

### L3.8 Chemical thermodynamics

Name	Symbol	Definition	SI unit	Notes
heat	$q, Q$		J	(1)
work	$w, W$		J	(1)
internal energy	$U$	$\Delta U = q + w$	J	(1)
enthalpy	$H$	$H = U + pv$	J	
thermodynamic temperature	$T$		K	
Celsius temperature	$\theta, t$	$\theta/^{\circ}\text{C} = T/\text{K} - 273.15$	$^{\circ}\text{C}$	(2)
entropy	$S$	$dS = dq_{\text{rev}}/T$	$\text{J K}^{-1}$	
Helmholtz energy, (Helmholtz function)	$A$	$A = U - TS$	J	(3)
Gibbs energy (Gibbs function)	$G$	$G = H - TS$	J	
surface tension	$\gamma, \sigma$	$\gamma = (\partial G/\partial A_s)_{T,p}$	$\text{J m}^{-2}, \text{N m}^{-1}$	
molar quantity $X$	$X_m, (\bar{X})$	$X_m = X/n$	(varies)	(4),(5)
specific quantity $X$	$x$	$x = X/m$	(varies)	(4),(5)

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- (1) Both  $q > 0$  and  $w > 0$  indicate an increase in the energy of the system;  $\Delta U = q + w$ . The given equation is sometimes written as  $dU = \overset{\delta}{d}q + \overset{\delta}{d}w$ , where  $\overset{\delta}{d}$  denotes an inexact differential.
  - (2) This quantity is sometimes misnamed 'centigrade temperature'.
  - (3) It is sometimes convenient to use the symbol  $F$  for Helmholtz energy in the context of surface chemistry, to avoid confusion with  $A$  for area.
  - (4) The definition applies to pure substance. However, the concept of molar and specific quantities (see section 2) may also be applied to mixtures.
  - (5)  $X$  is an extensive quantity. The unit depends on the quantity. In the case of molar quantities the entities should be specified.

*Example* molar volume of B,  $V_m(\text{B}) = V/n_{\text{B}}$

<i>Name</i>	<i>Symbol</i>	<i>Definition</i>	<i>SI unit</i>	<i>Notes</i>
pressure coefficient	$\beta$	$\beta = (\partial p / \partial T)_V$	Pa K <sup>-1</sup>	
relative pressure coefficient	$\alpha_p$	$\alpha_p = (1/p)(\partial p / \partial T)_V$	K <sup>-1</sup>	
compressibility, isothermal	$\kappa_T$	$\kappa_T = -(1/V)(\partial V / \partial p)_T$	Pa <sup>-1</sup>	
isentropic	$\kappa_S$	$\kappa_S = -(1/V)(\partial V / \partial p)_S$	Pa <sup>-1</sup>	
linear expansion coefficient	$\alpha_l$	$\alpha_l = (1/l)(\partial l / \partial T)$	K <sup>-1</sup>	
cubic expansion coefficient	$\alpha, \alpha_V, \gamma$	$\alpha = (1/V)(\partial V / \partial T)_p$	K <sup>-1</sup>	(6)
heat capacity, at constant pressure	$C_p$	$C_p = (\partial H / \partial T)_p$	J K <sup>-1</sup>	
at constant volume	$C_V$	$C_V = (\partial U / \partial T)_V$	J K <sup>-1</sup>	
ratio of heat capacities	$\gamma, (\kappa)$	$\gamma = C_p / C_V$	1	
Joule-Thomson coefficient	$\mu, \mu_{JT}$	$\mu = (\partial T / \partial p)_H$	K Pa <sup>-1</sup>	
virial coefficient, second	$B$	$pV_m = RT(1 + B/V_m$	m <sup>3</sup> mol <sup>-1</sup>	
third	$C$	$+ C/V_m^2 + \dots)^m$	m <sup>6</sup> mol <sup>-2</sup>	
van der Waals coefficients	$a$	$(p + a/V_m^2)(V_m - b) = RT$	J m <sup>3</sup> mol <sup>-2</sup>	(7)
	$b$		m <sup>3</sup> mol <sup>-1</sup>	(7)
compression factor, (compressibility factor)	$Z$	$Z = pV_m / RT$	1	

(6) This quantity is also called the coefficient of thermal expansion, or the expansivity coefficient.

(7) For a gas satisfying the van der Waals equation of state, given in the definition, the second virial coefficient is related to the parameters  $a$  and  $b$  in the van der Waals equation by  $B = b - a/RT$

<i>Name</i>	<i>Symbol</i>	<i>Definition</i>	<i>SI unit</i>	<i>Notes</i>
partial molar quantity $X$	$X_B, (\bar{X}_B)$	$X_B = (\partial X / \partial n_B)_{T, p, n_{j \neq B}}$	(varies)	(8)
chemical potential, (partial molar Gibbs energy)	$\mu$	$\mu_B = (\partial G / \partial n_B)_{T, p, n_{j \neq B}}$	$\text{J mol}^{-1}$	(9)
standard chemical potential	$\mu^\theta, \mu^\circ$		$\text{J mol}^{-1}$	(10)
absolute activity	$\lambda$	$\lambda_B = \exp(\mu_B / RT)$	1	(9)
(relative) activity	$a$	$a_B = \exp\left[\frac{\mu_B - \mu_B^\circ}{RT}\right]$	1	(9),(11)
standard partial molar enthalpy	$H_B^\circ$	$H_B^\circ = \mu_B^\circ + TS_B^\circ$	$\text{J mol}^{-1}$	(9), (10)
standard partial molar entropy	$S_B^\circ$	$S_B^\circ = -(\partial \mu_B^\circ / \partial T)_p$	$\text{J mol}^{-1} \text{K}^{-1}$	(9), (10)

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- (8) The symbol applies to entities B which should be specified. The bar may be used to distinguish partial molar  $X$  from  $X$  when necessary.

*Example* The partial molar volume of  $\text{Na}_2\text{SO}_4$  in aqueous solution may be denoted  $\bar{V}(\text{Na}_2\text{SO}_4, \text{aq})$ , in order to distinguish it from the volume of the solution  $V(\text{Na}_2\text{SO}_4, \text{aq})$ .

- (9) The definition applies to entities B which should be specified.
- (10) The symbol  $^\theta$  or  $^\circ$  is used to indicate standard. They are equally acceptable. Whenever a standard chemical potential  $\mu$  or a standard equilibrium constant  $K$  or other standard quantity is used, the standard state must be specified.
- (11) In the defining equation given here the pressure dependence of the activity has been neglected as is often done for condensed phases at atmospheric pressure.

An equivalent definition is  $a_B = \lambda_B / \lambda_B$ , where  $\lambda_B = \exp(\mu_B / RT)$ . The definition of  $\mu$  depends on the choice of the standard state.

<i>Name</i>	<i>Symbol</i>	<i>Definition</i>	<i>SI unit</i>	<i>Notes</i>
standard reaction Gibbs energy (function)	$\Delta_r G^\circ$	$\Delta_r G^\circ = \sum_B \nu_B \mu_B^\circ$	$\text{J mol}^{-1}$	(10),(12),(13),(14)
affinity of reaction	$A, ( )$	$A = -(\partial G / \partial \xi)_{p, T}$ $= \sum_B \nu_B \mu_B$	$\text{J mol}^{-1}$	(13)
standard reaction enthalpy	$\Delta_r H^\circ$	$\Delta_r H^\circ = \sum_B \nu_B H_B^\circ$	$\text{J mol}^{-1}$	(10),(12)
standard reaction entropy	$\Delta_r S^\circ$	$\Delta_r S^\circ = \sum_B \nu_B S_B^\circ$	$\text{J mol}^{-1} \text{K}^{-1}$	(10), (12), (13)
reaction quotient	$Q$	$Q = \prod_B a_B^{\nu_B}$	1	(15)
equilibrium constant	$K^\circ, K$	$K^\circ = \exp(-\Delta_r G^\circ / RT)$	1	(10),(13),(16)

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- (12) The symbol r indicates reaction in general. In particular cases r can be replaced by another appropriate subscript, e.g.  $\Delta_r H^\circ$  denotes the standard molar enthalpy of formation.
- (13) The reaction must be specified for which this quantity applies.
- (14) Reaction enthalpies (and reaction energies in general) are usually quoted in  $\text{kJ mol}^{-1}$ . In older literature  $\text{kcal mol}^{-1}$  is also common, where  $1 \text{ kcal} = 4.184 \text{ kJ}$ .
- (15) This quantity applies in general to a system which is not in equilibrium.
- (16) This quantity is equal to the value of  $Q$  in equilibrium, when the affinity is zero. It is dimensionless and its value depends on the choice of standard state, which must be specified.

<i>Name</i>	<i>Symbol</i>	<i>Definition</i>	<i>SI unit</i>	<i>Notes</i>
equilibrium constant, pressure basis	$K_p$	$K_p = \prod_B p_B^{v_B}$	$\text{Pa}^{\sum v}$	(13), (17)
concentration basis	$K_c$	$K_c = \prod_B c_B^{v_B}$	$(\text{mol m}^{-3})^{\sum v}$	(13), (17)
molality basis	$K_m$	$K_m = \prod_B m_B^{v_B}$	$(\text{mol kg}^{-1})^{\sum v}$	(13), (17)
fugacity	$f, \mathcal{P}$	$f_B \lambda_B = \lim_{p \rightarrow 0} (p_B / \lambda_B)_T$	Pa	(9)
fugacity coefficient	$\phi$	$\phi_B = f_B / p_B$	1	
Henry's law constant	$k_H$	$k_{H,B} = \lim_{x_B \rightarrow 0} (f_B / x_B)$ $= (\partial f_B / \partial x_B)_{x_B=0}$	Pa	(9), (18)

- (17) These quantities are not in general dimensionless. One can define in an analogous way an equilibrium constant in terms of fugacity  $K_f$ , etc. At low pressures  $K_p$  is approximately related to  $K^\circ$  by the equation  $K^\circ \approx K_p / (p^\circ)^{\sum v}$ , and similarly in dilute solutions  $K_c$  is approximately related to  $K^\circ$  by  $K^\circ \approx K_c / (c^\circ)^{\sum v}$ ; however the exact relations involve fugacity coefficients or activity coefficients.

The equilibrium constant of dissolution of an electrolyte (describing the equilibrium between excess solid phase and solvated ions) is often called a solubility product, denoted  $K_{\text{sol}}$  or  $K_s$  (or  $K_{\text{sol}}^\circ$  or  $K_s^\circ$  as appropriate). In a similar way the equilibrium constant for an acid dissociation is often written  $K_a$ , for base hydrolysis  $K_{\text{hidr}}$  and for water dissociation  $K_w$ .

- (18) Henry's law is sometimes expressed in terms of molalities or concentrations and then the corresponding units of the Henry's law constant are  $\text{Pa kg mol}^{-1}$  or  $\text{Pa m}^3 \text{mol}^{-1}$ , respectively.

<i>Name</i>	<i>Symbol</i>	<i>Definition</i>	<i>SI unit</i>	<i>Notes</i>
activity coefficient				
referenced to Raoult's law	$f$	$f_B = a_B/x_B$	1	(9), (19)
referenced to Henry's law				
molality basis	$\gamma_m$	$a_{m,B} = \gamma_{m,B} m_B/m^\circ$	1	(9), (20)
concentration basis	$\gamma_c$	$a_{c,B} = \gamma_{c,B} c_B/c^\circ$	1	(9), (20)
mole fraction basis	$\gamma_x$	$a_{x,B} = \gamma_{x,B} x_B$	1	(9), (20)
ionic strength,				
molality basis	$I_m, I$	$I_m = \frac{1}{2} \sum m_B z_B^2$	mol kg <sup>-1</sup>	
concentration basis	$I_c, I$	$I_c = \frac{1}{2} \sum c_B z_B^2$	mol m <sup>-3</sup>	
osmotic coefficient,				
molality basis	$\phi_m$	$\phi_m = \frac{\mu_A^* - \mu_A}{RT \sum m_B}$	1	
mole fraction basis	$\phi_x$	$\phi_x = \frac{\mu_A - \mu_A^*}{RT \ln x_A}$	1	
osmotic pressure	$\Pi$	$\Pi = c_B RT$	Pa	(21)

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(19) This quantity applies to pure phases, substances in mixtures, or solvents.

(20) This quantity applies to solutes.

(21) The defining equation applies to ideal dilute solutions. The entities B are individually moving solute molecules, ions, etc. regardless of their nature. Their amount is sometimes expressed in osmoles (meaning a mole of osmotically active entities), but this use is discouraged.

## Other symbols and conventions in chemical thermodynamics

### (i) Symbols used as subscripts to denote a chemical process or reaction

These symbols should be printed in roman (upright) type, without a full stop (period).

vaporization, evaporation (liquid → gas)	vap
sublimation (solid → gas)	sub
melting, fusion (solid → liquid)	fus
transition (between two phases)	trs
mixing of fluids	mix
solution (of solute in solvent)	sol
dilution (of a solution)	dil
adsorption	ads
displacement	dpl
immersion	imm
reaction in general	r
atomization	at
combustion reaction	c
formation reaction	f

### (ii) Recommended superscripts

standard	$\theta^\circ$
pure substance	*
infinite dilution	$\infty$
ideal	id
activated complex, transition state	‡
excess quantity	E

### (iii) Examples of the use of these symbols

The subscripts used to denote a chemical process, listed under (i) above, should be used as subscripts to the  $\Delta$  symbols to denote the change in an extensive thermodynamic quantity associated with the process.

*Example*       $\Delta_{\text{vap}}H = H(\text{g}) - H(\text{l})$ , for the enthalpy of vaporization, an extensive quantity proportional to the amount of substance vaporized.