# INDEX

Activity, 324 in binary systems containing compounds, 459 calculation from phase diagrams, 397 of: N in liquid Fe, 457 in the system Fe-X, 494 of O in liquid Fe, 479 relationship with free energy of solution, 379 of S in liquid Fe, 476 in the system: Fe-C, 426 Fe-Co, 356 Fe-Cr, 325 Fe-Cr-O, 512 Fe-Cu, 347 Fe-Ni, 353 Fe-O, 478, 482 Fe-Si, 424 Mg-Al, 540 PbO-SiO<sub>2</sub>, 534, 538 Tl-Sn, 363 U-C, 474 Activity coefficient, 338 Henrian, 419 mean ionic, 545 one weight percent, 421 Activity quotient, 412 Adiabatic, 15 processes, reversible, 25, 46 Alpha function, 343, 360 Anode, 527

Anolyte, 527 Aqueous solutions, thermodynamics of, 542 Avogadro's hypothesis, 7 Avogadro's number, 80

Beattie-Bridgeman equation of state, 204 Belton-Freuhan treatment of Gibbs-Duhem equation, 348 Berthelot equation of state, 204 Boiling temperature, 169 Boltzmann's constant, 80 Boltzmann's equation, 82, 87 Boyle's law, 5

Calomel half-cell, 546 Calorie, 16 15° calorie, 16 thermochemical, 16 Carnot cycle, 49 Cathode, 527 Catholyte, 527 Charles' law, 5 Chemical potential, 102, 155 Clapeyron equation, 166 Clausius-Clapeyron equation, 168 Coefficient of thermal expansion, 6 Complexion, 76 Component, 9

## 608

Compressibility factor, 192, 214 isothermal variation with pressure for several gases, 192 variation with reduced pressure at constant reduced temperature, 194 Concentration cell, 532 Convention: regarding: direction of heat flow, 17 enthalpy reference state, 128 sign of EMF of a galvanic cell: European convention, 555 US convention, 527 work, 17 Constitution diagram, 9 (See also Phase diagram) Critical point of a gas, 190

Dalton's law of partial pressure, 207 Daniell cell, 525 Davy, Humphrey, 15 Debye, P., 117 Debye frequency, 118 Debye temperature, 118 Debye T<sup>3</sup> law, 118 Degree of freedom, 173 Dieterici equation of state, 204 Dulong and Petit's law, 114

Einstein, A., 114 Einstein: characteristic temperature, 116 crystal, 114 Elastic vibration, 117 Electrochemical reaction, 522 Electrochemical series, 550 Electrolyte, 527 Electromotive force, 524 Ellingham diagram, 272 for chlorination of Fe, 285 CO/CO, nomographic scale, 292 effect of: nonunit activity, 413 phase transformation, 280 pressure, 288 H<sub>2</sub>/H<sub>2</sub>O nomographic scale, 294 for metallurgically important oxides, 287 for oxidation of: Ag, 272 C, 290 Co, 274 Cu, 283

Fe, 490 Mn. 274 oxygen pressure nomographic scale, 276 Endothermic, 125 Energy, 8 degradation of, 38 internal, 16 quantization of, 74 theoretical calculation of, 116 (See also Free energy, Gibbs free energy, Helmholtz free energy, Internal energy) Enthalpy, 20, 93 convention regarding reference state, 128 of evaporation and sublimation, 168 as a function of: pressure, 145 pressure, volume, and temperature, 107 temperature and composition, 125 of phase transition, 126 of reaction, 128 (See also Heat) Entropy, 36 absolute value, 138 configurational, 85 experimental entropy change, 139 of formation of an ideal solution, 335 as a function of: internal energy and volume, 61 temperature, 134 temperature and volume, 63 pressure, 145 irreversible, 44, 57 of phase transition, 141 thermal, 85 Third Law entropy change, 139 Equilibrium, 4 heterogeneous, 9 homogeneous, 9 in a one component system, 155 in the system: C, 181 C-O, 286 Cu-H, O, 569 Cu-O, 266 Fe-C-Ti, 499 Fe-O, 482 Fe-O-C, 498 Fe-O-Si, 496 H<sub>2</sub>O, 177, 179 M-C-O, 295 Mg-C-O, 266 N<sub>2</sub>-H<sub>2</sub>-NH<sub>3</sub>, 248

#### INDEX

Equilibrium, in the system (Cont.): S-O, 237 SiO<sub>2</sub>, 180 V-O-S, 440 Equilibrium constant, 229 effect of: pressure, 232 temperature, 230 Excess thermodynamic function, 361 Exothermic, 125

Faraday's constant, 524 First Law of Thermodynamics, 18 Formation cell, 530 Free energy: in binary system containing compounds, 459 direct calculation of, 355 of evaporation, 270 of formation of ions, 545 generation from phase diagram, 397 Gibbs, 99 Helmholtz, 93 relationship with activity, 379 of solution formation, 328 Free energy function, 501 Fugacity, 212, 244 Fundamental equation, 104

Galvanic cell, 524 concentration, 528 formation, 530 Gas: constant, 7, 16 ideal, 8 Gay-Lussac's law, 6 Gibbs-Duhem equation, 327 alpha function of, 343 application to activity determination of, 340 Belton-Freuhan treatment of, 348 Gibbs free energy, 99 as a function of: pressure, 164, 198 temperature, 156 temperature and pressure, 164 (See also Free energy) Gibbs-Helmholtz equation, 110 Gibbs phase rule, 176, 433

Graphical representation of reaction equilibria, 295 Harmonic oscillator, 114 Heat: effects in galvanic cells, 541 engine, 48 of evaporation, 143 of formation of: an ideal solution, 333 a nonideal solution, 339 of fusion, 73, 142 calculation from phase diagram, 407 as a function of temperature, 125 reversible, 42 sign convention, 17 (See also Enthalpy) Heat capacity, 21 at constant: pressure, 21, 113 volume, 21, 113 electronic contribution to, 122 empirical representation of, 122 as a function of temperature for several elements, 124 lattice contribution to, 121 theoretical calculation of, 114 Helmholtz free energy, 93 Henrian standard state, 419 Henry's law, 320 relationship with Raoult's law, 346 Hess's law, 125 Heterogeneous, 9 Hildebrand, J. H., 360 Homogeneous, 9

Ideal gas, 8 entropy of mixing, 212 free energy of mixing, 211 heat of mixing, 210 isothermal variation of free energy with pressure for, 205 law, 8, 188 standard state, 206 temperature scale, 7 Ideal mixing, 88 Imperfect gas, 212 Integral free energy of solution, 328 Interaction coefficient, 491 Interaction parameter, 492

## 610

Internal energy, 16 as a function of: entropy and volume, 61 pressure, volume and temperature, 106

Joule, J., 15 Joule (unit), 8

Kammerlingh-Onnes equation of state, 205 Kelvin temperature scale, 52 Kopp's rule, 125

Law of corresponding states, 193 Le Chatelier's principle, 132, 231, 232 Lever rule, 12 Lime-stabilized zirconia, 533 Liter-atmosphere, 8

Macrostate, 77 Margules, M., 360 Maxwell's relations, 105 Mean ionic activity coefficient, 545 Mean ionic molality, 544 Mechanical equivalent of heat, 16 Microstate, 77 Molality, 542 Molarity, 542 Mole fraction, 206

Nernst heat theorem, 135 Nonideal gas, 212 standard state, 212 isothermal variation of free energy with pressure for, 216 Nonideal solution, 338

One weight percent standard state, 421 Oxide phases of variable composition, 480

Partial molar free energy of solution, 328 Partial molar property, 208 Partition function, 79 Perfect gas, 189 (See also Ideal gas) pH, 554

Phase, 10 Phase diagram, 9 of a one-component system in terms of: pressure and temperature, 169 for carbon, 181 for silica, 180 for sulfur, 177 for the system: Bi-Cd, 402 Cu-Ni, 11 Fe-C, 434 Fe-O, 12, 482  $Mn_2SiO_4$ -Fe<sub>2</sub>SiO<sub>4</sub>, 394 U-C. 470 for the systems alkali oxide-silica, 406 for systems containing compounds, 459 for water, 179 Phase rule, 176, 433 Planck, M., 136 Planck's constant of action, 115 Pourbaix diagram, 555 for Cu-H, O, 569 Pressure, 155 critical, 190 reduced, 193 partial, 207 Processes: irreversible, 37 natural, 37 reversible, 40 reversible adiabatic, 25 spontaneous, 37 Property: extensive, 9 intensive, 9 partial molar, 208 Quantization of energy, 74 Quasi-chemical model of solutions, 366 Raoult's law, 320 relationship with Henry's law, 346 properties of Raoultian solutions, 332 Raoultian standard state, 419 Regular solution, 358 criteria of phase stability in, 384 free energy of, 382 relationship between free energy, activity, and phase diagram, 397

Richards' rule, 142

### Rumford, Count, 15

#### INDEX

Second Law method, 505 Second Law of Thermodynamics, 55 Sievert's law, 475 Single electrode potential, 549 Solubility of gases in metals, 473 of N in liquid Fe, 475 of O in liquid Fe, 478 of S in liquid Fe, 477 Solubility product, 550 Solutions containing several dilute solutes, 489 Standard free energy of reaction, 225 variation with temperature, 267 Standard oxidation potential, 551 Standard state: Henrian, 419 ideal gas, 206 liquid, 388 nonideal gas, 212 one weight percent, 421 Raoultian, 419 solid, 388 species in a condensed state, 388 unit molality, 542 State: equation of, 2 function, 4 ideal gas, equation of, 8 macroscopic, 1, 76 microscopic, 1, 76 thermodynamic, 1 Stirling's approximation, 77, 336

Tabular representation of thermodynamic data, 501 Tangential intercepts, 330 Temperature, 155 absolute zero, 7 critical, 190 galvanic cell, coefficient of, 541 reduced, 193 Thermodynamic temperature scale, 52 Third Law method, 505 Third Law of Thermodynamics, 134 experimental verification of, 138 Transformation formula, 107 Triple point, 11, 170 Trouton's rule, 142

Valency, 522 van der Waals gas, 193 van Laar, J. H., 360 van't Hoff equation, 231 Vapor pressure: saturated, 96, 168 of several elements, 172 Variable: dependent, 2 extensive, 9 independent, 2 intensive, 9 Virial equation of state, 205 coefficient, 205 Volume: change of ideal solution formation, 332 critical, 190 reduced, 193

Work, 8 electrochemical, 524 maximum, 43, 57 other than P-V, 104 sign convention concerning, 17