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PHYSICAL CHEMISTRY DIVISION
COMMISSION ON THERMODYNAMICS*

STANDARD QUANTITIES IN CHEMICAL THERMODYNAMICS

**Fugacities, Activities, and Equilibrium Constants for
Pure and Mixed Phases**

(IUPAC Recommendations 1994)

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Standard quantities in chemical thermodynamics. Fugacities, activities and equilibrium constants for pure and mixed phases (IUPAC Recommendations 1994)

Synopsis. The standard chemical potential μ is defined in terms of a specified state of aggregation, a specified temperature and a specified standard pressure. Other standard thermodynamic quantities are obtained from μ by the usual mathematical operations.

In this report definitions are given for the standard chemical potential of a substance B in the following states of aggregation: gas phase whether pure or mixed, condensed phase whether pure or mixed, solvent substance in solution, and solute substance in solution. Fugacities and virial coefficients are introduced in the discussion of gases and activity, activity coefficients, and osmotic coefficients in the discussion of condensed phases.

Expressions for the standard equilibrium constant are given for a reaction in the gas phase, in a condensed phase and in a solution. Some numerical examples are given and relative magnitudes of various terms in the equations are illustrated.

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PREFACE

In the past, the IUPAC recommendations on symbols and terminology in physical chemistry have been published in three editions (respectively 1969, 1973, and 1979) of the *Manual of Symbols and Terminology for Physicochemical Quantities and Units* (Green Book). Recommendations in the field of chemical thermodynamics were contained in two appendices to this manual: appendix I on "Activities and related quantities", and appendix IV on "Notation for states and processes and the significance of the word *standard* in chemical thermodynamics".

In 1988, a completely revised and extended version of the Green Book was published under the title *Quantities, Units and Symbols in Physical Chemistry*; a revised edition of which was published in 1993. The extensions include a substantial part of Appendix IV.

In anticipation of these developments, the Commission on Thermodynamics decided at the IUPAC General Assembly at Lyngby in 1983 to start the preparation of a new document on chemical thermodynamics with the following aims:

1. to combine the closely related topics of Appendix I and Appendix IV in one publication,
2. to give a more extended treatise on the thermodynamic basis of equilibrium constants, and
3. to adjust the text in view of the content of the new Green Book and by introducing examples.

A Task Group was established at the 1986 meeting of the Commission in Lisbon, whose membership is printed on the preceding page.

1. INTRODUCTION

The chemical potential μ_B of a substance B in a mixture of substances B, C, ... is related to the Gibbs energy G of the mixture by

$$\mu_B = (\partial G / \partial n_B)_{T,p,n_{C \neq B}} \quad (1)$$

where T is the thermodynamic temperature, p is the pressure, and n_B, n_C, \dots are the amounts of substance of B, C, ... For a pure substance B, the chemical potential μ_B^* is given by

$$\mu_B^* = G^*/n_B = G_m^* \quad (2)$$

where G_m^* is the molar Gibbs energy, and where the superscript * attached to a symbol denotes the property of the pure substance. The superscript $^\ominus$ or $^\circ$ attached to a symbol may be used to denote a standard thermodynamic quantity. Consequently, the standard chemical potential of substance B may be written as μ_B^\ominus or μ_B° , but in this document the superscript $^\ominus$ has been used to denote standard thermodynamic quantities.

The word **mixture** is used to describe a gaseous or liquid or solid phase containing more than one substance, when the substances are all treated in the same way. It is sometimes convenient to treat a mixture of constant composition, such as air, as a pure substance.

The word **solution** is used to describe a liquid or solid phase containing more than one substance, when for convenience one (or more) substance, which is called the **solvent**, is treated differently from the other substances, which are called solutes. When, as is often but not necessarily the case, the sum of the mole fractions of the **solutes** is small compared with unity, the solution is called a **dilute solution**. In the definitions given in Section 5, the solvent substance is denoted by A and the solute substances by B, C, ... (Note a) The superscript $^\infty$ attached to the symbol for a property of a solution denotes the property in the limit of infinite dilution.

The nomenclature and notation used in this document are consistent with the recommendations given in "Quantities, Units and Symbols in Physical Chemistry" (ref. 1), the IUPAC "Green Book", and ISO 31/8 (ref. 2).

Note a: The solvent is often denoted by the subscript 1 and the solutes by the subscripts 2, 3, ...

2. STANDARD THERMODYNAMIC QUANTITIES

Absolute values of some thermodynamic quantities, such as chemical potential and entropy, are not needed in most applications of thermodynamics. Only changes in these quantities, such as may result from variation of temperature or pressure or composition, can be measured easily or calculated. It is therefore important to define a reference value of each thermodynamic quantity to which such changes may be referred. Suitable reference values, known as **standard thermodynamic quantities**, can be derived if the standard chemical potential is defined.

The **standard chemical potential** is defined in terms of a specified state of aggregation, a specified temperature, and an arbitrarily chosen but specified standard pressure. For a solute substance in a solution {see section 5(a)} an arbitrarily chosen but specified standard molality is also required. Other standard thermodynamic quantities are obtained from the standard chemical potential by the usual mathematical operations.

For example, the standard molar entropy S_B^\ominus of a substance B is defined by $S_B^\ominus(z, T) = -d\mu_B^\ominus(z, T)/dT$, where z denotes the state of aggregation.

For a specified standard pressure, and in the case of a solute for a specified standard molality, all standard thermodynamic quantities are independent of pressure and composition, but they remain functions of temperature. Consequently, standard thermodynamic quantities are often required at many temperatures. However, for quantities such as $\{H_m^\ominus(T) - H_m^\ominus(T')\}$ and $\Delta_f H_m^\ominus(T')$ it is generally more convenient to choose the reference temperature T' as one of a relatively small number of values: zero, 273.15 K, 293.15 K, or 298.15 K. The most widely used values are $T' = 0$, for example with the quantity $\{H_m^\ominus(T) - H_m^\ominus(0)\}$ and $T' = 298.15$ K, for example with the quantity $\Delta_f H_m^\ominus(298.15 \text{ K})$. Because the quantity "298.15 K" occurs so frequently, workers may find it convenient to use a special symbol for this quantity. No recommendation is made for a special symbol for "298.15 K" but T_a , T' , and T^\ominus have all been used. Since T^\ominus would mean a standard temperature in general, the use of T^\ominus to mean exclusively 298.15 K is strongly discouraged. The value of any reference temperature for standard thermodynamic quantities should *always* be stated when the numerical value of any standard thermodynamic quantity is given and any special symbol used to denote the quantity "298.15 K" should *always* be defined.

The **standard pressure** is denoted by p^\ominus and the recommended value for standard thermodynamic quantities is 10^5 Pa. (Note b)

Note b: The non-SI unit "bar" is defined exactly by $1 \text{ bar} = 10^5 \text{ Pa}$.

Most data published before 1982 used a standard pressure of 1 “standard atmosphere” (a non-SI unit equal to 101325 Pa). If the value of p^\ominus changes from p_1^\ominus to p_2^\ominus then the difference in the standard chemical potential (see sections 3 to 5) is given by one of the following three equations.

(a) For a gaseous (g) substance **B**, whether pure or mixed,

$$\mu_{\text{B}}^\ominus(\text{g}, T, p_2^\ominus) - \mu_{\text{B}}^\ominus(\text{g}, T, p_1^\ominus) = RT \ln(p_2^\ominus/p_1^\ominus) \quad (3)$$

(b) For a substance **B** in a condensed phase (cd), whether pure or mixed, or for a solvent substance **B** in a solution

$$\mu_{\text{B}}^\ominus(\text{cd or solvent}, T, p_2^\ominus) - \mu_{\text{B}}^\ominus(\text{cd or solvent}, T, p_1^\ominus) = \int_{p_1^\ominus}^{p_2^\ominus} V_{\text{B}}^* dp \quad (4)$$

where $V_{\text{B}}^* = V_{\text{B}}^*(\text{cd}, T, p)$ is the molar volume of pure substance **B**.

(c) For a solute substance **B** in a solution

$$\mu_{\text{B}}^\ominus(\text{solute}, T, p_2^\ominus) - \mu_{\text{B}}^\ominus(\text{solute}, T, p_1^\ominus) = \int_{p_1^\ominus}^{p_2^\ominus} V_{\text{B}}^\infty dp \quad (5)$$

where $V_{\text{B}}^\infty = V_{\text{B}}^\infty(\text{solute}, T, p)$ is the partial molar volume of the solute **B** at infinite dilution.

Consequently with $p_1^\ominus = 101325$ Pa and $p_2^\ominus = 10^5$ Pa the differences in standard thermodynamic quantities for condensed phases will nearly always be negligible compared with the uncertainties in current data, but for gases the differences, though small, may not be negligible. For example if p^\ominus decreases from 101325 Pa to 10^5 Pa then, for a gaseous substance, the standard chemical potential decreases by about $0.013 RT$ and the standard molar entropy increases by about $0.013 R$. The **standard molar enthalpy** $H_{\text{B}}^\ominus(\text{g}, T)$ of a gas **B**, and its derivatives with respect to temperature, do not depend in any way on the value chosen for the standard pressure p^\ominus . Instances may occur when it is desirable to adopt other values for p^\ominus but in any case the value adopted for p^\ominus should *always* be stated when the numerical value of any standard thermodynamic quantity is given.

Notwithstanding the above, the word “**normal**” in for example “normal boiling temperature” continues to mean the value at a pressure of 101325 Pa.

The **standard molality** is denoted by m^\ominus and for standard thermodynamic quantities the recommended value, which is used almost exclusively, is 1 mol kg^{-1} . Nevertheless, the value of m^\ominus adopted should always be stated when the numerical value of any standard thermodynamic quantity of a solute is given. If the amount-of-substance concentration c_{B} is used in place of molality then the value adopted for the **standard concentration** c^\ominus should always be stated when the

numerical value of any standard thermodynamic quantity of a solute is given; the recommended value for standard thermodynamic quantities is $c^\ominus = 1 \text{ mol dm}^{-3}$.

In sections 3 to 5, definitions are given for the standard chemical potential of a substance **B** in the following states of aggregation: gas phase whether pure or mixed, condensed phase whether pure or mixed, solvent substance in a solution, and solute substance in a solution. The term "standard state" is often used to imply the values of the standard thermodynamic functions that are taken as a reference, but, for gaseous substances and for solute substances in solution, the standard chemical potential does not correspond to conditions that can be achieved experimentally. (Note c)

However, the difference ($\mu_{\text{B}} - \mu_{\text{B}}^\ominus$), between the chemical potential of substance **B** and its standard chemical potential for the same temperature and state of aggregation, can always be calculated and measured using the definitions of sections 3 to 5. Standard methods may be used to determine more general differences in chemical potential.

Sections 3 to 5 also give definitions for additional quantities that represent differences in chemical potential that are especially important for a particular state of aggregation. Consequently, fugacities and virial coefficients are introduced in the discussion of gases so that the dependence of the chemical potential on pressure can be represented succinctly. For condensed phases and solutions (where the dependence of the chemical potential on composition is often more important than the dependence on pressure) activities, activity coefficients, and osmotic coefficients are introduced. All of these quantities may be determined experimentally or calculated from appropriate theories.

3. GASES AND GASEOUS MIXTURES

The partial pressure p_{B} of a substance **B** in a gaseous mixture is a quantity with the same dimension as pressure defined by

$$p_{\text{B}} = y_{\text{B}}p \quad (6)$$

where y_{B} is the mole fraction of **B** in the gaseous mixture and p is the pressure. Equation (6) is the definition of partial pressure recommended by IUPAC (ref. 1) and has the important property that $\sum_{\text{B}} p_{\text{B}} = p$. However for a real gas, $y_{\text{B}}p$ could not be obtained from the rate of change of momentum through collisions at a wall of known area and, in this sense, $y_{\text{B}}p$ is not a true pressure. To avoid ambiguity,

Note c: The "standard states" for gaseous and for solute substances in solution have been described as hypothetical.

partial pressure p_B is not used again in this document.

The standard chemical potential μ_B^\ominus of a gas B, whether a pure substance or a component of a gaseous mixture, is defined by

$$\mu_B^\ominus(g, T) = \mu_B(g, T, p, y) - RT \ln(y_B p / p^\ominus) - \int_0^p (V_B - RT/p) dp \quad (7)$$

where y denotes the set of mole fractions y_B, y_C, \dots of B, C, \dots , p^\ominus is the standard pressure, and $V_B = V_B(g, T, p, y)$ is the partial molar volume of B. The integral in equation (7) results from the pressure dependence of the chemical potential and is of central importance in the study of gases; for a perfect gas mixture the integrand in equation (7) is zero.

The fugacity f_B of the gas B in a gaseous mixture containing mole fractions y_B, y_C, \dots of the substances B, C, \dots is a quantity with the same dimension as pressure defined by

$$f_B = y_B p \exp \left[\int_0^p \{V_B / (RT) - 1/p\} dp \right] \quad (8)$$

The symbol \tilde{p} is sometimes used in place of f to denote fugacity especially when the discussion also involves the activity coefficients (see section 4) of substances in a liquid mixture.

It follows from the definitions of μ_B^\ominus and of f_B that the chemical potential μ_B of a gas B in a gaseous mixture is given by

$$\mu_B(g, T, p, y) = \mu_B^\ominus(g, T) + RT \ln(f_B / p^\ominus) \quad (9)$$

The ratio $f_B / (y_B p)$, sometimes denoted by the symbol ϕ_B , may be called the fugacity coefficient of the gas B. It follows from the definition of f_B that

$$\lim_{p \rightarrow 0} \{f_B / (y_B p)\} = \lim_{p \rightarrow 0} \phi_B = 1 \quad (10)$$

A perfect gas mixture of B, C, \dots is defined as one for which

$$pV = (n_B + n_C + \dots)RT$$

Consequently, $f_B = y_B p$, $f_C = y_C p$, \dots , and $\phi_B = \phi_C = \dots = 1$ for a perfect gas mixture.

The fugacity of a substance B in a liquid mixture may be defined by an equation similar to (8) but with liquid mole fraction x_B in place of gaseous mole fraction y_B

and the partial molar volume $V_B = V_B(l, T, p, x)$ of the substance B in the liquid mixture in place of $V_B(g, T, p, y)$.

When $y_B = 1$, the definitions given in this section for a gas B in a gaseous mixture reduce to those for a pure gas. Consequently for a pure gas B, the fugacity f_B^* is defined by

$$f_B^* = p \exp \left[\int_0^p \{V_B^*/(RT) - 1/p\} dp \right] \quad (11)$$

where $V_B^* = V_B^*(g, T, p)$ is the molar volume of the pure gas B, and the chemical potential μ_B^* is given by

$$\mu_B^*(g, T, p) = \mu_B^\ominus(g, T) + RT \ln(f_B^*/p^\ominus) \quad (12)$$

It follows from the definitions of f_B^* that

$$\lim_{p \rightarrow 0} (f_B^*/p) = 1 \quad (13)$$

A pure perfect gas B is defined as one for which $pV = n_B RT$. Consequently $f_B^* = p$ for a pure perfect gas B.

The fugacity of a pure liquid B may be defined by an equation similar to (11) but with the molar volume $V_B^* = V_B^*(l, T, p)$ of the pure liquid B in place of $V_B^*(g, T, p)$.

It is often convenient to express the thermodynamic properties of a gas in terms of virial coefficients. At low to moderate pressures, the molar volume V_m of a gaseous mixture may be obtained from

$$V_m = RT/p + B(y) + \dots \quad (14)$$

where the second virial coefficient $B(y)$ of the mixture is defined by

$$B(y) = \lim_{p \rightarrow 0} (V_m - RT/p) \quad (15)$$

For a binary mixture $\{(1 - y)A + yB\}$, the second virial coefficient is given by

$$B(y) = (1 - y)^2 B_{AA} + 2y(1 - y)B_{AB} + y^2 B_{BB} \quad (16)$$

where B_{AA} and B_{BB} are the second virial coefficients for pure A and B, and B_{AB} results from interactions of A with B. Alternatively,

$$B(y) = (1 - y)B_{AA} + yB_{BB} + y(1 - y)\delta_{AB} \quad (17)$$

where

$$\delta_{AB} = 2B_{AB} - (B_{AA} + B_{BB}) \quad (18)$$

The partial molar volume V_B for component B in the mixture is given by

$$V_B = RT/p + B_{BB} + (1 - y)^2\delta_{AB} + \dots \quad (19)$$

and, since all virial coefficients are independent of pressure, the fugacity f_B and chemical potential μ_B of B in the mixture are given by

$$\ln\{f_B/(y_B p)\} = \{B_{BB} + (1 - y)^2\delta_{AB}\}p/(RT) + \dots \quad (20)$$

$$\mu_B(g, T, p, y) = \mu_B^\ominus(g, T) + RT \ln(y_B p/p^\ominus) + p\{B_{BB} + (1 - y)^2\delta_{AB}\} + \dots \quad (21)$$

When $y = 1$, these equations reduce to those for a pure gas at low to moderate pressures. The use of some of these equations is illustrated by the following numerical example.

At 373.15 K values for the second virial coefficients of $n\text{-C}_4\text{H}_{10}$ and $n\text{-C}_6\text{H}_{14}$ are -422 and $-1031 \text{ cm}^3 \text{ mol}^{-1}$ and, for mixtures of $n\text{-C}_4\text{H}_{10}$ and $n\text{-C}_6\text{H}_{14}$, δ_{AB} is $153 \text{ cm}^3 \text{ mol}^{-1}$.

For the mixture ($0.8000\text{C}_4\text{H}_{10} + 0.2000\text{C}_6\text{H}_{14}$) at pressure $p = 100.000 \text{ kPa}$, equation (17) gives

$$B(y)/(\text{cm}^3 \text{ mol}^{-1}) = (-0.8000 \times 422 - 0.2000 \times 1031 + 0.2000 \times 0.8000 \times 153) = -519$$

For the butane in the mixture ($y_A = 1 - y = 0.8000$), where A denotes $n\text{-C}_4\text{H}_{10}$, equations (19) and (8) give

$$(V_A - RT/p)/(\text{cm}^3 \text{ mol}^{-1}) = (-422 + 0.2000^2 \times 153) = -416$$

$$\begin{aligned} f_A/\text{kPa} &= 0.8000 \times 100.000 \exp\{-416 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \times 10^5 \text{ Pa} \\ &\quad / (8.31451 \text{ J K}^{-1} \text{ mol}^{-1} \times 373.15 \text{ K})\} \\ &= 80.000 \exp(-0.01341) = 78.935 \end{aligned}$$

and, for $p^\ominus = 100.000$ kPa, equation (9) gives

$$\begin{aligned}\mu_A(\text{g}, 373.15 \text{ K}, 10^5 \text{ Pa}, 0.8000) - \mu_A^\ominus(\text{g}, 373.15 \text{ K}) \\ &= (8.31451 \text{ J K}^{-1} \text{ mol}^{-1} \times 373.15 \text{ K}) \ln(78.935 \text{ kPa}/100.000 \text{ kPa}) \\ &= -733.90 \text{ J mol}^{-1}\end{aligned}$$

Similarly, for the hexane in the mixture ($y_B = y = 0.2000$), where B denotes $n\text{-C}_6\text{H}_{14}$,

$$(V_B - RT/p)/(cm^3 \text{ mol}^{-1}) = (-1031 + 0.8000^2 \times 153) = -933$$

$$\begin{aligned}f_B/\text{kPa} &= 0.2000 \times 100.000 \exp\{-933 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \times 10^5 \text{ Pa} \\ &\quad / (8.31451 \text{ J K}^{-1} \text{ mol}^{-1} \times 373.15 \text{ K})\} \\ &= 20.000 \exp(-0.03007) = 19.408\end{aligned}$$

and, for $p^\ominus = 100.000$ kPa,

$$\begin{aligned}\mu_B(\text{g}, 373.15 \text{ K}, 10^5 \text{ Pa}, 0.2000) - \mu_B^\ominus(\text{g}, 373.15 \text{ K}) \\ &= (8.31451 \text{ J K}^{-1} \text{ mol}^{-1} \times 373.15 \text{ K}) \ln(19.408 \text{ kPa}/100.000 \text{ kPa}) \\ &= -5086.6 \text{ J mol}^{-1}\end{aligned}$$

The results of these calculations are summarized in table 1 together with those obtained when the mixture is treated as an ideal mixture of imperfect gases ($\delta_{AB} = 0$) and when the mixture is treated as a perfect gas mixture ($f_A = y_A p$ and $f_B = y_B p$ or at these conditions $B_{AA} = B_{BB} = \delta_{AB} = 0$).

TABLE 1. Partial molar volumes V_B , fugacities f_B , and differences ($\mu_B - \mu_B^\ominus$) in chemical potential for $(0.8000n\text{-C}_4\text{H}_{10} + 0.2000n\text{-C}_6\text{H}_{14})$ at a temperature of 373.15 K and a pressure of 100.000 kPa for $p^\ominus = 100.000$ kPa.

| $\frac{\delta_{AB}}{\text{cm}^3 \text{ mol}^{-1}}$ | B | $\frac{B_{BB}}{\text{cm}^3 \text{ mol}^{-1}}$ | $\frac{V_B - RT/p}{\text{cm}^3 \text{ mol}^{-1}}$ | $\frac{f_B}{\text{kPa}}$ | $\frac{(\mu_B - \mu_B^\ominus)}{\text{J mol}^{-1}}$ |
|--|--------------------------------|---|---|--------------------------|---|
| 153 | C ₄ H ₁₀ | -422 | -416 | 78.935 | -733.90 |
| 153 | C ₆ H ₁₄ | -1031 | -933 | 19.408 | -5086.6 |
| 0 | C ₄ H ₁₀ | -422 | -422 | 78.919 | -734.53 |
| 0 | C ₆ H ₁₄ | -1031 | -1031 | 19.346 | -5096.5 |
| 0 | C ₄ H ₁₀ | 0 | 0 | 80.000 | -692.32 |
| 0 | C ₆ H ₁₄ | 0 | 0 | 20.000 | -4993.4 |

4. PURE CONDENSED PHASES AND MIXED CONDENSED PHASES

For a substance **B** in a condensed phase which is a pure substance or a component in a mixture the **standard chemical potential** μ_B^\ominus is defined by

$$\mu_B^\ominus(\text{cd}, T) = \mu_B^*(\text{cd}, T, p) + \int_p^{p^\ominus} V_B^* dp \quad (22)$$

where p^\ominus is the standard pressure and $V_B^* = V_B^*(\text{cd}, T, p)$ is the molar volume of pure **B**. The integral in equation (22) represents the pressure dependence of the chemical potential and often, especially when $p \approx p^\ominus$, the integral is small and the last term in equations (22) and (24) is neglected.

For example, if $|p^\ominus - p| < 100$ kPa, then the contribution of the integral to equations (22) and (24) is usually less than about 10 J mol^{-1} , which is small compared with $(\mu_B - \mu_B^\ominus) \approx -1700 \text{ J mol}^{-1}$ for an ideal mixture with $x_B = 0.5$ at ambient temperature.

The definition (22) of the standard chemical potential of a substance **B** in a condensed phase is identical with the definition in section 5(b) of the standard chemical potential of a solvent substance **A** in a solution.

The **activity coefficient** f_B of a substance **B** in a liquid or solid mixture containing mole fractions x_B, x_C, \dots of the substances **B, C, \dots** is a dimensionless quantity defined in terms of the chemical potential μ_B of **B** in the mixture by

$$RT \ln (x_B f_B) = \mu_B(\text{cd}, T, P, x) - \mu_B^*(\text{cd}, T, p) \quad (23)$$

where x denotes the set of mole fractions x_B, x_C, \dots .

It follows from the definitions of μ_B^\ominus and f_B that the **chemical potential** μ_B of the substance **B** in the mixture is given by

$$\mu_B(\text{cd}, T, p, x) = \mu_B^\ominus(\text{cd}, T) + RT \ln (x_B f_B) - \int_p^{p^\ominus} V_B^* dp \quad (24)$$

The (relative) **activity** a_B of a substance **B** in a liquid or solid mixture is a dimensionless quantity defined in terms of the chemical potential μ_B by

$$RT \ln a_B = \mu_B - \mu_B^* \quad (25)$$

It follows from the definitions of f_B and a_B that

$$a_B = x_B f_B \quad (26)$$

and that

$$\lim_{x_B \rightarrow 1} a_B = 1 \quad (27)$$

A mixture of substances **B, C, \dots** is called an **ideal mixture** when $a_B = x_B, a_C = x_C, \dots$ or $f_B = 1, f_C = 1, \dots$.

Additional quantities are sometimes used to describe the (gas + liquid) equilibrium of a mixture. The **Henry's law constant** $k_{H,B}$ of a substance **B** in a liquid mixture is a quantity with the same dimension as pressure defined by

$$k_{H,B} = \lim_{x_B \rightarrow 0} (\tilde{p}_B/x_B) = (\partial \tilde{p}_B / \partial x_B)_{x_B=0} \quad (28)$$

where \tilde{p}_B is the fugacity of the substance **B** in the *gaseous* mixture and x_B is the mole fraction of **B** in the *liquid* mixture; here the alternative (ref. 1) symbol \tilde{p} has been used to denote fugacity to avoid any confusion with the use of f to denote activity coefficient. It is important to note that Henry's law applies to a substance **B** at high dilution ($x_B \rightarrow 0$) in a liquid mixture. By contrast, with the composition limit $x_B \rightarrow 1$, equation (28) becomes

$$\lim_{x_B \rightarrow 1} (\tilde{p}_B/x_B) = (\partial \tilde{p}_B / \partial x_B)_{x_B=1} = \tilde{p}_B^* \quad (29)$$

where \tilde{p}_B^* is the fugacity of the pure gas **B**. Since equations (28) and (29) refer to a (gas + liquid) equilibrium, the fugacities \tilde{p}_B and \tilde{p}_B^* are evaluated at the vapour pressure of the mixture or of the pure fluid **B**. If the pure gas **B** is a perfect gas, then $\tilde{p}_B = p_B^{g+1}$, where p_B^{g+1} is the vapour pressure of pure **B**, and equation (29) becomes a statement of **Raoult's law**.

In general, the activities and activity coefficients defined in this section for a substance in a mixed condensed phase are functions of temperature, pressure, and composition.

5. SOLUTIONS

(a) Solute substance in a solution

The **standard chemical potential** μ_B^\ominus of a solute substance **B** in a solution (especially a dilute liquid solution) of **B**, **C**, ... in a solvent substance **A** is defined by

$$\mu_B^\ominus(\text{solute}, T) = \{ \mu_B(\text{solute}, T, p, m) - RT \ln(m_B/m^\ominus) \}^\infty + \int_p^{p^\ominus} V_B^\infty dp \quad (30)$$

where m denotes the set of molalities m_B, m_C, \dots of the solutes **B**, **C**, ... in the solvent **A**, m^\ominus is the standard molality, $^\infty$ denotes the limit at infinite dilution, p^\ominus is the standard pressure, and $V_B^\infty = V_B^\infty(\text{solute}, T, p)$ is the partial molar volume of the solute **B** at infinite dilution. In equation (30), both the terms inside $\{\dots\}^\infty$ diverge as $m_B \rightarrow 0$, but their difference remains finite. The integral in equation (30) results from the pressure dependence of the chemical potential and often, especially when $p \approx p^\ominus$, the integral is small and the last term in equations (30) and (32) is neglected.

For example, if $|p^\ominus - p| < 100 \text{ kPa}$, then the contribution of the integral to equations (30) and (32) is usually less than about 10 J mol^{-1} which is small compared with $(\mu_B - \mu_B^\ominus) \approx -5700 \text{ J mol}^{-1}$ for an ideal dilute solution with $m/m^\ominus = 0.1$ at ambient temperature.

The **activity coefficient** γ_B of a solute **B** in a solution (especially a dilute liquid solution) containing molalities m_B, m_C, \dots of solutes **B, C, \dots** in a solvent **A** is a dimensionless quantity defined in terms of the chemical potential μ_B by

$$RT \ln (m_B \gamma_B / m^\ominus) = \mu_B - \{\mu_B - RT \ln (m_B / m^\ominus)\}^\infty \quad (31)$$

It follows from the definitions of μ_B^\ominus (solute) and γ_B that the **chemical potential** μ_B of the solute **B** in a solution containing molalities m_B, m_C, \dots of solutes **B, C, \dots** in a solvent **A** is given by

$$\begin{aligned} \mu_B(\text{solute}, T, p, m) = & \mu_B^\ominus(\text{solute}, T) + RT \ln (m_B \gamma_B / m^\ominus) \\ & - \int_p^{p^\ominus} V_B^\infty dp \end{aligned} \quad (32)$$

The name activity coefficient with the symbol $\gamma_{c,B}$ may be used for the quantity defined in a way similar to γ_B but with amount concentration c_B in place of molality m_B and a standard concentration c^\ominus in place of the standard molality m^\ominus .

The **activity** a_B of a solute **B** in a solution (for example in a dilute liquid solution) containing molalities m_B, m_C, \dots of solutes **B, C, \dots** in a solvent **A**, is a dimensionless quantity defined in terms of the chemical potential μ_B by

$$RT \ln a_B = \mu_B - \{\mu_B - RT \ln (m_B / m^\ominus)\}^\infty \quad (33)$$

The name relative activity is sometimes used instead of the name activity for this quantity.

It follows from the definitions of γ_B and a_B that

$$a_B = \gamma_B m_B / m^\ominus \quad (34)$$

and that

$$(a_B m^\ominus / m_B)^\infty = 1 \quad (35)$$

The name activity with the symbol $a_{c,B}$ may be used for the quantity defined in a way similar to a_B but with concentration c_B in place of molality m_B and a standard concentration c^\ominus in place of the standard molality m^\ominus .

A solution of solutes **B, C, \dots** in a solvent **A** is called an **ideal-dilute solution** when $a_B = m_B / m^\ominus, a_C = m_C / m^\ominus, \dots$ or $\gamma_B = 1, \gamma_C = 1, \dots$.

(b) Solvent substance in a solution

The **standard chemical potential** μ_A^\ominus for the solvent A in a liquid or solid solution is defined by

$$\mu_A^\ominus(\text{solvent}, T) = \mu_A^*(cd, T, p) + \int_p^{p^\ominus} V_A^* dp \quad (36)$$

where p^\ominus is the standard pressure and $V_A^* = V_A^*(cd, T, p)$ is the molar volume of pure A. The integral in equation (36) represents the pressure dependence of the chemical potential and often, especially when $p \approx p^\ominus$, the integral is small and the last term in equation (36) is neglected. This definition of the standard chemical potential of the solvent A in a solution is identical with the definition in section 4 of the standard chemical potential of any substance B in a condensed phase.

The **osmotic coefficient** ϕ of the solvent A in a solution (especially a dilute liquid solution) containing molalities m_B, m_C, \dots of solutes B, C, \dots is a dimensionless quantity defined in terms of chemical potential μ_A of the solvent A in the solution by

$$\phi = (\mu_A^* - \mu_A) / \left(RT M_A \sum_B m_B \right) \quad (37)$$

where μ_A^* is the chemical potential of the pure solvent A at the same temperature and pressure, the sum over the solutes B, C, \dots is denoted by \sum_B , and M_A is the molar mass of the solvent A.

For an **ideal dilute solution** as defined in sections 5(a) it can be shown that $\phi = 1$.

It follows from the definitions of μ_A^\ominus and ϕ that the **chemical potential** μ_A of the solvent A in the solution is given by

$$\begin{aligned} \mu_A(\text{solvent}, T, p, m) = & \mu_A^\ominus(\text{solvent}, T) - RT\phi M_A \sum_B m_B \\ & - \int_p^{p^\ominus} V_A^* dp \end{aligned} \quad (38)$$

where m denotes the set of molalities m_B, m_C, \dots . Often, especially when $p \approx p^\ominus$, the integral in equation (38) is small and the last term is neglected. However, in practice the integral is not always negligible compared with $RT\phi M_A \sum_B m_B$, although $|\mu_A - \mu_A^\ominus|$ for the solvent substance in solution is usually very much less than $|\mu_B - \mu_B^\ominus|$ for the solutes (especially for an electrolyte solute) in the same solution.

For example, if $p^\ominus = 100$ kPa and $p \ll p^\ominus$, as is the case for isopiestic measurements with aqueous solutions near ambient temperature, then the contribution of the integral in equations (36) and (38) is about 2 J mol^{-1} which is comparable with $(\mu_A - \mu_A^\ominus) \approx -4.5 \text{ J mol}^{-1}$ but small compared with $(\mu_B - \mu_B^\ominus) \approx -5700 \text{ J mol}^{-1}$ for an ideal dilute solution with $\sum_B m_B = 0.1 \text{ mol kg}^{-1}$.

The **activity** a_A of the solvent A in a solution (especially a dilute liquid solution) containing molalities m_B, m_C, \dots , of solutes B, C, \dots is a dimensionless quantity defined in terms of the chemical potential μ_A of the solvent A in the solution by

$$RT \ln a_A = \mu_A - \mu_A^* = -RT \phi M_A \sum_B m_B \quad (39)$$

This definition of the activity of the solvent A in a solution is identical with the definition in section 4 of the activity of any substance in a mixture.

In general, the activities, activity coefficients, and osmotic coefficients defined in this section for solutes and solvents are functions of temperature, pressure, and composition.

6. COMPOSITION VARIABLES AND ACTIVITY COEFFICIENTS

Sometimes the same mixed condensed phase will have been studied by one group of workers as a mixture and by another group as a solution, and the results must be adjusted before the different measurements can be compared. The mole fraction x_A of the solvent A in a solution containing molalities $m_B = n_B / (n_A M_A)$, m_C, \dots of the solutes B, C, \dots is given by

$$x_A = 1 / \left(1 + M_A \sum_B m_B \right) \quad (40)$$

where M_A is the molar mass of the solvent A. The mole fraction x_B , molality m_B , and concentration c_B of the (solute) substance B are related to each other by

$$x_B = m_B M_A / \left(1 + M_A \sum_B m_B \right) \quad (41)$$

$$m_B = x_B / (x_A M_A) \quad (42)$$

and

$$c_B / m_B = \rho / \left(1 + \sum_B m_B M_B \right) = \rho - \sum_B c_B M_B \quad (43)$$

where M_B is the molar mass of the solute B and ρ is the density of the solution.

For a given mixed condensed phase, the activity coefficient f_B of the substance B with mole fraction x_B in the mixture, the activity coefficient γ_B of the solute B with molality m_B in the solution, and the activity coefficient $\gamma_{c,B}$ of the solute B with concentration c_B in the solution will, in general, be different. These activity

coefficients are related to each other by

$$f_B/f_B^\infty = \gamma_B \left(1 + M_A \sum_B m_B \right) = \gamma_{c,B} \left(\rho + M_A \sum_B c_B - \sum_B c_B M_B \right) / \rho_A^* \quad (44)$$

$$\gamma_B = (f_B/f_B^\infty) x_A \quad (45)$$

and

$$\gamma_B = \gamma_{c,B} \left(\rho - \sum_B c_B M_B \right) / \rho_A^* = \gamma_{c,B} (c_B / m_B \rho_A^*) \quad (46)$$

where ρ_A^* is the density of the pure (solvent) substance A and f_B^∞ denotes the activity coefficient of the substance B in the mixture at infinite dilution when $x_A \rightarrow 1$. Note that whereas $\gamma_B^\infty = 1$, in general $f_B^\infty \neq 1$; this is a direct consequence of the differences between the definition of the standard chemical potential of a solute in a solution and the definition of the standard chemical potential of a substance in a mixture. However, the chemical potential μ_B of the substance B in a mixed condensed phase is the same whether the phase is treated as a mixture with the composition described in terms of mole fraction, or as a solution with the composition described in terms of molality, or as a solution with the composition described in terms of concentration.

7. EQUILIBRIUM CONSTANT

The standard equilibrium constant K^\ominus for a chemical reaction is defined by

$$RT \ln \{K^\ominus(T)\} = - \sum_B \nu_B \mu_B^\ominus(z, T) = -\Delta_r G^\ominus(T) \quad (47)$$

where z denotes the state of aggregation and ν_B denotes the stoichiometric number of the substance B in the chemical reaction

$$0 = \sum_B \nu_B B \quad (48)$$

$\Delta_r G^\ominus$ is the change in the molar Gibbs energy due to the reaction. It follows from this definition that K^\ominus and $\Delta_r G^\ominus$ are, like all standard thermodynamic quantities, independent of pressure and composition, and that K^\ominus is a dimensionless quantity.

The Green Book (ref. 1) recommends the symbol K^\ominus , K° , or K for the equilibrium constant defined by equation (47); the name "thermodynamic equilibrium constant" with the symbol K has also been used by IUPAC (ref. 3). ISO 31/8 (ref. 2) recommends the name "standard equilibrium constant" with the symbol K^\ominus or K° . In this document the name **standard equilibrium constant** with symbol K^\ominus (K° would be an equivalent symbol) has been used for the equilibrium constant defined by equation (47) to distinguish it from other equilibrium

constants that are often used in practice although they are not constant at fixed temperature and need not be dimensionless. In the following paragraphs, definitions are given for some of these equilibrium constants; they have been given the symbol K and their dependence on temperature, pressure, and composition has been explicitly indicated; where appropriate, the conditions under which K becomes constant at constant temperature and becomes dimensionless (that is the conditions under which K approaches K^\ominus) are noted. It is assumed that all quantities refer to the state of chemical equilibrium.

The **standard equilibrium constant for a reaction in the gas phase** is given by

$$K^\ominus(g, T) = \prod_{\text{B}} (f_{\text{B}}/p^\ominus)^{\nu_{\text{B}}} \quad (49)$$

$$= \lim_{p \rightarrow 0} \prod_{\text{B}} (y_{\text{B}}p/p^\ominus)^{\nu_{\text{B}}} \quad (50)$$

Equation (50) provides the most direct method of determining $K^\ominus(g, T)$ experimentally and is useful when, as is often the case, the fugacity f_{B} is not known for each gas B in the reaction mixture. In many instances the extrapolation to zero pressure is not carried out and, at least at low to moderate pressures, is not necessary. In practice the quantity

$$K_p(g, T, p, y) = \prod_{\text{B}} (y_{\text{B}}p)^{\nu_{\text{B}}} \quad (51)$$

which has the dimension of (pressure) $^{\sum_{\text{B}} \nu_{\text{B}}}$, is often used. At constant temperature, K_p may be approximately constant, especially at low pressures where

$$\lim_{p \rightarrow 0} K_p(g, T, p, y) = K_f(g, T) = \prod_{\text{B}} (f_{\text{B}})^{\nu_{\text{B}}} \quad (52)$$

which is independent of pressure but need not equal K^\ominus .

The **standard equilibrium constant for a reaction in a condensed phase** is given by

$$K^\ominus(\text{cd}, T) = \left\{ \prod_{\text{B}} (x_{\text{B}}f_{\text{B}})^{\nu_{\text{B}}} \right\} \exp \left[- \int_p^{p^\ominus} \sum_{\text{B}} \{ \nu_{\text{B}} V_{\text{B}}^* / (RT) \} dp \right] \quad (53)$$

where x_{B} and f_{B} are the mole fraction and activity coefficient of the substance B in the reaction mixture at equilibrium; V_{B}^* is the molar volume of pure substance B .

Often, especially when $p \approx p^\ominus$, the pressure integral is small and the quantity

$$K_{x_f}(\text{cd}, T, p) = \prod_{\text{B}} (x_{\text{B}}f_{\text{B}})^{\nu_{\text{B}}} \quad (54)$$

is a good approximation to $K^\ominus(\text{cd}, T)$. If it is assumed that the reaction mixture

is an ideal mixture then K_{xf} reduces to

$$K_x(\text{cd}, T, p, x) = \prod_{\text{B}} (x_{\text{B}})^{\nu_{\text{B}}} \quad (55)$$

which is often used in practice. However, since few real mixtures are even approximately ideal, K_x usually varies with composition and is often a poor approximation to $K^\ominus(\text{cd}, T)$.

The **standard equilibrium constant for a reaction in a solution** of solutes B, C, ... in a solvent A is given by

$$K^\ominus(\text{solution}, T) = (a_{\text{A}})^{\nu_{\text{A}}} \left\{ \prod_{\text{B}} (a_{\text{B}})^{\nu_{\text{B}}} \right\} \\ \times \exp \left[- \int_p^{p^\ominus} \left\{ \left(\nu_{\text{A}} V_{\text{A}}^* + \sum_{\text{B}} \nu_{\text{B}} V_{\text{B}}^\infty \right) / (RT) \right\} dp \right] \quad (56)$$

where a denotes activity, V_{A}^* is the molar volume of the pure solvent, and V_{B}^∞ is the partial molar volume of the solute B at infinite dilution. Often, especially when $p \approx p^\ominus$ the pressure integral is small and the quantity

$$K_a(\text{solution}, T, p) = (a_{\text{A}})^{\nu_{\text{A}}} \prod_{\text{B}} (a_{\text{B}})^{\nu_{\text{B}}} \quad (57)$$

$$= \exp \left(-\nu_{\text{A}} \phi M_{\text{A}} \sum_{\text{B}} m_{\text{B}} \right) \prod_{\text{B}} (m_{\text{B}} \gamma_{\text{B}} / m^\ominus)^{\nu_{\text{B}}} \quad (58)$$

varies with pressure but may still be a good approximation to K^\ominus . If the solvent term $\exp(-\nu_{\text{A}} \phi M_{\text{A}} \sum_{\text{B}} m_{\text{B}})$, which is often close to unity, is neglected then the resulting quantity

$$K_{m\gamma}(\text{solution}, T, p, m) = \prod_{\text{B}} (m_{\text{B}} \gamma_{\text{B}} / m^\ominus)^{\nu_{\text{B}}} \quad (59)$$

varies with composition but may still be a good approximation to K^\ominus . The quantity

$$K_m(\text{solution}, T, p, m) = \prod_{\text{B}} (m_{\text{B}})^{\nu_{\text{B}}} \quad (60)$$

which has dimension $(\text{molality})^{\sum_{\text{B}} \nu_{\text{B}}}$, is often used in practice. Although K_m may be approximately constant, especially in a dilute solution at $p \approx p^\ominus$, it need not equal K^\ominus .

By contrast

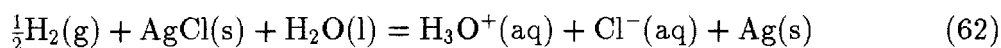
$$K^\ominus(\text{solution}, T) = \lim_{\sum_{\text{B}} m_{\text{B}} \rightarrow 0} \prod_{\text{B}} (m_{\text{B}} / m^\ominus)^{\nu_{\text{B}}}, \quad (p = p^\ominus) \quad (61)$$

This equation provides the most direct method of determining $K^\ominus(\text{solution}, T)$ experimentally (provided $p = p^\ominus$) and is useful when, as is often the case, the osmotic coefficient ϕ for the solvent and the activity coefficients γ_{B} , γ_{C} , ... for the solutes are not known.

If amount concentration c_B is used in place of molality m_B with a standard concentration c^\ominus in place of the standard molality m^\ominus , then equations (57) to (59) and (61) are modified by writing $a_{c,B}$ in place of a_B and $\gamma_{c,B}$ in place of γ_B ; as indicated in sections 4 and 5(b), the activity a_A of the solvent is not altered by changing the variable used to describe the composition of a mixture or solution. Since concentration, unlike molality, varies with both temperature and pressure, it is not possible to define a standard equilibrium constant $K^\ominus(\text{solution}, T)$ for a reaction in solution when the composition of the solution is described in terms of concentration.

In practice, many chemical reactions involve more than one phase, and the expressions for the standard equilibrium constant are necessarily more complicated than those given above for reactions in a single phase. Since it is not possible to consider all combinations, the general procedure is illustrated here by a single example.

The chemical reaction:



involves four phases and may be studied using a galvanic cell. The standard equilibrium constant contains a term from equation (49) for the gas (H_2), a term from equation (53) for each of the pure solid phases (Ag and AgCl), and terms from equation (56) for the solvent (H_2O) and solute (HCl). The complete expression is

$$K^\ominus(T) = \left\{ (a_{\text{HCl}}/a_{\text{H}_2\text{O}}) (p^\ominus/f_{\text{H}_2})^{1/2} \right\} \\ \times \exp \left[- \int_p^{p^\ominus} \{ (V_{\text{HCl}}^\infty - V_{\text{H}_2\text{O}}^* + V_{\text{Ag}}^* - V_{\text{AgCl}}^*) / (RT) \} dp \right]$$

and $K^\ominus(298.15 \text{ K}) \approx 5694$ when $p^\ominus = 100 \text{ kPa}$. The contributions of the various terms to K^\ominus are considered in some detail below; for this reaction, a change of 0.01 mV in the electromotive force (emf) of the galvanic cell corresponds to 0.04 per cent in K^\ominus .

If the volumes of the condensed phases are independent of pressure, then the contribution of the integral to K^\ominus is a factor

$$\exp \left\{ - (p^\ominus - p) (V_{\text{HCl}}^\infty - V_{\text{H}_2\text{O}}^* + V_{\text{Ag}}^* - V_{\text{AgCl}}^*) / (RT) \right\} \\ \approx 1 + 6 \times 10^{-6} (p^\ominus - p) / \text{kPa}$$

which is often negligible.

At 298.15 K, the second virial coefficient of H_2 is about $15 \text{ cm}^3 \text{ mol}^{-1}$ and, using equation (20), the fugacity coefficient ϕ_{H_2} for H_2 is

$$\phi_{\text{H}_2} = f_{\text{H}_2} / (y_{\text{H}_2} p) = 1 + 6 \times 10^{-6} (p / \text{kPa})$$

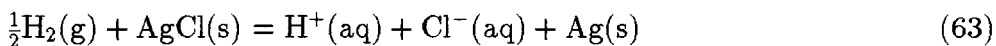
Consequently, the gas imperfections contribute a factor 1.0003 to K^\ominus at a total pressure $p = 100$ kPa. While this factor may be neglected for many measurements, the vapour pressure of the solution is close to that of pure water (about 3.2 kPa at 298.15 K) so $y_{\text{H}_2} \approx 0.968$ at $p = 100$ kPa and, when $p^\ominus = 100$ kPa,

$$(f_{\text{H}_2}/p^\ominus)^{1/2} \approx (y_{\text{H}_2}p/p^\ominus)^{1/2} \approx 1 - 0.016$$

which corresponds to 0.4 mV in the emf of the galvanic cell.

The activity of $a_{\text{H}_2\text{O}}$ of H_2O differs from unity by about $M_{\text{A}} \sum_{\text{B}} m_{\text{B}} = 2M_{\text{A}}m_{\text{HCl}}$ and contributes more than 0.04 per cent to K^\ominus (or more than 0.01 mV to the emf) for molalities m_{HCl} of HCl greater than about 0.01 mol kg⁻¹. Consequently, $a_{\text{H}_2\text{O}}$ should be considered for precise work except at high dilution.

Alternatively, the chemical reaction may be written



and the solvent no longer enters the expression for K^\ominus . It should be noted that for a given solution, $m(\text{H}^+) \neq m(\text{H}_3\text{O}^+)$ and that K^\ominus is different for reactions (62) and (63).

The above discussion indicates that for many purposes the gas imperfections and the pressure dependence of the chemical potentials for the condensed phases may be neglected. Consequently, for the reaction (63), which also avoids $a_{\text{H}_2\text{O}}$, the standard equilibrium constant may be written

$$\begin{aligned} K^\ominus(T) &= a_{\text{HCl}} \{p^\ominus / (y_{\text{H}_2}p)\}^{1/2} \\ &= \{m_{\text{H}^+}m_{\text{Cl}^-} / (m^\ominus)^2\} (\gamma_{\text{H}^+}\gamma_{\text{Cl}^-}) \{p^\ominus / (y_{\text{H}_2}p)\}^{1/2} \\ &= (m_{\pm}\gamma_{\pm} / m^\ominus)^2 \{p^\ominus / (y_{\text{H}_2}p)\}^{1/2} \end{aligned}$$

where m_{\pm} and γ_{\pm} are the mean ionic molality and mean ionic activity coefficient for HCl in the aqueous solution. As with most electrolyte solutions, the activity coefficients of HCl can be neglected only for very approximate calculations. For example, $\gamma_{\pm} = 0.796$ for an aqueous HCl solution of molality 0.1 mol kg⁻¹ and an equilibrium constant calculated with $\gamma_{\pm} = 1$ differs from K^\ominus by almost 40 per cent; even when $m_{\pm} = 10^{-4}$ mol kg⁻¹, γ_{\pm} accounts for about 2.3 per cent of K^\ominus .

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