text{Fe}^{+2}-\text{FeCl}_2^{+1}$	3.4	2.48	2.50	13.1	15.1
$\text{Ce}^{+3}-\text{Ce}^{+4}$	9.3	5.52	5.48	19.1	18.0

^a All energy values in kcal./mole for $D = 78$. ^b Fitted value.

It is of interest to examine the variation of the calculated free energies of activation with the individual parameters of this model. The results are illustrated in Figs. 3, 4 and 5. Figure 3 shows the variation of the calculated free energy of activation with the tunnelling distance. The curves represented in the three figures have been calculated by varying only the specific parameter named, while holding the other parameters constant. The $\text{Fe}^{+2}-\text{Fe}^{+3}$ system has been the one chosen for these figures, although any of the other systems would have served as well. Figure 4 shows the relationship between the calculated free energy of activation

and (a) the charge (Z^*) on the central ion of smaller ionization potential and (b) the product $n_a n_b$, of the charges of the reactant complex ions. Both these curves show that as the charges on ions are increased, there is a corresponding increase of the free energy of activation. This in turn corresponds to the well known fact observed in electron-exchange studies that the reaction will be speeded up as the total charge on the reactant cations is reduced either by complexing with anions or by hydrolysis.

Figure 5 shows the variation of the calculated free energy of activation with the reciprocal of the dielectric constant. This relation is particularly important, for it provides a convenient experimental approach for testing the correctness of the proposed model by studying the kinetics of an exchange reaction in media of varying dielectric constant. The dependence of the calculated free energy of activation on the value of r_0 , which, in turn, is a function of the principal and orbital quantum numbers of the exchanging electron, is also given in Fig. 5. Here it is seen that s, p, d and f electrons will exchange more rapidly in the order given, and

that the principal quantum number is only of secondary importance in determining the probability of exchange. Recently W. F. Libby¹⁸ reported some approximate quantum-mechanical calculations of the frequencies of electron exchange in the hydrogen molecular-ion. He found appreciable frequencies of exchange for 3d electrons at distances of the order of 30 Å.

Though the expression for the free energy of activation is a complicated function of the temperature because of its dependence on r_{ab}^* which in turn inversely depends on $T^{1/2}$, calculations show that over a limited temperature range ΔF^\ddagger varies linearly with temperature. As mentioned earlier, the great speed of electron-exchange reactions involving two anions is presumably due to a low value for ΔF_r^\ddagger , in accord with their decreased tendency to hydrate.

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THE ABSTRACTION OF HYDROGEN ATOMS FROM MERCAPTANS BY 2,2-DIPHENYL-1-PICRYLHYDRAZYL

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The reaction between 2,2-diphenyl-1-picrylhydrazyl and mercaptans in solution is a process of hydrogen atom abstraction in which the radical concentration is accurately known. The activation energy is approximately constant at 15.0 kcal./mole for a number of mercaptans, and A factors for the normal mercaptans are in the range $2-6 \times 10^{11}$. *t*-Butyl mercaptan has a much lower rate constant than the normal mercaptans and this is reflected chiefly in a lower A factor. The results are discussed in relation to other hydrogen abstraction reactions in solution and in the gas phase.

Hydrogen abstraction reactions of the type



have been widely investigated in recent years.¹ The results are initially expressed in terms of the rate of combination of methyl radicals, but an accurate study of this latter reaction² has resulted in the evaluation of absolute rate constants for reaction 1. Data for the abstraction of hydrogen atoms in the gas phase from some fifty compounds are now available.³

Investigation of hydrogen atom abstraction in solution has been limited mainly to the study of chain transfer in polymerization processes.⁴ A relationship between rate of polymerization and molecular weight of the polymer produced gives the ratio of the rate constants for transfer and propaga-

tion, and the recent measurement of rate constants for the propagation process⁵ permits the evaluation of absolute transfer constants.

Edwards and Mayo⁶ have studied the decomposition of acetyl peroxide in mixtures of carbon tetrachloride and various solvents, and have compared the ease of abstraction of a hydrogen atom from the solvent with ease of abstraction of a chlorine atom from carbon tetrachloride. The results compare very well with those for methyl radical reactions in the gas phase,³ but it is not certain whether methyl or acetate radicals are involved in the reaction in solution.

The problem of studying hydrogen abstraction reactions in solution is simplified if the concentration of the attacking radical is accurately known, and if the system is not complicated by possible cage effects. The radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) was chosen for the present work because it does not dimerize⁷ and the problem of a

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(2) R. Gomer and G. B. Kistiakowsky, *ibid.*, **19**, 85 (1951).

(3) A. F. Trotman-Dickenson, *Quart. Revs. (London)*, **7**, 198 (1953).

(4) R. A. Gregg and F. R. Mayo, *Discs. Faraday Soc.*, **2**, 328 (1947).

(5) E.g., M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *J. Am. Chem. Soc.*, **73**, 1700 (1951).

(6) F. G. Edwards and F. R. Mayo, *ibid.*, **72**, 1265 (1950).

(7) E. Müller, I. Müller-Rodloff and W. Runge, *Ann.*, **520**, 235 (1935).

cage effect does not arise. In addition it is highly colored and its concentration at any time can be estimated by its absorption in the visible. It would be expected that activation energies for hydrogen atom abstraction with DPPH would be higher than those with the more reactive methyl radical, but otherwise the work should provide a comparison between reactions in the gas phase and in solution.

Experimental

Materials.—2,2-Diphenyl-1-picrylhydrazine and DPPH were prepared by the method of Goldschmidt and Renn.⁸ The DPPH was further purified by recrystallization from an ether-chloroform mixture.

n-Butyl mercaptan (Eastman Kodak Co.) and isobutyl and *t*-butyl mercaptans (Matheson Co.) were distilled at atmospheric pressure in a 15-plate column, the fractions collected having boiling point ranges less than 0.05°. *n*-Hexyl and *n*-octyl mercaptans (Matheson Co.) were distilled at reduced pressure in an atmosphere of nitrogen. Middle fractions of boiling point range less than 0.25° were collected. The mercaptans were given one further distillation in the high vacuum apparatus and stored at -80°.

Benzene (Mallinckrodt Analytical Reagent) was degassed in the vacuum apparatus. Cyclohexane (Matheson Co.) was shaken with sulfuric acid, and washed with sodium carbonate solution and water, and, after drying with calcium chloride, distilled in the 15-plate column. It was degassed in the vacuum apparatus.

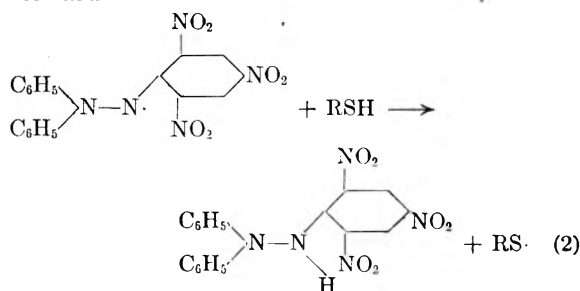
Procedure.—About 0.0005 g. of DPPH was placed in a reaction tube of 1 cm. diameter and the tube pumped out to 10⁻⁴ mm. on the vacuum apparatus. A known amount of mercaptan was added by freezing down the vapor contained in a 500-ml. bulb, and between 3–10 ml. of solvent, usually benzene, were distilled into the tube. It was sealed off and heated to the reaction temperature. At the end of the reaction, the tube was emptied and the weight of solvent determined by difference.

The reaction was followed by taking measurements of optical density with a Fisher electrophotometer using a 650 m μ filter.⁹ Temperatures of 20, 30, 45 and 60° were used. Three or four experiments were performed at each temperature, the mercaptan concentration varying over a threefold range. With the normal mercaptans this concentration was of the order of 10⁻³ mole/cc. and with *t*-butyl mercaptan it was of the order of 10⁻⁴ mole/cc.

The rate of disappearance of DPPH in pure benzene is negligible, being less than 1%/day at 60°.

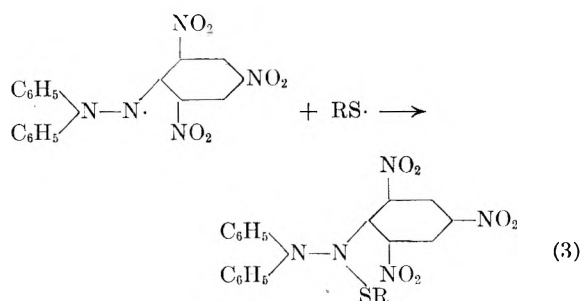
Results and Discussion

The examination of the reaction products gave evidence that a mixture of substances is obtained by the reaction of DPPH with a mercaptan, one of which is 2,2-diphenyl-1-picrylhydrazine. It is well known that the S-H bond in mercaptans is relatively weak, and that the hydrogen atom is readily removed by free radicals in polymerization reactions. The following mechanism for the reaction between DPPH and a mercaptan is therefore put forward



(8) S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922).

(9) C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).



The product from the reaction of *n*-hexyl mercaptan with DPPH was investigated. Its absorption spectrum in the region 380–550 m μ was almost identical with that of 2,2-diphenyl-1-picrylhydrazine. Solid product of melting point about 50° below that of 2,2-diphenyl-1-picrylhydrazine was isolated from the reaction mixture. It gave a positive test for sulfur and was oxidized to DPPH in fair yield by treatment with lead dioxide. Its infrared spectrum was almost identical with that of 2,2-diphenyl-1-picrylhydrazine over the range 650–3500 cm.⁻¹. In particular the N-H stretching vibration at 3290 cm.⁻¹ occurred in both spectra. The product also showed medium absorptions at 2850, 2920 and 2950 cm.⁻¹ and these are probably C-H stretching vibrations from hexyl groups. The product thus appears to be a mixture of 2,2-diphenyl-1-picrylhydrazine and a sulfur-containing compound of related structure, in agreement with the mechanism put forward in equations 2 and 3.

A typical curve for the disappearance of DPPH in a benzene solution of a mercaptan is shown in Fig. 1. The order in the early stages is somewhat less than one but over the major part of the reaction the first order law is followed. In any single experiment the mercaptan is in sufficient excess for its concentration to be considered constant. From experiments in which the mercaptan concentration was varied it was shown that the reaction is first order with respect to mercaptan. These results can be summarized in the form

$$R_{\text{DPPH}} = 2k[\text{DPPH}][\text{RSH}]$$

where R_{DPPH} is the rate of disappearance of DPPH. Since reaction 3 is rapid, and reaction 2 is slow and rate determining, the rate of the hydrogen abstraction reaction is given by $1/2 R_{\text{DPPH}}$, and

$$1/2 R_{\text{DPPH}} = k[\text{DPPH}][\text{RSH}]$$

Values of the second-order rate constant k were obtained at temperatures of 20, 30, 45 and 60° for *n*-butyl, isobutyl, *t*-butyl, *n*-hexyl and *n*-octyl mercaptans. From these values, activation energies were calculated for the hydrogen abstraction reactions by means of the Arrhenius equation

$$k = Ae^{-E/RT}$$

and A factors were also deduced. No allowance was made in these calculations for the temperature coefficient of the collision rate. Table I contains values of k at 60° in cc./mole/sec., together with activation energies and A factors. It is estimated that the activation energies are correct to about 0.5 kcal./mole, and this corresponds to an error of a factor of 2 in A .

TABLE I

Mercaptan	k at 60° (cc./mole/ sec.)	E (kcal./mole)	A
<i>n</i> -Butyl	73	14.6	2.8×10^{11}
Isobutyl	57	15.3	6.3×10^{11}
<i>t</i> -Butyl	3.8	15.3	4.2×10^{10}
<i>n</i> -Hexyl	76	15.1	6.2×10^{11}
<i>n</i> -Octyl	46	14.6	1.8×10^{11}

The activation energy for the abstraction of a hydrogen atom from these mercaptans by DPPH is 15.0 ± 0.4 kcal./mole. The variation is within the estimated experimental error, and it is thought that the differences between mercaptans are probably not significant. The value of 15 kcal./mole compares with 7 kcal./mole derived from the work of Gregg, Alderman and Mayo¹⁰ and Matheson, *et al.*,⁵ for the activation energy of the reaction between polystyryl radicals and *t*-butyl mercaptan. Such a difference is to be expected from the comparatively low reactivity of the DPPH radical. Activation energies also can be derived⁴ for hydrogen atom abstraction by polystyryl radicals from benzene (22.6 kcal./mole), toluene (17.9), ethylbenzene (13.3) and diphenylmethane (10.5). The value for benzene is very much higher than that for *t*-butyl mercaptan, and accounts for the fact that in the present work with DPPH, benzene can be used as a solvent for the mercaptan.

The high reactivity of polystyryl radicals compared with DPPH radicals has been noted above, but methyl radicals are even more reactive than polystyryl radicals. Thus activation energies for hydrogen abstraction from benzene and toluene in the gas phase are about 9.2 and 8.3 kcal./mole, respectively.³ No data are available for the reaction between methyl radicals and mercaptans, but the activation energy is probably of the order of 3 kcal./mole.

The variation of A factors among the normal mercaptans is within the experimental error but there is a considerable change in the case of *t*-butyl mercaptan. The low A factor for this compound is ascribed to a steric effect, the methyl groups of the *t*-butyl mercaptan hindering the attack of the DPPH radical. Such an effect is also observed with chain transfer of growing polymer chains with mercaptans. Mayo, *et al.*,¹⁰ found that at 60° dodecyl mercaptan was four times as effective as *t*-butyl mercaptan in the transfer reaction with a polystyryl radical. The present work shows a ratio of rate constants of about 20 for *n*-butyl and *t*-butyl mercaptans, and this would be even higher if the *t*-butyl mercaptan contains a slight amount of an isomeric mercaptan as impurity.

The A factors for the reactions between DPPH and the normal mercaptans do not differ greatly from 4×10^{11} . Trotman-Dickenson's review³

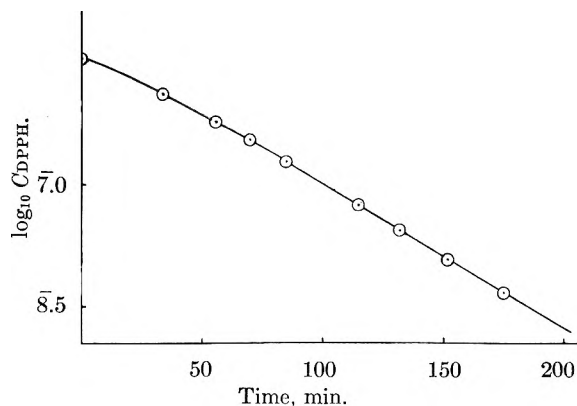


Fig. 1.—The disappearance of DPPH in a benzene solution of *n*-butyl mercaptan (1.13×10^{-4} mole/cc.) at 30°.

shows that nearly all the hydrogen abstraction reactions of methyl radicals have A factors of 10^{11} within a factor of 10. The work with DPPH in solution thus substantiates the conclusion already reached for hydrogen atom abstraction in the gas phase that A factors of about 10^{11} are usually to be expected, compared with the "normal" collision theory value of the order of 10^{14} .

In solution it is found that A factors for the reaction between polystyryl radicals and hydrocarbons are generally in the range 10^9 – 10^{12} . These results are obtained by combining the data of Gregg and Mayo⁴ for chain transfer in styrene polymerization, referred to the propagation reaction, with the results of Matheson, *et al.*, for the propagation process.⁵ The A factors for benzene and *t*-butylbenzene are of the order of 10^{14} , however, considerably higher than values reported for any other hydrogen abstraction reaction. Gregg and Mayo note that there is an approximate correspondence between high activation energy and high frequency factor, a conclusion which applies to a number of bimolecular reactions.¹¹

The effect of changing the solvent from benzene to cyclohexane was investigated for the reaction between DPPH and *n*-hexyl mercaptan. The rate constants were nearly twice as large as the rate constants in benzene. Benzene forms a weak complex with DPPH,⁷ and it is possible that solvation of the DPPH is to some extent the reason for the lower rate constants in benzene. The activation energy and A factor were 14.8 kcal./mole and 7.4×10^{11} , respectively, showing that a change of solvent is unlikely to alter the general conclusions discussed here. With reactions in cyclohexane as well as in benzene, the order is at first less than one with respect to DPPH, but it is between 0.9 and 1 over the major part of the reaction. The reason for this effect is not known. It occurs whatever the initial concentration of DPPH, and is some peculiarity of the initial stage of the reaction.

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PHYSICAL PROPERTIES OF *n*-HEXADECANE, *n*-DECYLCYCLOPENTANE, *n*-DECYLCYCLOHEXANE, 1-HEXADECENE AND *n*-DECYLBENZENE¹

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For *n*-hexadecane, *n*-decylcyclopentane, *n*-decylcyclohexane, 1-hexadecene and *n*-decylbenzene, highly purified hydrocarbons of the API Research series, the following properties were measured: densities at 20, 25 and 30°; refractive indices at seven wave lengths at 20, 25 and 30°; and boiling points and vapor pressures from 50 to 760 mm. The data on refractive indices were correlated by means of modified Cauchy and Hartmann equations, and values of the constants are given for each compound, to permit precise evaluation of the refractive index as a function of wave length. The data on vapor pressures were correlated with the three-constant Antoine equation and values of the constants are given for each compound. Also included are calculated values of the specific dispersions, $(n_F - n_C)/d$ and $(n_g - n_D)/d$.

The American Petroleum Institute Research Project 6 has so far reported data on the densities, refractive indices and boiling points and vapor pressures for 76 different API Research hydrocarbons.²⁻⁷ In this paper are reported similar data for an additional 5 API Research hydrocarbons representing different normal alkyl series, namely, *n*-hexadecane, *n*-decylcyclopentane, *n*-decylcyclohexane, 1-hexadecene and *n*-decylbenzene.

process of publication⁸ by other workers. The purity of the samples measured was as follows, in mole per cent.: *n*-hexadecane, 99.96 ± 0.04; *n*-decylcyclopentane, 99.80 ± 0.18, *n*-decylcyclohexane, 99.88 ± 0.11; 1-hexadecene, 99.93 ± 0.06; and *n*-decylbenzene, 99.88 ± 0.10.

The measurements of density were made at 20, 25 and 30°, with a density balance previously described.⁹ The experimental values of density are

TABLE I
VALUES OF DENSITY

Compound	Formula	Density ^a			Temp. coefficient of density at 25°
		20°	25°	30°	
<i>n</i> -Hexadecane	C ₁₆ H ₃₄	0.77344	0.76996	0.76643	0.000701
<i>n</i> -Decylcyclopentane	C ₁₅ H ₃₀	.81097	.80739	.80383	.000714
<i>n</i> -Decylcyclohexane	C ₁₆ H ₃₂	.81858	.81517	.81183	.000675
1-Hexadecene	C ₁₆ H ₃₂	.78112	.77759	.77409	.000703
<i>n</i> -Decylbenzene	C ₁₆ H ₂₆	.85553	.85189	.84833	.000720

^a For air-saturated hydrocarbons in the liquid state at 1 atm.

These API Research hydrocarbons were made available by the American Petroleum Institute through the API Research Project 44 at the Carnegie Institute of Technology. The samples were purified by the API Research Project 6 from material supplied by the following laboratories: *n*-hexadecane and 1-hexadecene by the API Research Project 6 at the Carnegie Institute of Technology; *n*-decylcyclopentane, *n*-decylcyclohexane and *n*-decylbenzene by the API Research Project 45 at The Ohio State University. Description of the purification and purity of these compounds is in

given in Table I. Individual measurements were reproducible within 0.00003 g./ml. The accuracy of the tabulated values is estimated to be ±0.00005 to ±0.00010 g./ml.

The refractive index was measured by means of the apparatus and procedure previously described.⁵ The calculations and correlations were similarly made as described previously.⁵ Table II gives the values of refractive index at 7 wave lengths at 20, 25 and 30° and the values of the constants of the modified Cauchy and Hartmann equations. The fourteenth and last columns of Table II give the root mean square values of the deviations of the observed from the calculated points. Individual measurements were reproducible within ±0.00002 to ±0.00003. The accuracy of the tabulated values is estimated to be ±0.00005 to ±0.00008.

Table III gives the values of the specific dispersions, $10^4(n_F - n_C)/d$ and $10^4(n_g - n_D)/d$, calculated from the values of refractive index in Table II and of density in Table I.

In previous reports,^{5,6} it was indicated that some correlation exists between the values of the con-

(1) This investigation was performed as part of the work of the American Petroleum Institute Research Project 6 in the Petroleum Research Laboratory of the Carnegie Institute of Technology, Pittsburgh, Pennsylvania. A portion of the work described was completed before June, 1950, when the Project was moved from the National Bureau of Standards to the Carnegie Institute of Technology. One of the authors, A. F. F., remained with the National Bureau of Standards, transferring to the American Dental Association Research Fellowship there.

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(3) A. F. Forziati and F. D. Rossini, *ibid.*, **43**, 473 (1949).

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(5) A. F. Forziati, *ibid.*, **44**, 373 (1950).

(6) A. F. Forziati, D. L. Camin and F. D. Rossini, *ibid.*, **45**, 406 (1950).

(7) F. D. Rossini, B. J. Mair and A. J. Streiff, "Hydrocarbons from Petroleum," Reinhold Publ. Corp., New York, N. Y., 1953.

(8) Unpublished data of the API Research Project 6, Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, Attention of Frederick D. Rossini.

(9) A. F. Forziati, B. J. Mair and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 513 (1945).

TABLE II
VALUES OF REFRACTIVE INDEX AT SEVEN WAVE LENGTHS AND THREE TEMPERATURES AND OF THE CONSTANTS OF THE MODIFIED CAUCHY AND HARTMANN EQUATIONS

Compound	Formula	Temp., °C.	Refractive index							Constants in the equation							
			Wave length in Angstrom units							n_{∞}	C	λ^*	$\frac{\rho \times 10^3}{10^6}$	$\frac{\Delta n}{10^3} = \frac{a \times X}{10^3} - \frac{b}{10^4} + \frac{c}{\lambda^2}$			
			6678.1	6562.8	5892.6	5460.7	5015.7	4861.3	4358.3								
			Hered	Hc	Nad	Hge	Heblue	Hf	Hgr								
<i>n</i> -Hexadecane	C ₁₆ H ₃₄	20	1.43204	1.43235	1.43453	1.43640	1.43888	1.43993	1.44119		1.42072	0.003787	0.09714	2.00	2.006	0.0095	4.24
		25	1.43001	1.43032	1.43250	1.43436	1.43684	1.43788	1.44213						2.006	0.0095	3.42
		30	1.42798	1.42829	1.43047	1.43232	1.43480	1.43583	1.44007								
<i>n</i> -Decylcyclopentane	C ₁₆ H ₃₀	20	1.44605	1.44637	1.44862	1.45056	1.45313	1.45420	1.45861		1.43441	0.003917	0.09720	1.20	2.013	0.0069	3.34
		25	1.44402	1.44434	1.44659	1.44852	1.45109	1.45216	1.45656						2.013	0.0069	2.83
		30	1.44199	1.44231	1.44456	1.44648	1.44905	1.45012	1.45451								
<i>n</i> -Decylcyclohexane	C ₁₆ H ₃₂	20	1.45074	1.45108	1.45338	1.45536	1.45798	1.45908	1.46357		1.43890	0.004057	0.09454	1.85	1.927	0.0166	3.27
		25	1.44878	1.44911	1.45141	1.45338	1.45599	1.45708	1.46156						1.927	0.0166	4.11
		30	1.44682	1.44714	1.44944	1.45140	1.45400	1.45508	1.45955								
1-Hexadecene	C ₁₆ H ₃₂	20	1.43845	1.43879	1.44120	1.44326	1.44601	1.44715	1.45188		1.42611	0.004144	0.09883	1.46	2.093	0.0112	3.23
		25	1.43633	1.43667	1.43907	1.44113	1.44387	1.44501	1.44973						2.093	0.0112	4.12
		30	1.43421	1.43455	1.43694	1.43900	1.44173	1.44287	1.44758								
<i>n</i> -Decylbenzene	C ₁₆ H ₂₆	20	1.47939	1.47986	1.48319	1.48607	1.48994	1.49158	1.49836		1.46380	0.005250	0.11501	1.25	1.930	0.0485	2.56
		25	1.47735	1.47782	1.48112	1.48398	1.48782	1.48944	1.49617						2.073	0.0189	2.36
		30	1.47523	1.47570	1.47899	1.48184	1.48567	1.48729	1.49400								

stants n_{∞} and C of the Hartmann equation and the number of carbon atoms in the normal alkyl radical for the normal paraffins, the 1-alkenes, and the normal alkylbenzenes. The values of n_{∞} and C for *n*-hexadecane, 1-hexadecene and *n*-decylbenzene from the present investigation are found to be in good accord with those previously reported for the lower members of these series.^{5,6}

The measurements and calculations of vapor pressures and boiling points were made as previously described,^{2,4,6} with the samples being introduced into the apparatus without contact with the air of the atmosphere.⁶ Because of a break in the multicontact mercury manometer, a new one was made for the apparatus, with resulting pressures for the given contacts that were slightly different from those of the previous manometer.² Due to the relatively high normal boiling points for the compounds of this investigation, it became necessary to use a procedure which minimized the time a given sample was kept at elevated temperatures (above 200°). This was done as follows: two samples of each compound were used, with one sample being used for the lower range of pressure (50 to 403 mm.) and the second sample being used for the higher pressures (403 to 760 mm.). For the measurements from 50 to 403 mm. the boiler and jacket were preheated to 100° before the sample was introduced. After introduction, the sample was quickly brought to equilibrium and temperature measurements were made at selected pressures from 50 to 403 mm. The first sample was then withdrawn and the apparatus was thoroughly cleaned. Before introducing the second sample, the boiler and jacket were preheated to 200° and the sample itself was preheated to 100°. When the sample had been introduced into the boiler, it was quickly brought to equilibrium and temperature measurements were made at selected pressures from 403 to 760 mm. After the measurement at 1 atmosphere, the pressure was reduced to 403 mm. and the temperature was remeasured as a check.

Table IV gives the experimental data on the temperature and pressures of the liquid-vapor equilibrium for the 5 compounds. Table V gives the values of the three constants of the Antoine equation, the normal boiling point at 760 mm., the pressure coefficient of the boiling point at 760 mm., and the range of measurement in pressure and in temperature. The last column of Table V gives the root mean-square value of the ratios of the deviations of the observed points from the Antoine equation to the expected standard deviation.⁴ Individual measurements of boiling points were reproducible within ±0.002 to ±0.003°. The accuracy of the tabulated values of the normal boiling point is estimated to be ±0.008 to ±0.015°.

In earlier reports,^{2,4,6} it was pointed out that some correlation exists between the values of the constants B and C of the Antoine equation for vapor pressures and the number of carbon atoms in the normal alkyl side chain for the members of the several normal alkyl series of hydrocarbons, as normal paraffins, normal alkylcyclopentanes, normal alkylcyclohexanes and normal alkylbenzenes, and the 1-alkenes. The values of the B and C constants for

TABLE III

Temp., °C.	CALCULATED VALUES OF THE SPECIFIC DISPERSION									
	$10^4(n_F - n_c)/d$	$10^4(n_g - n_D)/d$	$10^4(n_F - n_c)/d$	$10^4(n_g - n_D)/d$	$10^4(n_F - n_c)/d$	$10^4(n_g - n_D)/d$	$10^4(n_F - n_c)/d$	$10^4(n_g - n_D)/d$	$10^4(n_F - n_c)/d$	$10^4(n_g - n_D)/d$
	<i>n</i> -Hexadecane		<i>n</i> -Decylcyclopentane		<i>n</i> -Decylcyclohexane		1-Hexadecene		<i>n</i> -Decylbenzene	
20	98.00	124.90	96.55	123.19	97.73	124.48	107.03	136.73	136.99	177.32
25	98.19	125.07	96.86	123.48	97.77	124.51	107.25	137.09	136.40	176.67
30	98.38	125.26	97.16	123.78	97.80	124.53	107.48	137.45	136.62	176.94

TABLE IV

EXPERIMENTAL DATA ON THE TEMPERATURES AND PRESSURES OF THE LIQUID-VAPOR EQUILIBRIUM									
<i>t</i> , °C.	<i>P</i> , mm.	<i>t</i> , °C.	<i>P</i> , mm.	<i>t</i> , °C.	<i>P</i> , mm.	<i>t</i> , °C.	<i>P</i> , mm.	<i>t</i> , °C.	<i>P</i> , mm.
<i>n</i> -Hexadecane		<i>n</i> -Decylcyclopentane		<i>n</i> -Decylcyclohexane		1-Hexadecene		<i>n</i> -Decylbenzene	
286.704	758.50	279.283	758.55	297.507	758.50	284.768	758.24	297.799	758.41
285.337	736.32	277.907	736.33	296.058	736.32	283.402	736.10	296.370	736.16
278.333	630.54								
268.540	503.11	260.943	503.23			266.590	503.01	278.950	503.12
259.336	403.36	251.676	403.47	268.976	403.47	257.440	403.38		
250.605	323.81	242.859	323.76	259.864	323.79	248.690	323.84	260.372	323.82
242.432	261.15								
235.145	214.20	227.251	214.10	243.758	214.15	233.203	214.17	244.331	214.18
227.336	171.66	219.377	171.73	235.626	171.71	225.397	171.68		
221.780	145.87	213.782	145.93	229.848	145.88	219.806	145.81	230.476	145.83
215.000	118.69								
208.962	98.24	200.861	98.25	216.465	98.22	206.981	98.06	217.156	98.17
203.437	82.14							211.392	82.04
199.273	71.49	191.085	71.48	206.361	71.50	197.257	71.56		
195.301	62.48							202.987	62.47
190.054	52.09	181.867	52.01	196.812	52.08	188.152	52.06		

TABLE V

SUMMARY OF THE RESULTS OF THE CORRELATION OF THE EXPERIMENTAL DATA WITH THE ANTOINE EQUATION FOR VAPOR PRESSURE

Compound	Formula	Constants of the Antoine equation $\log_{10} P = A - B/(C + t)$ or $t = B/(A - \log_{10} P) - C$ <i>P</i> in mm. Hg; <i>t</i> in °C.			Normal boiling point at 760 mm., °C.	Pressure coefficient dt/dP at 760 mm., °C./mm.	Range of measurement		Measure of precision, ρ
		<i>A</i>	<i>B</i>	<i>C</i>			Pressure, mm.	Temp., °C.	
<i>n</i> -Hexadecane	C ₁₆ H ₃₄	7.03044	1831.317	154.528	286.793	0.06077	52-760	190.0-286.8	1.30
<i>n</i> -Decylcyclopentane	C ₁₅ H ₃₀	7.00349	1825.748	163.479	279.376	.06138	52-760	181.8-279.4	1.04
<i>n</i> -Decylcyclohexane	C ₁₆ H ₃₂	7.01640	1896.974	161.106	297.589	.06338	52-760	196.8-297.6	1.55
1-Hexadecene	C ₁₆ H ₃₂	7.04437	1843.581	157.917	284.873	.06077	52-760	188.1-284.8	1.71
<i>n</i> -Decylbenzene	C ₁₆ H ₂₆	7.03642	1904.132	160.318	297.890	.06301	62-760	202.9-297.9	1.50

each of the five compounds of the present investigation are found to be in good accord with those previously reported for the lower members of these series.^{2,4,6}

CORRELATION OF CRITICAL TEMPERATURES WITH THERMAL EXPANSION COEFFICIENTS OF ORGANIC LIQUIDS^{1,2}

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Two equations relating thermal expansion coefficients with critical temperatures of organic liquids are presented. One of these equations is derived from the Ramsay-Shields-Eotvos and the McLeod and Sugden relations. The other equation has been obtained empirically with the aid of experimentally determined critical temperatures and densities. A comparison of the two equations is made.

The thermal expansion coefficient of a liquid is of interest because of relations involving this coefficient and the heat capacity of the liquid and also because of the purely practical use of liquid expansion in thermoregulating devices. A fairly complete review of methods for predicting critical temperatures and thermal expansion coefficients is given by Partington.³ The ideal method for making such predictions should be applicable to different classes of compounds and should involve only data which are already available or are easily measured.

Lautie,⁴ using the Ramsay-Shields-Eotvos equation relating surface tension and temperature

$$\gamma \left(\frac{M}{d}\right)^{2/3} = k(T_c - T - 6) \quad (1)$$

and the parachor relation of McLeod and Sugden

$$[P] = \left(\frac{M}{d}\right) \gamma^{1/4} \quad (\text{neglecting vapor density}) \quad (2)$$

derived the relation

$$\left(\frac{d}{M}\right)^{10/3} \frac{[P]^4}{k} + T + 6 = T_c \quad (3)$$

Since $[P]^4/k$ in the above relation is constant for a given liquid at a definite temperature, the relation may be written

$$\left(\frac{d}{M}\right)^{10/3} k' + T + 6 = T_c \quad (4)$$

Assuming k' to be independent of temperature, which is a valid assumption in cases where no chemical change occurs, a relation is obtained involving only density and temperature.

$$\left(\frac{d_1}{d_2}\right)^{10/3} = 1 + \frac{T_2 - T_1}{T_c - T_2 - 6} \quad (5)$$

The expansion coefficient, α , for a liquid is defined as $1/v(\partial v/\partial T)_P$. If finite temperature intervals are used and the reciprocals of the densities substituted for volumes, the definition of α becomes $(d_1/d_2 - 1)/(T_2 - T_1)$. Substituting for d_1/d_2 its equivalent from eq. 5 we have

$$[\alpha(T_2 - T_1) + 1]^{10/3} = \frac{T_2 - T_1}{T_c - T_2 - 6} + 1 \quad (6)$$

(1) This paper is based on theses presented by Sheldon Greenbaum, March, 1946, and Gene P. Rutledge, June, 1948, in partial fulfillment of the requirements for the M.S. degree. The work was sponsored by the Fulton-Sylphon Company, Knoxville, Tennessee.

(2) Presented at the 115th meeting of the American Chemical Society, San Francisco, California, March, 1949.

(3) J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. I, Longmans, Green and Company, London, 1949, pp. 646-652; Vol. II, 1951, pp. 43-49.

(4) R. Lautie, *Bull. soc. chim. France*, [5] 2, 155, 2234 (1935).

Upon rearrangement three more convenient forms of the equation are obtained.

$$\alpha = \frac{\left(1 + \frac{\Delta T}{T_c - T_2 - 6}\right)^{0.3} - 1}{\Delta T} \quad (6A)$$

$$T_c = \frac{\Delta T}{(\alpha \cdot \Delta T + 1)^{10/3} - 1} + T_2 + 6 \quad (6B)$$

$$T_c = \frac{\Delta T}{(d_1/d_2)^{10/3} - 1} + T_2 + 6 \quad (6C)$$

The expansion coefficient for any temperature interval may then be calculated from the critical temperature of the liquid or the critical temperature may be calculated from the densities at two known temperatures.

Equation 6 shows that the coefficient of expansion of a liquid rises with the temperature and its value is a function of the magnitude of the interval between the temperature at which the densities are measured and the critical temperature as well as a function of ΔT .

Table I affords a comparison of T_c calculated using eq. 6C and T_c obtained by direct measurements on 74 organic compounds. T_c was calculated over a smaller range, usually approximately 30°, and a larger range, which ordinarily extended from 0 to within about 10° of the boiling point. The table

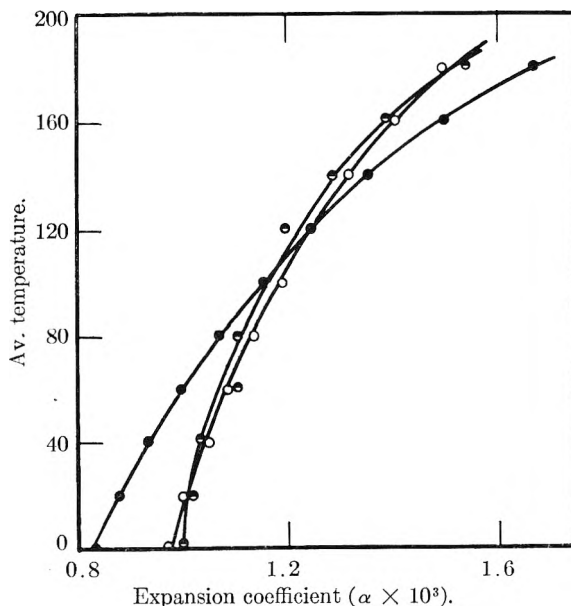


Fig. 1.—Thermal expansion coefficients for undecane (ref. *b* and *d* of Table I): ○ calcd. from density measurements; ●, predicted from critical temperature (eq. 6A); ○, predicted from critical temperature (eq. 7A).

TABLE I
 EXPERIMENTAL AND CALCULATED CRITICAL TEMPERATURES

Compound	Density ^a at temp., °K.		Density ^a at temp., °K.		Critical temp., °K.			Dev. from exptl., %		
					Calcd. Eq. 6B	Calcd. Eq. 7B	Exptl. ^b	Eq. 6B (smaller interval)	Eq. 6B (larger interval)	Eq. 7B
Toluene	0.877940 ^c	281.2	0.779703	383.2	599.0	587.7	593.8		0.9	1.0
Benzene	.891806 ^c	281.2	.813835	353.2	561.1	544.7	561.7		0.1	3.0
<i>o</i> -Xylene	.91595 ^d	250.25	.80573	379.55	628.3	640.2	631.5		0.5	1.4
<i>m</i> -Xylene	.88113 ^d	273.2	.77172	399.2	632.0	631.7	618.8		2.1	2.1
<i>p</i> -Xylene	.86544 ^d	288.1	.76658	398.75	627.0	623.1	617.6		1.5	0.9
Propionitrile	.77152 ^d	303.2	.69837	372.35	554.0	523.7	564.4		1.8	7.2
Butyronitrile	.78165 ^d	303.2	.71762	368.8	574.0	555.9	582.2		1.4	4.5
Capronitrile	.79704 ^d	303.2	.74005	370.35	616.0	623.7	622.2		1.0	0.2
Chlorobenzene	1.0978 ^d	301.2	1.0100	381.8	640.0	656.2	632.2		1.2	3.8
Ethylbenzene	0.88458 ^d	273.2	0.77016	399.1	619.6	610.6	619.2		0.1	1.4
Propylbenzene	.87864 ^d	273.2	.76608	403.2	634.0	631.7	638.8		0.8	1.1
Cyclohexane	.78315 ^d	288.2	.70080	372.4	566.0	541.5	554.1		2.1	2.3
Methylcyclohexane	.78650 ^d	273.2	.69825	372.70	583.0	567.6	574.7		1.4	1.3
Acetone	.81250 ^d	273.2	.77933	303.2	510.3	494.1	508.2	0.4		2.8
Carbon disulfide	1.29270 ^d	273.2	1.24817	303.2	551.0	559.3	546.2	0.9		2.4
Pentane	0.64543 ^d	273.2	0.61607	303.2	487.6	460.7	470.4	3.6		2.1
2-Methylbutane	.63945 ^d	273.2	.62470	288.2	479.6	455.7	461.0	4.0		1.2
Hexane	.67704 ^d	273.2	.65055	303.2	519.8	508.8	508.0	2.3		0.2
Heptane	.70048 ^d	273.2	.67522	303.2	539.6	531.5	540.2	0.1		1.6
3-Ethylpentane	.7160 ^d	273.2	.6442	353.2	543.5	525.0	540.8		0.5	2.9
Octane	.71850 ^d	273.2	.69450	303.2	560.0	573.1	569.1	1.5		0.7
2,5-Dimethylhexane	.71020 ^d	273.2	.68551	303.2	548.8	555.3	550.0	0.2		1.0
Isooctane	.7078 ^d	273.2	.6303	363.2	559.8	536.5	544.3		2.8	1.4
Nonane	.73300 ^d	273.2	.70988	303.2	577.5	600.7	596.0	1.9		0.8
Decane	.74487 ^d	273.2	.72238	303.2	588.2	583.7	603.6	2.6		3.3
Undecane	.75483 ^d	273.2	.73282	303.2	599.0	642.8	642.6	6.8		0.0
	.7182 ^d	323.2	.6224	443.2	645.4	624.1	642.6		0.4	2.9
Dodecane	.75248 ^d	288.2	.74157	303.2	610.4	661.8	658.2	7.2		0.5
Pentadecane	.77197 ^d	288.2	.76146	303.2	629.7	700.1	717.6	12.2		2.4
Tridecane	.77049 ^d	273.2	.74915	303.2	614.3	673.3	683.2	10.0		1.4
Dotriacontane	.77910 ^d	348.2	.75185	391.2	849.8	833.5	882.2		3.7	5.5
Methyl formate	1.00317 ^d	273.2	.97421	293.2	494.3	474.6	487.2	1.5		2.6
Ethyl formate	0.94815 ^d	273.2	.90958	303.2	511.4	495.2	508.5	0.6		2.6
	(1.00000) ^e	273.2	(1.07882)	326.1	515.9	490.4	508.5		1.5	3.6
Ethyl acetate	0.92453 ^d	273.2	0.88851	303.2	521.2	508.3	523.3	0.4		2.9
	(1.00000) ^e	273.2	(1.11094)	346.7	527.6	496.9	523.3		0.8	5.0
Ethyl propionate	0.91251 ^d	273.2	0.87903	303.2	535.3	533.0	546.1	2.0		2.4
	(1.00000) ^e	273.2	(1.12890)	363.7	551.4	523.1	546.1		1.0	4.2
Ethyl butyrate	0.89998 ^d	273.2	0.86871	303.2	549.2	555.5	566.2	3.0		1.9
	(1.00000) ^e	273.2	(1.15864)	387.6	574.1	543.7	566.2		1.4	4.0
Ethyl nonate	0.88156 ^d	273.2	0.85693	303.2	612.5	668.0	673.2	9.0		0.8
Ethyl octanoate	.88351 ^d	273.2	.85802	303.2	601.9	648.9	659.2	8.6		1.6
	(1.0000) ^f	273.2	(1.1798)	428.5	645.7	633.5	659.2		2.0	3.9
Acetic anhydride	1.0870 ^d	288.2	1.0443	323.2	574.0	584.4	569.2	0.9		2.7
Propyl acetate	(1.00000) ^e	273.2	(1.13422)	368.7	557.7	529.9	549.4		1.5	3.5
Propyl butyrate	(1.00000) ^e	273.2	(1.17389)	404.1	595.4	566.8	600.2		0.8	5.6
Methyl isobutyrate	(1.00000) ^e	273.2	(1.12288)	360.3	550.9	524.5	540.8		1.9	3.0
Isobutyl isobutyrate	(1.00000) ^e	273.2	(1.03402)	305.6	586.2	618.6	602.2	2.7		2.7
	(1.00000) ^e	273.2	(1.16397)	399.9	598.2	574.2	602.2		0.7	4.7
Isobutyl butyrate	(1.00000) ^e	273.2	(1.03425)	306.3	590.9	626.5	611.2	3.3		2.5
	(1.00000) ^e	273.2	(1.18388)	414.7	608.0	580.1	611.2		0.5	5.1
Isobutyl formate	(1.00000) ^e	273.2	(1.04225)	309.1	557.8	566.7	551.2	1.2		2.8
	(1.00000) ^e	273.2	(1.13352)	371.8	567.9	543.9	551.2		3.0	1.3
Isobutyl propionate	(1.00000) ^e	273.2	(1.03114)	302.2	577.7	605.6	592.2	2.4		2.7
	(1.00000) ^e	273.2	(1.17933)	404.5	589.6	557.3	592.2		0.4	5.9
Propyl isobutyrate	(1.00000) ^e	273.2	(1.04098)	310.2	574.3	594.5	589.2	2.5		0.9
	(1.00000) ^e	273.2	(1.17875)	403.1	587.0	554.1	589.2		0.3	6.0
Propyl propionate	(1.00000) ^e	273.2	(1.03424)	304.0	569.2	589.7	578.2	1.6		2.0
	(1.00000) ^e	273.2	(1.15902)	389.21	578.2	548.4	578.2		0.0	5.2
Methyl acetate	(1.00000) ^e	273.2	(1.07353)	322.8	514.7	490.2	506.9		1.5	3.3
Methyl propionate	(1.00000) ^e	273.2	(1.10789)	347.6	536.3	509.3	530.6		1.0	4.0

TABLE I (Continued)

Compound	Density ^a at temp., °K.		Critical temp., °K.			Dev. from exptl., %	
	Density ^a at temp., °K.	Density ^a at temp., °K.	Eq. 6B	Eq. 7B	Eq. 7B	Eq. 6B (smaller interval)	Eq. 6B (larger interval)
Methyl butyrate	(1.00000) ^e 273.2	(1.13183) 367.5	558.0	531.0	554.5		0.6 4.2
Pyridine	1.0031 ^d 273.2	0.9164 358.2	605.9	616.2	617.2		1.8 0.2
Phenol	1.0499 ^d 323.2	1.0325 343.2	697.6	797.2	692.2	0.8	15.2
Aniline	1.03905 ^d 273.2	1.01317 303.2	651.6	753.2	699.2	6.8	7.7
Anisole	1.01243 ^d 273.2	0.98462 303.2	618.1	678.5	642.2	3.7	5.7
Chloroform	1.52638 ^d 273.2	1.47060 303.2	536.3	534.6	536.2	0.0	0.3
Carbon tetrachloride	1.63255 ^d 273.2	1.57480 303.2	544.4	564.6	556.3	2.1	1.5
Methylamine	0.76903 ^d 199.0	0.71124 252.2	437.0	409.1	430.0		1.6 4.7
Ethylamine	0.7854 ^d 200.55	0.6949 283.3	453.8	417.0	456.4		0.6 8.6
Acetic acid	1.04926 ^d 293.2	1.02679 313.2	586.5	611.9	594.8	1.3	2.9
	(1.0000) ^e 273.2	(1.1229) 380.2	614.6	612.9	594.8		3.3 3.0
Propionic acid	1.01503 ^d 273.2	0.98260 303.2	571.7	594.3	612.7	6.7	3.0
	(1.00000) ^e 273.2	(1.16161) 405.8	616.5	669.1	612.7		0.6 9.2
Butyric acid	0.97762 ^d 273.2	0.94797 303.2	586.7	621.0	628.2	6.6	1.1
	(1.0000) ^e 273.2	(1.1537) 404.7	626.0	617.5	628.2		0.4 1.7
Isobutyric acid	0.96815 ^d 273.2	0.93782 303.2	577.7	604.1	609.2	5.2	0.8
Valeric acid	.95744 ^d 273.2	.93017 303.2	605.9	656.2	652.2	7.1	0.6
	(1.0000) ^e 273.2	(1.1576) 416.7	650.9	651.9	652.2		0.2 0.0
3-Methylbutyric acid	0.94462 ^d 273.2	0.91708 303.2	599.0	642.9	634.2	5.5	1.4
Methanol	.80999 ^g 273.2	.78184 303.2	549.0	555.4	513.2	7.0	8.2
Ethanol	.79784 ^g 283.2	.77203 313.2	578.4	598.2	516.3	12.0	15.9
Butanol-1	(1.0000) ^e 273.2	(1.0362) 312.5	630.6	696.2	560.2	12.5	24.3
	(1.0000) ^e 273.2	(1.1203) 381.7	623.3	629.9	560.2		11.2 12.4
Butanol-2 (racemic)	0.82273 ^d 273.2	0.79898 303.2	601.8	648.5	538.2	11.8	20.5
2-Methylpropanol-1	.81707 ^d 273.2	.79437 303.2	614.6	671.5	538.2	14.1	24.8
2-Methylpropanol-2	.78760 ^d 293.2	.77090 308.2	517.4	500.9	508.2	1.8	1.4
2-Methylbutanol-2	.82718 ^d 273.2	.79974 303.2	561.3	576.3	545.2	3.0	5.7
3-Methylbutanol-1	.82392 ^d 273.2	.80179 303.2	625.0	692.8	580.2	7.7	19.4
Heptanol-1	(1.0000) ^e 273.2	(1.0362) 316.8	669.1	769.7	638.2	4.6	20.6
	(1.0000) ^e 273.2	(1.1722) 429.6	657.5	653.2	638.2		3.0 2.4
Octanol-1	(1.0000) ^e 273.2	(1.0229) 302.1	676.0	798.3	658.2	2.7	21.3
	(1.0000) ^e 273.2	(1.2076) 459	677.4	664.9	658.2		1.4 1.0

^a Values in the density column which are enclosed by parentheses represent relative volumes, the volume at 0° being taken as 1.00000. ^b The values for the experimental critical temperatures for the hydrocarbons were taken from M. P. Doss, "Physical Constants of the Principal Hydrocarbons," 3rd. Ed., The Texas Co., New York, N. Y., 1941. All others are from C. D. Hodgman, "Handbook of Physics and Chemistry," 25th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1941, p. 1703. ^c J. S. Burlew, *J. Am. Chem. Soc.*, 62, 690 (1940). ^d "Annual Tables of Physical Constants," Princeton, Frick Chemical Laboratories, New Jersey, 1942. ^e A. Zander, *Ann.*, 224, 61ff. (1884). ^f R. Gardenmeister, *ibid.*, 323, 286 (1886). ^g "International Critical Tables," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 28.

shows that, in fifteen of the eighteen cases where T_c was calculated using the larger and smaller temperature intervals, there is closer agreement between T_c calculated and observed when the larger temperature range is used in the calculation. The table also indicates that highly polar liquids such as acids and alcohols depart more from the general relation than the less polar types. This, of course, might be expected since both $[P]$ and k vary with temperature for these substances. Out of the forty-four compounds used in calculating T_c from the larger intervals, only three (acetic acid, butanol-1 and dotriacontane) give values deviating by more than 3% from observed values. Twenty-two of the forty-four differ by 1% or less.

A more extensive evaluation of eq. 6A can be accomplished by actually predicting expansion coefficients calculated for a series of small uniform (20°) temperature intervals from the critical temperature of a substance. Undecane is taken as an example (Fig. 1). It is evident from Fig. 1 that eq. 6A gives a curve which crosses the experimental curve. Although the agreement between values on the two curves is fairly good, the trend is unmis-

takable. A larger temperature interval used in the calculation usually will give better agreement between the two curves since the deviations may tend to cancel.

A rotation of the curve predicted using small ΔT values is necessary to give agreement over the entire temperature range. Since the expansion coefficient is a function of $(T_c - T_{av})$ where T_{av} is the average temperature of the interval over which the expansion coefficient is determined the nature of the curve suggests the empirical equation

$$\alpha = a(T_c - T_{av})^b \quad (7)$$

Using the critical temperature and density measurements of 29 organic compounds (including anhydrides, acids, hydrocarbons, alcohols, fluorocarbons, esters, ketones, nitriles, ethers and others) the best curve, ($\Delta T = 30^\circ$ or less) by the method of least squares, is represented by the equation (see Fig. 2)

$$\alpha = 0.04314(T_c - T_{av})^{-0.6410} \text{ or} \quad (7A)$$

$$T_c = \left(\frac{\alpha}{0.04314} \right)^{-1.56} + T_{av} \quad (7B)$$

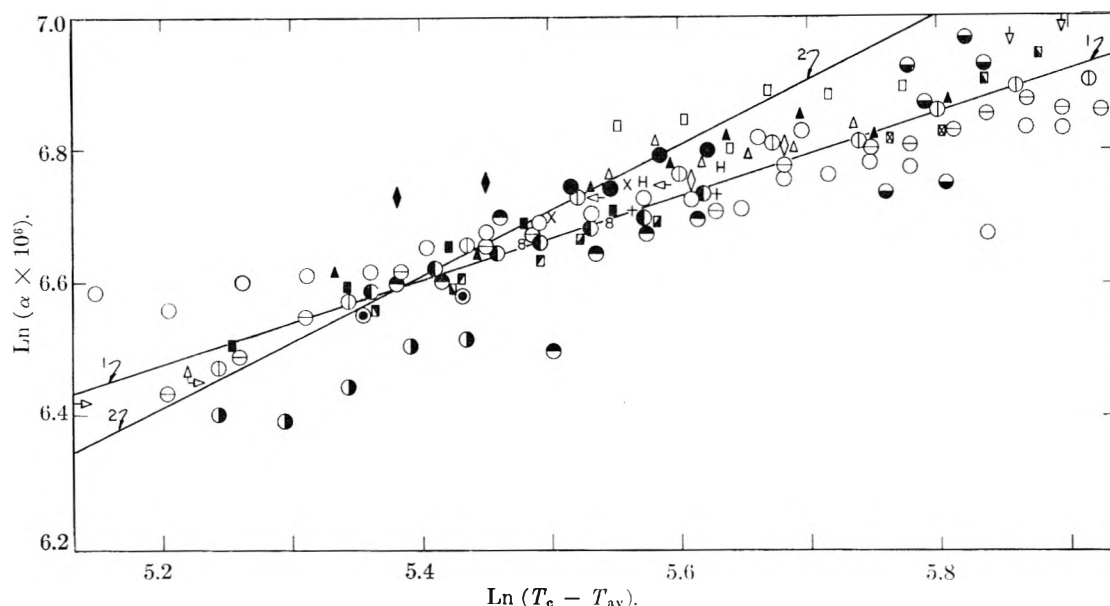


Fig. 2.—(Curve 1), least squares plot for evaluation of constants^a in eq. 7A; (curve 2), plot for both Pettinelli's eq. and for eq. 6B using $\Delta T = 8^\circ$ and calculating α for assumed values of $T_c - T_{av}$: ●, acetic anhydride; ○, 2,2-dimethylpentane; x, heptane; ▲, toluene; △, capronitrile; ■, cyclohexane; □, chlorobenzene; ⊖, 3-ethylpentane; ⊕, undecane; ⊙, pyridine; ⊗, acetonitrile; ⊚, butyronitrile; ⊛, benzene; ⊘, acetic acid; ⊙, propionic acid; ⊚, ethyl propionate; ⊛, ethyl formate; ⊚, ethyl acetate; ⊙, acetone; ⊚, *n*-propanol; ◆, methanol; ◇, thiophene; II, fluorobenzene; 8, chloroform; +, carbon tetrachloride; <, carbon disulfide; ∇, anisole; >, ethyl ether; ⚡, perfluoroheptane.

^a Data on perfluoroheptane from A. V. Grosse and G. H. Cady, *Ind. Eng. Chem.*, **39**, 367 (1947), and R. D. Fowler, J. D. Hamilton, J. S. Kasper, C. E. Weber, W. B. Buford and H. C. Anderson, *ibid.*, **39**, 375 (1947). All other data from same sources as in Table I.

This equation generally gives better agreement than eq. 6A for smaller temperature ranges (see Fig. 1).

Either T_c or α are very easily obtained for different substances using a general plot of $(T_c - T_{av})$ vs. α (see Fig. 3).

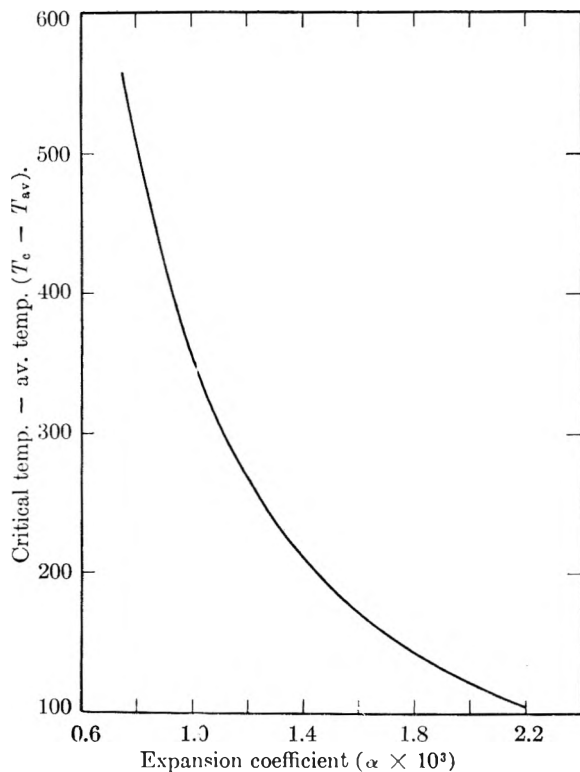


Fig. 3.—Plot of eq. 7A.

An equation of the same form as (7A) has been published by Pettinelli.⁵ Pettinelli assumed that b , the slope of the line on plotting $\ln \alpha$ vs. $\ln (T_c - T_{av})$, is -1 whereas here it is found to be -0.6410 . Pettinelli's constant, a , the y intercept of the $\ln \alpha$ vs. $\ln (T_c - T_{av})$ plot, varied from 0.289 to 0.359 for the 14 compounds he tested with an average value of 0.319. Values of α calculated for several $T_c - T_{av}$ values using eq. 6A and assuming ΔT is 30° give $b = -1.051$ and $a = 0.4182$ when substituted in eq. 7. When $\Delta T = 12^\circ$ the values so obtained are $b = -1.036$ and $a = 0.3795$. At $\Delta T = 8^\circ$ the constants, $b = -0.998$ and $a = 0.2947$, compare closely with the constants in Pettinelli's equation. By plotting these values on Fig. 2, it is evident that eq. 7A gives the best agreement over the entire temperature range. This is also evident in Fig. 1. Pettinelli used the expansion coefficient of a liquid at only one temperature in evaluating the constants. Table I shows that eq. 6C, using smaller ΔT values and excluding alcohols, gives 16 out of 39 compounds differing from the experimentally determined T_c by more than 3%, whereas for eq. 7B only 4 out of the 39 differ by more than 3%.

Since so many variables are involved, a statistical evaluation of the accuracy of these equations is essentially impossible; however, a suggested accuracy of $\pm 3\%$ for T_c is given for eq. 6C using larger ΔT 's and eq. 7B using smaller ΔT 's. If several density values are known, several predicted values for T_c may be obtained. In this case it is suggested that the average of the several predicted T_c values be used. If the expansion coefficient is not accurately known, the pre-

(5) F. Pettinelli, *J. phys.*, **1**, 596 (1906).

dicted T_c cannot be reliable. A 3% difference in T_c is roughly equivalent to a 5% difference in α .

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NOTE

THE EVALUATION OF CONSTANTS IN FIRST-ORDER CONSECUTIVE IRREVERSIBLE REACTIONS

BY ELIAS KLEIN AND T. F. FAGLEY

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Received January 30, 1954

Swain¹ has treated consecutive irreversible first-order kinetics for the case in which both products

B and C in the reaction $A \rightarrow B \rightarrow C$ are analyzed as a single chemical species. A study of a first-order consecutive reaction in this Laboratory reveals a reaction in which the only species which can be measured with any experimental precision is the species C represented in the equation $A \xrightarrow{k_1} B \xrightarrow{k_2} C$. If k_1 and k_2 are to be evaluated from this measurement alone, a series of tedious approximations has been the usual procedure in the past.

Pairs of graphs (y/a)	(y'/a)	Offset	$\log K$	$\log m$	K	$k_1 t$	k_1
0.3	0.4	0.100	-0.285				
					Tangency of curves		
.3	.6	.274	-.300	0.476	0.502	2.99	0.0997
.3	.7	.359	-.302	.562	.499	3.65	.1007
.4	.6	.173	-.301	.475	.500	2.99	.0997
.4	.7	.258	-.301	.561	.500	3.69	.1004
					Av. 0.500 ₂₅		0.1001 ₂₅
					$k_2 = K$	$k_1 = 0.0500$	

TABLE OF K vs. m VALUES

K	m				K	m			
	$y/a = 0.3$	$y/a = 0.4$	$y/a = 0.6$	$y/a = 0.7$		$y/a = 0.3$	$y/a = 0.4$	$y/a = 0.6$	$y/a = 0.7$
0.01000	36.6700	52.0900	92.6300	121.4000	1.5000	0.9028	1.1346	1.6742	2.0252
.01053	34.8935	49.5330	88.0460	115.3870	2.0000	.7925	1.0008	1.4899	1.8118
.01111	33.1020	46.9260	83.4750	109.3590	3.0000	.6710	0.8539	1.2965	1.5956
.01176	31.3225	44.4295	78.8885	103.3430	4.0000	.6024	.7736	1.1971	1.4888
.01250	29.5360	41.7600	74.3120	97.3280	5.0000	.5581	.7228	1.1373	1.4265
.01333	27.7575	39.3150	69.7275	91.3050	6.0000	.5270	.6878	1.0979	1.3861
.01429	25.9770	36.7640	65.1490	85.2880	7.0000	.5039	.6623	1.0704	1.3581
.01539	24.1930	34.2095	60.5670	79.2675	8.0000	.4860	.6429	1.0497	1.3375
.01667	22.4100	31.6560	55.9860	73.2480	9.0000	.4719	.6278	1.0341	1.3218
.01818	20.6250	29.1060	51.4030	67.2265	10.000	.4604	.6158	1.0216	1.3093
.02000	18.8457	26.5500	46.8250	61.2100	15.000	.4255	.5798	0.9853	1.2730
.02222	17.0640	23.9985	42.2460	55.1880	20.000	.4080	.5621	.9676	1.2553
.02500	15.2800	21.4440	37.6640	49.1720	25.000	.3975	.5516	.9571	1.2448
.02857	13.4995	18.8930	33.0855	43.1550	30.000	.3906	.5447	.9502	1.2379
.03333	11.7180	16.3410	28.5060	37.1370	35.000	.3857	.5398	.9453	1.2330
.04000	9.9375	13.7900	23.9275	31.1200	40.000	.3820	.5361	.9416	1.2293
.05000	8.1600	11.2420	19.3520	25.1060	45.000	.3792	.5333	.9388	1.2264
.06667	6.3825	8.6970	14.7795	19.0950	50.000	.3769	.5310	.9365	1.2242
.10000	4.6040	6.1580	10.2160	13.0930	55.000	.3750	.5292	.9346	1.2223
.11111	4.2471	5.6502	9.3069	11.8962	60.000	.3735	.5276	.9331	1.2208
.12500	3.8880	5.1432	8.3976	10.7000	65.000	.3722	.5263	.9318	1.2195
.14290	3.5273	4.6361	7.4928	9.5067	70.000	.3711	.5252	.9307	1.2184
.16667	3.1620	4.1268	6.5874	8.3166	75.000	.3701	.5242	.9297	1.2174
.20000	2.7905	3.6140	5.6865	7.1325	80.000	.3692	.5234	.9289	1.2166
.25000	2.4096	3.0944	4.7884	5.9552	85.000	.3685	.5227	.9281	1.2158
.33333	2.0130	2.5617	3.8895	4.7868	90.000	.3678	.5220	.9275	1.2151
.50000	1.5868	2.0016	2.9798	3.6236	95.000	.3673	.5214	.9268	1.2146
.66667	1.3542	1.7019	2.5113	3.0378	100.000	.3667	.5209	.9263	1.2140

(1) C. G. Swain, *J. Am. Chem. Soc.*, **66**, 1696 (1944).

If $(a - x)$, $(x - y)$ and y represent the amount or

concentration of A, B and C, respectively, where a is the amount or concentration of A at time $t = 0$, the rates may be written

$$dx/dt = k_1(a - x) \quad (1)$$

$$dy/dt = k_2(x - y) \quad (2)$$

and the integration leads to

$$x = a(1 - e^{-k_1 t}) \quad (3)$$

$$y = a\{1 - [1/(k_1 - k_2)](k_2 e^{-k_1 t} - k_1 e^{-k_2 t})\} \quad (4)$$

If the following substitutions are made in equation 4, one obtains

$$K = k_2/k_1; \quad m = k_1 t \\ (y/a - 1)(1 - K) = Ke^{-m} - e^{-mK} \quad (5)$$

The value y/a represents the degree of completion of the reaction at any time. If for, say, two values, y/a and y'/a , the solution of (5) is tabulated within the range of $K = 0.01$ to $K = 100.0$, the specific reaction rate constants can be evaluated in the following way.

For each value, y/a and y'/a , plot a graph of K versus $\log m$. This, from the definition of m , is seen to have the abscissa $\log kt$. If the graph paper is transparent, the abscissas of the two graphs may be equated by off-setting one graph from the other by an amount equal to $\log t - \log t'$, where t

corresponds to the time where y/a completion has occurred. The intersection of the two graphs must then give the unique solution for K . This generally applicable solution then resolves itself into a tabulation of K versus m values for three or four values of y/a . The values of $y/a = 0.3, 0.4, 0.6$ and 0.7 would allow several determinations of K at various stages of completion of the kinetic process. From equation 5 it can be seen that there is no algebraic method for expressing m explicitly and that only a series of approximations would lead to a value of m for a given set of values y/a and K . Solutions were obtained by using successive approximations with the aid of mathematical tables.² The values of m , K and y/a are given in Table I. The method was tested by applying it to the hypothetical reaction for which $k_1 = 0.1 \text{ min.}^{-1}$ and $k_2 = 0.05 \text{ min.}^{-1}$ for which the times for $y/a = 0.3, 0.4, 0.6$ and 0.7 are 15.87, 20.02, 29.80 and 36.24 minutes, respectively. Graphs constructed on sufficiently large paper to permit a precision of four significant figures in $\log t$ and three in $\log m$ were offset on one another by $\log t - \log t'$ and K read off directly.

(2) Tables of Exponential Functions, Federal Works Agency, Works Project Administration (Under Sponsorship of Natl. Bur. Standards), 1939; "A New Manual of Logarithms," K. C. Bruhns, Rev. ed., The Charles T. Powner Co., Chicago, Illinois, 1942.

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				Wt. % A	
1 A	Argon	-186	Nonazeotrope, V-I.		164
2 A	Nitrogen, 500-1500 mm.	-195	Nonazeotrope		255
3 A	Silver Chloride	1580	Nonazeotrope		263
4 A	Lead chloride	954			263
5 A	Boron Chloride	11.5		77.2	263
	Hydrogen chloride	-92.5		62	262
		-100		60	262
		-92		65	262
		100		80	262
		100		42	262
		100		52	262
		100		62	262

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