

Materials 2B03

EQUATION TOOLBOX

Chapter 2 – The First Law of Thermodynamics

$$dU = \delta q - \delta w$$

Isothermal Process	Adiabatic Process
$\delta w = \delta q = nRT \ln \left(\frac{V_2}{V_1} \right)$	$\delta w = -nc_v dT = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$ $\delta q = 0$ $PV^\gamma = \text{constant for reversible process only}$
Isochoric Process	Isobaric Process
$\delta w = 0$ $\delta q = nc_v dT$	$\delta w = P\Delta V$ $\delta q = nc_p dT$

Chapter 3 – The Second Law of Thermodynamics

$$dS = \int \left(\frac{q}{T} \right) dT$$

Isothermal Process	Adiabatic Process
$dS = \int \left(\frac{nRT \ln \left(\frac{V_2}{V_1} \right)}{T} \right) dT$ $\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$	$dS = \int \left(\frac{q}{T} \right) dT$ $\Delta S = 0$ <p>*a reversible adiabatic process is isentropic!*</p>
Isochoric Process	Isobaric Process
$dS = \int \left(\frac{nc_v}{T} \right) dT$ $\Delta S = nc_v \ln \left(\frac{T_2}{T_1} \right)$	$dS = \int \left(\frac{nc_p}{T} \right) dT$ $\Delta S = nc_p \ln \left(\frac{T_2}{T_1} \right)$

Chapter 5 – Auxiliary Functions

Enthalpy (H)	$H = U + PV$ $\Delta H = (U_2 + PV_2) - (U_1 + PV_1)$	<ul style="list-style-type: none">• If a closed system performs P-V work, the enthalpy change is equal to the heat entering/leaving the system.
Helmholtz Free Energy (A)	$A = U - TS$ $\Delta A = (q - w) - (T_2S_2 - T_1S_1)$	<ul style="list-style-type: none">• At constant T and V, a spontaneous reaction will decrease A.
Gibbs Free Energy (G)	$G = H - TS$ $\Delta G = \Delta H - T\Delta S$	<ul style="list-style-type: none">• At constant T and P, a spontaneous reaction will decrease G.

Chapter 5 – Auxiliary Functions

Equation	When to Apply	Notes
<p>Clapeyron Equation</p> $\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$	Two condensed phases (liquids and/or solids) in equilibrium with each other.	--
<p>Clausius-Clapeyron Equation</p> $\ln p = \frac{-\Delta H}{RT} + \text{constant}$	A condensed phase (liquid or solid) in equilibrium with its gas	Boiling occurs when vapour pressure is equal to atmospheric pressure.

Chapter 6 – Heat Capacity, Entropy, Enthalpy, and the Third Law of Thermodynamics

Pure elements in their most stable form at room temperature	$\Delta H_{pure}^o = 0$
Temperature dependence without phase transformations	$\Delta H^T = \int_{298K}^T nc_p dT$
Temperature dependence with a phase transformation	$\Delta H^{T_{final}} = \int_{298K}^{T_{trans}} nc_p^{phase2} dT + \Delta H_{transformation} + \int_{T_{trans}}^{T_{final}} nc_p^{phase1} dT$
Reaction	$\Delta H_{reaction} = \sum \Delta H_{products} - \sum \Delta H_{reactants}$

Chapter 7 – Phase Equilibrium in a One-Component System

Equation	When to Apply
<p>Clapeyron Equation</p> $\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T\Delta V_{(l \rightarrow s)}}$	<p>Need to simultaneously adjust temperature and pressure to keep a solid and liquid in equilibrium</p>
<p>Clausius-Clapeyron Equation</p> $d \ln P = \frac{\Delta H}{RT^2} dT \quad \frac{d \ln P}{dT} = \frac{\Delta H}{RT^2}$	<p>Need to simultaneously adjust temperature and pressure to keep a condensed phase (solid or liquid) and gas in equilibrium.</p>

at any temperature:

$$\Delta H_{s \rightarrow l} + \Delta H_{l \rightarrow v} = \Delta H_{s \rightarrow v}$$

Chapter 7 – Phase Equilibrium in a 1-Component System

Variation of G with...	Interpretation	Equation
Temperature, at constant pressure	The negative of the entropy change	$\left(\frac{\partial G}{\partial T}\right)_P = -S$, and $\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$
Pressure, at constant temperature	Volume	$\left(\frac{\partial G}{\partial P}\right)_T = V$, and $\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V$
Number of moles in the system, at constant temperature and pressure	Chemical potential	$\left(\frac{\partial G'}{\partial n_i}\right)_{T,P} = \mu_i$

Chapter 8 – The Behaviour of Gases

Van der Waals Gases

Correction term for interactions among particles

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT$$

Correction term for finite particle volume

For n other than 1:
$$\left(P + a \frac{n^2}{V^2} \right) (V - nb) = nRT$$

We can rewrite the Van der Waals equation as a cubic function of V :

$$PV^3 - (Pb + RT)V^2 + aV - ab = 0$$

Critical point

$$\begin{cases} T_{cr} = \frac{8a}{27bR} \\ V_{cr} = 3b \\ P_{cr} = \frac{a}{27b^2} \end{cases}$$

Compressibility Factor Z for Gases Modelled as a Virial Expansion

$$\frac{PV}{RT} = Z = 1 + BP + CP^2 + DP^3 + \dots$$

Fugacity (f):

An effective partial pressure which replaces the mechanical partial pressure in an accurate computation of the chemical equilibrium constant.

In other words: fugacity is equal to the pressure of an ideal gas which has the same chemical potential as the real gas.

$$\frac{f}{P} = \frac{P}{P_{ideal}} \quad \ln \left(\frac{f}{P} \right)_{P=P} = \int_{P=0}^{P=P} \frac{Z-1}{P} dP$$

Chapter 8 – The Behaviour of Gases

For Mixtures of Ideal Gases

$$\Delta H^{mix} = 0$$

$$\Delta S^{mix} = -nR \sum_i X_i \ln X_i = -nR [(X_A \ln X_A) + (X_B \ln X_B) + \dots]$$

$$\Delta G^{mix} = \Delta H^{mix} - T \Delta S^{mix} = \sum_i n_i RT \ln X_i = n_A RT \ln X_A + n_B RT \ln X_B + \dots$$

Since mole fractions are always less than 1, the logarithms are negative. This means ΔG^{mix} is negative, therefore mixing is always spontaneous!

Chapter 11 – Reactions Involving Gases

$$\Delta G_{\text{reaction}}^{\circ} = -RT \ln K_p$$

$$K_p = \frac{P_{AB}^2}{P_A P_B}$$

Diagram illustrating the components of the equilibrium constant expression K_p :

- Product gases in the numerator:** Indicated by a blue arrow pointing to the numerator P_{AB}^2 . The exponent 2 is circled in red.
- Reactant gases in the denominator:** Indicated by a blue arrow pointing to the denominator $P_A P_B$.
- Exponents are the corresponding coefficients in the balanced reaction:** Indicated by a red arrow pointing from the circled 2 to this text box.

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} = \frac{X_C^c X_D^d}{X_A^a X_B^b} \frac{P^c P^d}{P^a P^b} = (K_x) P^{(c+d-a-b)}$$

Procedure

1. Set up ICE table for number of moles
2. Find total number of moles and mole fractions
3. Calculate ΔG for the temperature of interest and solve for K_p
4. Derive an expression for K_x and solve for x
5. Substitute x into the expressions for final number of moles

Chapter 15 – Electrochemistry

- For the general reaction: $aA + bB \rightarrow cC + dD$

$$\varepsilon^\circ = \varepsilon^\circ_{\text{cathode}} - \varepsilon^\circ_{\text{anode}}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

$$\Delta G = -zF\varepsilon$$

$$\varepsilon = \varepsilon^\circ - \frac{RT}{ZF} \ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

ΔG : Gibbs energy for the cell

ΔG° : Gibbs energy of the cell for reactants and products in their standard states

R: gas constant (8.314 J/molK)

T: temperature (K)

a_i : activities of component i raised to the power of its coefficient (products in numerator, reactants in denominator)

ε : EMF of the cell

ε° : EMF of the cell for reactants and products in their standard states

R: gas constant (8.314 J/molK)

T: temperature (K)

Z: valence

F: Faraday's constant (96,487 C)

a_i : activities of component i raised to the power of its coefficient (products in numerator, reactants in denominator)

Chapter 15 – Electrochemistry

- Concentration cell: cell with identical electrodes inserted into solutions differing only in concentration
- The driving force is the diffusion of electrolyte from high to low concentration.
- Example: $\text{CuSO}_4^{\text{high}} \rightarrow \text{CuSO}_4^{\text{low}}$

$$\varepsilon = \varepsilon^o - \frac{RT}{ZF} \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} = 0 - \frac{RT}{2F} \ln \frac{a_{\text{low conc. CuSO}_4}}{a_{\text{high conc. CuSO}_4}}$$

standard EMF is 0 for concentration cells

Chapter 15 – Electrochemistry

- **Effect of temperature:**

- For any cell reaction at constant temperature and pressure:

$$\Delta G = -zF\varepsilon$$

- The molar entropy and enthalpy changes for the cell reaction are:

$$\Delta S = zF \left(\frac{\partial \varepsilon}{\partial T} \right)_P \qquad \Delta H = -zF\varepsilon + zFT \left(\frac{\partial \varepsilon}{\partial T} \right)_P$$