A DICTIONARY OF THERMODYNAMICS

A.M. JAMES

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PREFACE

The idea of a dictionary of thermodynamics arose as a result of difficulties encountered during 25 years' experience of teaching the subject at all levels in university courses. At the start of a study of thermodynamics, students are not familiar with the language, while at the end of the course they require a thumb-nail sketch of the important concepts. In subsequent years, including periods of postgraduate study, students still need reminding of the basic concepts, equations, formulae, etc. and also their applications. While all these aspects are well and adequately covered in the many standard textbooks on thermodynamics, nevertheless in such books it is often impossible to locate readily a given topic and then to disentangle it from the context of the chapter. The fulfilment of these various needs has been uppermost in my mind during the writing of the book, in which the entries are listed in alphabetical sequence rather than by any of the methods arising from any conventional treatment of the subject.

Many thermodynamic courses and textbooks are devoted to the so-called 'rigorous' treatment of the subject, which generally means the derivation of all the standard equations. At the end, students have been treated to a course of mathematical gymnastics but they do not necessarily understand the significance or the application of the various concepts or equations to real systems. In this book, equations are quoted without derivation and their applications and limits are discussed; to all practising scientists this is a very important aspect.

The book is written essentially for scientists who have a minimum of G.C.E. 'A' level, or its equivalent, in a physical science subject. Biologists, Biochemists, Chemists, The Medical Profession, Geologists, Microbiologists, Pharmacists, Physiologists, Physicists and perhaps other scientists will, it is hoped, find this a useful reference book, which in addition to definitions of the various quantities, etc. also contains much useful tabulated thermodynamic data and provides access to standard reference texts for more detailed treatment. While not specifically aimed at schools, it is hoped that copies of the book will be available in the library for more advanced students.

Comments and suggestions for improvements would be most welcome.

Preface

I am indebted to Dr. W.H. Lee of Surrey University for many helpful discussions during the early stages of the preparation of the manuscript. The writing of any book consumes a large amount of time which would otherwise have been spent with the family. My sincere thanks are due to my wife, Dr. Mary P. Lord, for her understanding, patience, help and encouragement during the preparation of the manuscript.

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USE OF THE DICTIONARY

Entries are arranged in alphabetical sequence with full cross-referencing where there is more than one acceptable or recognised name.

Symbols and abbreviations are used in the text without definition; reference should be made to the list of Principal Symbols on page viii.

In the text, a word in italics followed by (q.v.) indicates a reference to another entry which would be of help; in some instances the reference to another entry is in parentheses. Thus in the sentence "The *work* (q.v.) done during the isothermal reversible expansion of a perfect gas (see *reversible process*) is equal to the heat absorbed by the gas", the reader is referred to entries 'work' and 'reversible process' for further information. A word in italics, followed by[+], e.g. *concentration cell*[+], indicates a reference to that entry in a companion Dictionary of Electrochemistry by C.W. Davies and A.M. James.

More detailed treatments of some of the entries can be found in standard textbooks; where appropriate, relevant references are indicated at the end of an entry by a simple code for the name of the author. All the books with the coding are listed in the Bibliography.

PRINCIPAL SYMBOLS

A	Helmholtz free energy; Debye–Hückel constant
B	Debye–Hückel constant
C	coulomb
C_p, C_V	Heat capacity at constant pressure, volume
E	Electromotive force of cell
$E(O,R), E(X^+X)$	Electrode potential
F	Faraday constant
G	Gibbs free energy function
$\bar{G}_i$	Partial molar free energy of ith component
H	Enthalpy or heat content
I	Ionic strength; Moment of inertia
J	joule
$\bar{J}$	Partial derivative
K	kelvin
K	Equilibrium constant with subscripts p,x, therm, s as appropriate
K_a, K_b	Acid and base ionisation constants
K_w	Ionisation constant of water
L_e, L_f	Molar heat of vaporisation, fusion
$M_r(X)$	Relative molecular mass of X
N	Total number of particles or molecules in a system
N	newton (SI unit of force)
N_A	Avogadro constant
P	Total pressure of system
P^*	Fugacity
Q	Partition function
R	Gas constant
S	Entropy
T	Temperature/K
U	Internal energy
V	Volume
V	volt
W	Statistical probability
$\bar{X}_A$	Partial molar X of A
a_A, a_B, a_i	Activity of A,B or ith component
$a_+, a_-, a_\pm$	Activity of cation, anion, mean ionic activity

c	Number of components (phase rule)
c_A	Concentration of A/mol dm^{-3}
e	Electron
f	Activity coefficient (mole fraction basis); Number of degrees of freedom (phase rule)
g	Gravitational constant; Statistical weight; Osmotic coefficient
g	gramme
k	Boltzmann constant
k	kilo (prefix), eg. kg = kilogramme = 10^3 g
k_c, k_e	Cryoscopic, ebullioscopic constant
l_e, l_f	Heat of vaporisation, fusion per kg
m	metre, milli (prefix), e.g. mm = millimetre = 10^{-3} m
m_A	Molality of A
$m_+, m_-, m_\pm$	Molality of cation, anion, mean ionic molality
n_A, n_B	Number of molecules of A,B in system
n_r	Number of particles in rth energy level
p	Number of phases (phase rule); Pressure above solution
p_i	Partial pressure of i in system
$p^\ominus$	Vapour pressure of pure solvent
p_i^*	Partial fugacity of ith component
q, dq	Heat absorbed by system
s	Second
t_+, t_-	Transport number of cation, anion
w, dw	Work done by system
w_A, w_B	Weight of A,B
x_A, x_B	Mole fraction of A,B in solution
y_A, y_B	Mole fraction of A,B in gaseous phase
z_A, z_B	Valence of A,B
α	Degree of association or dissociation
γ	Ratio of heat capacities C_p/C_V; Surface tension
$\gamma_i, \gamma_+, \gamma_-$	Activity coefficient (molality scale)
$\gamma_\pm$	Mean ionic activity coefficient
ε	Permittivity
ε_r	Energy of particle in rth energy level
μ	micro (prefix), e.g. μm = micrometre = 10^{-6} m
μ_A, μ_B	Chemical potential of A,B
μ_{JT}	Joule–Thomson coefficient

Principal symbols

v, v_+, v_-	Number of ions, cations, anions formed from 1 mole of electrolyte, $v = v_+ + v_-$
π	Ratio of circumference to diameter of circle $= 3.14159$; Osmotic pressure
ρ	Density
σ	Symmetry number; Area
Γ_A	Surface excess concentration of A
Δ	Increase in thermodynamic function, e.g. $\Delta X = X_2 - X_1$
ΔX_f	Increase in X for formation of compound from its elements

Superscripts

$\ominus$	Indicating a standard value of a property

Subscripts

A,B...	Referring to substances A,B...
i	Referring to typical ionic species i, or component
$p, V, T, S ...$	Indicating constant pressure, volume, temperature, entropy, etc.
f,e,s,t	Referring to fusion (or formation), evaporation, sublimation, transition
$+, -$	Referring to positive or negative ion
1,2	Referring to different systems or states of system
g,l,s (or c)	Referring to gaseous, liquid or solid states, respectively

Other abbreviations

b.p.	Boiling point
f.p.	Freezing point
m.p.	Melting point
v.p.	Vapour pressure
e.m.f.	Electromotive force
$\neq$	not equal to
$\equiv$	identically equal to
$\approx$	approximately equal to
$\propto$	proportional to
∞	infinity
$<$	smaller than
$>$	larger than
$\leqslant$	smaller than or equal to
$\geqslant$	larger than or equal to

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$\ll$	much smaller than
$\gg$	much larger than
$p!$	factorial $p = 1 \times 2 \times 3 \ldots \times (p-1) \times p$
$\displaystyle\sum_i$	sum of i terms
$\displaystyle\prod_i$	product of i terms
$f(x)$	function of x
$\dfrac{\mathrm{d}f}{\mathrm{d}x}, \mathrm{d}f/\mathrm{d}x,$	differential coefficient of $f(x)$ with respect to x
$\left(\dfrac{\partial f}{\partial x}\right)_{y\ldots}$	partial differential coefficient of $f(x,y\ldots)$ with respect to x when $y\ldots$ are held constant
$e^x, \exp(x)$	exponential of x
e	base of natural logarithms
$\ln x$	natural logarithm of x
$\log x$	common logarithm of x (to base 10), $\ln x = 2.303 \log x$

A

Absolute molar entropy

The absolute molar entropy of a substance, $S^{\ominus}(T)$, is evaluated from heat capacity data by the equation:

$$S^{\ominus}(T) = S_0^{\ominus} + \int_0^T C_p^{\ominus} \, d \ln T + \sum \frac{\Delta H(\text{trans})}{T(\text{trans})}$$

For substances conforming to the *third law of thermodynamics* (q.v.), $S_0^{\ominus} = 0$.

Acids and bases

Arrhenius defined an acid as a compound which dissociated in solution to yield a hydrogen ion, and a base as a compound which yielded an hydroxyl ion. On this basis the process of neutralisation is simply

$$H^+ + OH^- \longrightarrow H_2O$$
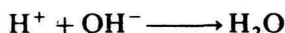
This definition is, however, limited to the use of water as the solvent.

Table A.1. Conjugate acids and bases by Lowry–Brønsted definition

	Acid		Proton +	Base	
↑	$HClO_4$	⇌	H^+ +	ClO_4^-	↓
	HBr	⇌	H^+ +	Br^-	
	H_2SO_4	⇌	H^+ +	HSO_4^-	
Increasing strength of acid	H_3O^+	⇌	H^+ +	H_2O	Increasing strength of base
	HSO_4^-	⇌	H^+ +	SO_4^{2-}	
	H_3PO_4	⇌	H^+ +	$H_2PO_4^-$	
	$[Co(NH_3)_4(H_2O)_2]^{3+}$	⇌	H^+ +	$[Co(NH_3)_4H_2O \cdot OH]^{2+}$	
	CH_3COOH	⇌	H^+ +	CH_3COO^-	
	NH_4^+	⇌	H^+ +	NH_3	
	HCO_3^-	⇌	H^+ +	CO_3^{2-}	
	H_2O	⇌	H^+ +	OH^-	
	NH_3	⇌	H^+ +	NH_2^-	
	CH_3OH	⇌	H^+ +	CH_3O^-	
	$(C_6H_5)_2NH$	⇌	H^+ +	$(C_6H_5)_2N^-$	

Lowry and Brønsted (1923) independently put forward a general definition of acids and bases which has been of great importance in unifying the dissociation of acids and bases, the hydrolysis of salts and the catalytic
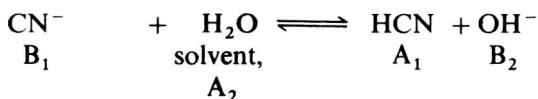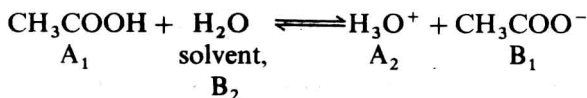
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action of acids and bases. In this, an acid is defined as a substance which can give up a proton, and a base as one that can accept a proton. An acid and a base are conjugate when related by the equation

$$\text{Acid} \rightleftharpoons \text{Proton} + \text{Base}$$

$$A \rightleftharpoons H^+ + B$$

An acid can only give up a proton if a base is present to accept it; hence, two acids and two bases must take part in any reaction involving transfer, i.e.

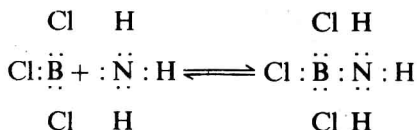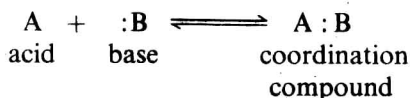$$A_1 + B_2 \rightleftharpoons A_2 + B_1$$

Free protons do not exist in solution; thus a potential acid can only function as such when it is the solute only if the solvent is a proton acceptor. Conversely for a base. Thus the acidic or basic function of a species cannot become apparent unless the solvent is capable of showing basic or acidic properties, respectively, e.g.

$$\underset{\substack{A_1}}{CH_3COOH} + \underset{\substack{\text{solvent,} \\ B_2}}{H_2O} \rightleftharpoons \underset{\substack{A_2}}{H_3O^+} + \underset{\substack{B_1}}{CH_3COO^-}$$

$$\underset{\substack{B_1}}{CN^-} + \underset{\substack{\text{solvent,} \\ A_2}}{H_2O} \rightleftharpoons \underset{\substack{A_1}}{HCN} + \underset{\substack{B_2}}{OH^-}$$

in which water can act, according to circumstances, as an acid or as a base. Thus the original Arrhenius theory, which applied to aqueous solutions only is extended to cover more substances. The nature of the solvent is thus important in deciding whether a substance will show acidic or basic properties in solution. There are three main types of solvent: (1) protogenic solvents, proton donors with acidic properties, e.g. glacial acetic acid; (2) protophilic solvents, proton acceptors with basic properties, e.g. ammonia; (3) aprotic solvents, which can neither accept nor donate protons, e.g. toluene, solutes dissolved in such solvents cannot show either acidic or basic properties. Water, alcohols, etc., which can be either protogenic or protophilic according to circumstances, are said to be amphiprotic.

G.N. Lewis extended the definition still further in his definition of an acid as a substance which can accept a pair of electrons from a donor substance, the base. Neutralisation is thus the formation of a covalent bond in which both electrons of the shared pair are provided by the base, e.g.

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$$A + :B \rightleftharpoons A:B$$

$$\text{acid} \quad \text{base} \quad \text{coordination}$$
$$\text{compound}$$

$$\begin{array}{ccccc} & Cl & H & & Cl & H \\ Cl: & \ddot{B} + & :\ddot{N}:H & \rightleftharpoons & Cl:\ddot{B}:\ddot{N}:H \\ & Cl & H & & Cl & H \end{array}$$

Donors which share electron pairs with cations are called ligands. The theory permits the classification as bases of such 'neutral' substances as H_2O, CO, Cl^-, SO_4^{2-}; the only qualification is that the species possesses an unshared electron pair. Lewis acids include metal ions, BF_3, $AlCl_3$, SiF_4 and any other electron pair acceptors. The relative strengths of Lewis acids vary widely with the strength of the base; thus, according to the Brønsted theory, OH^- is a stronger base than is ammonia, but, according to the Lewis theory, OH^- is a weaker base than is ammonia when reacting with Ag^+, although it is stronger than ammonia when reacting with H^+. There are some obvious examples of acids (e.g. HCl, H_2SO_4) which do not naturally fit the Lewis definition since they cannot plausibly accept electrons.

The coordination compound $A:B$ has been formed from two reactants, each capable of an independent existence in solution, by the sharing of the electrons of the donor. Thus it is easy to distinguish this process from an ordinary oxidation–reduction process:

$$\text{Oxidised state} + n\,e \rightleftharpoons \text{Reduced state}$$
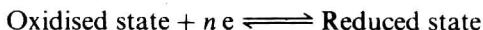
in which electrons are transferred between donor and acceptor and in which the resulting species have an independent existence.

The *equilibrium constant* (q.v.) for the general reaction, defined

$$K = \frac{[A:B]}{[A][:B]}$$

where [ ] refers to the active masses, is called a stability or formation constant.

If two ligands can add to the acceptor (e.g. in the silver–ammonia complex), the second step is

$$A:B + :B \rightleftharpoons B:A:B$$

and the formation constant is

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$$K = \frac{[B:A:B]}{[A:B][:B]}$$

If a ligand can add to a series of acceptors (e.g. metal–ammonia complexes), the formation constant is largest for the reaction leading to the greatest amount of coordination compound; the greater the stability, the greater the formation constant.

The Lewis acids of principal interest in biological sciences are the metal ions, e.g. in coordination compounds such as haemoglobin, chlorophyll, the vitamin B_{12} group, cytochromes and metalloenzymes.

Dissociation constants

The dissociation of an acid HA in water is written

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

for which

$$K_a = \frac{a(H_3O^+) \, a(A^-)}{a(HA)}$$

and of the base A^-,

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

for which

$$K_b = \frac{a(HA) \, a(OH^-)}{a(A^-)}$$

Hence, $K_a K_b = a(H_3O^+) \, a(OH^-) = K_w = 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$, i.e. the conjugate base (acid) of a strong acid (base) is weak. K_a may be written in terms of concentrations and *activity coefficients* (q.v.) of the various species:

$$K_a = \frac{c(H_3O^+) \, c(A^-)}{c(HA)} \times \frac{\gamma(H_3O^+) \, \gamma(A^-)}{\gamma(HA)} = K_c \frac{\gamma(H_3O^+) \, \gamma(A^-)}{\gamma(HA)}$$

where the equilibrium constant, K_c, can be obtained from the original concentration of acid and the equilibrium concentration of one product. In dilute solution $\gamma(HA) = 1$ and $\gamma(H_3O^+)$ and $\gamma(A^-)$ can be obtained from the *Debye–Hückel activity equation* (q.v.), whence

$$\log K_a = \log K_c + 2 A \, I^{1/2}$$

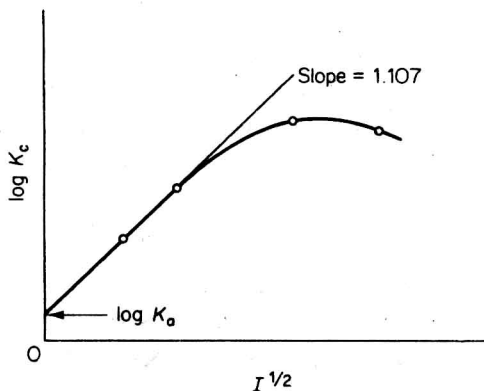The graph of $\log K_c$ against $I^{1/2}$ is linear (figure A.1) and of intercept $\log K_a$.

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Figure A.1 Plot of log K_c against $I^{1/2}$ for a weak acid.

Alternatively, if α is the degree of dissociation and $c/\mathrm{mol\ dm}^{-3}$ is the initial concentration of acid,

$$K_a = \frac{\alpha^2 c}{1 - \alpha} \times \frac{\gamma(H_3O^+)\,\gamma(A^-)}{\gamma(HA)}.$$

If activity coefficients are neglected, the classical dissociation constant is given by Ostwald's dilution law:

$$K_c = \alpha^2 c/(1 - \alpha)$$

Dissociation constants provide a measure of the strengths of acids and bases; the larger K_a, the stronger the acid. Values of K_a are often so small that they are tabulated (Table A.X, p. 257) as pK_a values, where $pK_a = -\log K_a$; thus for acetic acid at 298 K, $K_a = 1.754 \times 10^{-5}\ \mathrm{mol\ dm}^{-3}$ and $pK_a = 4.756$.

In the ionisation of polyprotic (polybasic) acids, each successive proton is removed from an ion of increased negative charge and so K_a for each step is less than that for the preceding step: e.g. for phosphoric acid $K_{a(1)} = 1.1 \times 10^{-2}$, $K_{a(2)} = 7.5 \times 10^{-8}$ and $K_{a(3)} = 4.8 \times 10^{-13}\ \mathrm{mol\ dm}^{-3}$.

For most organic acids, α is small and is approximately given by $\alpha = (K_a/c)^{1/2}$; hence, for a weak acid, $c(H^+) = c\alpha = (K_a\,c)^{1/2}$. Assuming $a(H^+) \approx c(H^+)$ (valid except in strongly acid solution), the pH of a solution of a weak acid is

$$pH = -\log c(H^+) = pK_a - \tfrac{1}{2}\log c$$

and that of a weak base is

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$$\mathrm{pH} = \mathrm{p}K_w - \tfrac{1}{2}\mathrm{p}K_b - \tfrac{1}{2}\log c$$

According to this theory, salt hydrolysis is simply the dissociation of a cation acid or anion base. An aqueous solution of ammonium chloride (the salt of a strong acid and weak base) contains NH_4^+, which reacts with the water thus:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

Thus what used to be called the hydrolysis constant of the ammonium salt is clearly the acid dissociation constant of the ammonium ion:

$$K_h = K_a = \frac{a(NH_3)\,a(H_3O^+)}{a(NH_4^+)} \approx \frac{c(NH_3)\,c(H_3O^+)}{c(NH_4^+)} \approx \frac{c\alpha^2}{1 - \alpha}$$

where $c/\mathrm{mol\ dm^{-3}}$ is the concentration of salt and α, the extent of hydrolysis, is given by

$$\alpha = \{K_a/c\}^{1/2} = \{K_w/K_b\,c\}^{1/2}$$

whence the pH of such a solution is

$$\mathrm{pH} = -\log c\alpha = \tfrac{1}{2}\,\mathrm{p}K_w - \tfrac{1}{2}\,\mathrm{p}K_b - \tfrac{1}{2}\log c$$

Similarly, for the salt of a weak acid and strong base,

$$\mathrm{pH} = \tfrac{1}{2}\,\mathrm{p}K_w + \tfrac{1}{2}\,\mathrm{p}K_a + \tfrac{1}{2}\log c$$

Thus the pH of a solution of the salt of a weak (strong) acid and a strong (weak) base is greater (less) than 7, i.e. alkaline (acidic) and increases (decreases) with increasing concentration of salt. For the salt of a weak acid and a weak base, the pH, given by

$$\mathrm{pH} = \tfrac{1}{2}\,\mathrm{p}K_w + \tfrac{1}{2}\,\mathrm{p}K_a - \tfrac{1}{2}\,\mathrm{p}K_b$$

depends on the relative strengths of the acid and base and is independent of concentration.

See also Dissociation constant; Potentiometric titration[†] ; and Ad, B, G, G & S, W & W.

Acid–base titrations
See Potentiometric titration[†].

Activity
Activity, a, is a function introduced by G.N. Lewis to aid the treatment of real systems. Like *fugacity* (q.v.), the activity permits the correlation of
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changes in *chemical potential* (q.v.) with experimentally measured quantities, such as concentration, through a relationship formally equivalent to that for an ideal system. Activity is defined as the ratio of the fugacity in a given state to the fugacity in a standard state, thus:

$$RT \ln a_i = \mu_i - \mu_i^\ominus = RT \ln \frac{p^*}{[p_i^*]^\ominus} \tag{A.1}$$

The use of the activity function for solids, liquids and gases is preferred to the fugacity, since it does not require comparison with an infinitely attenuated gas. For a pure gas, the standard state is that of unit fugacity; hence, $a_i = p_i^*$. Activity, defined as the ratio of fugacities, is dimensionless and, as such, its numerical value is meaningless unless a standard reference state is defined. Comparison of equation (A.1) with that for an ideal system:

$$RT \ln x_i = \mu_i - \mu_i^\ominus$$

suggests the introduction of an *activity coefficient* (q.v.), f_i, defined as $f_i = a_i/x_i$. The deviation of f_i from unity is a measure of the deviation of the system from ideal behaviour. When the composition variable is molality, the activity coefficient, $\gamma_i = a_i/m_i$, is the practical activity coefficient, since molality is the most common method of expressing concentrations, particularly of dilute solutions.

Activity is a function of the temperature, pressure and composition of the system:

$$\left(\frac{\partial \ln a_i}{\partial P} \right)_{T,x} = \frac{\bar{V}_i}{RT}$$

$$\left(\frac{\partial \ln a_i}{\partial T} \right)_{P,x} = \frac{\bar{H}_i - \bar{H}_i^\ominus}{RT^2}$$

where $\bar{H}_i$ and $\bar{H}_i^\ominus$ are the partial molal enthalpy values in the given and standard states, respectively.

Since no method has been devised to determine individual ion activities (a_+, a_-), the mean ionic activity $a_\pm$ for dissociated electrolytes is defined:

$$a_\pm = a_2^{1/\nu} = (a_+^{\nu^+} a_-^{\nu^-})^{1/\nu}$$

where a_2 is the activity of the undissociated electrolyte.

The variation of a or $a_\pm$ for sucrose and various electrolytes is shown in figure A.2.

Thermodynamic *equilibrium constants* (q.v.) are defined in terms of the

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