

UNIVERSITY OF MANITOBA, DEPARTMENT OF CHEMISTRY
Chemistry 2290, Winter 2012, G. Schreckenbach

Formula Sheet (Midterm 2)

This formula sheet can be taken home after the exam

Gas Laws (Ideal and Real Gases)

Ideal gas law: $PV = nRT$

Compression factor: $Z = \frac{PV_m}{RT}$

van der Waals equation: $\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$

Virial equation of state: $Z = \frac{PV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots$

Law of corresponding states $\left(P_R + \frac{3}{V_{R,m}^2}\right)\left(V_{R,m} - \frac{1}{3}\right) = \frac{8}{3}RT_R$

where $P_R = \frac{P}{P_C}$; $V_R = \frac{V}{V_C}$; $T_R = \frac{T}{T_C}$

First Law of Thermodynamics

First law: $\Delta U = q + w$ (where q and w are the heat transferred **to** the system and the work done **on** the system, respectively)

Reversible pV work: $w_{rev} = -\int_{V_1}^{V_2} PdV$; $\delta w_{rev} = -PdV$

Enthalpy (definition): $H = U + PV$

Heat capacity at constant volume: $C_V = \frac{\delta q_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V$

Heat capacity at constant pressure: $C_P = \frac{\delta q_P}{dT} = \left(\frac{\partial H}{\partial T}\right)_P$

For an ideal gas: $C_{P,m} = C_{V,m} + R$

Ideal gas, reversible isothermal process: $\left(\frac{\partial U}{\partial V}\right)_T = 0$, and $w_{rev} = -q_{rev} = nRT \ln \frac{V_1}{V_2}$

Ideal gas, reversible adiabatic process: $P_i V_i^\gamma = P_f V_f^\gamma$ where $\gamma = \frac{C_P}{C_V}$

Second Law of Thermodynamics

Carnot cycle, work and heat: $q_{cycle} = R(T_{hot} - T_{cold}) \ln \frac{V_b}{V_a} = -w_{cycle}$ (per mole of ideal gas)

Carnot cycle, thermodynamic efficiency: $\varepsilon \equiv \frac{-w_{cycle}}{q_{hot}} = 1 - \frac{T_{cold}}{T_{hot}}$

Entropy (definition) $\Delta S_{A \rightarrow B} = S_B - S_A \equiv \int_A^B \frac{\delta q_{rev}}{T}$ or $dS \equiv \frac{\delta q_{rev}}{T}$

Second Law of Thermodynamics: $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$;

Clausius inequality $dS \geq \frac{\delta q}{T}$

Ideal gas, entropy change: $\Delta S = n \int_{T_1}^{T_2} C_{V,m} \frac{dT}{T} + nR \ln \frac{V_2}{V_1}$

Ideal gas, molar entropy of mixing: $\Delta S_m = -R(x_1 \ln x_1 + x_2 \ln x_2)$

Entropy of fusion (melting): $\Delta S = \frac{q_{fus}}{T_{fus}} = \frac{\Delta H_{fus}}{T_{fus}}$ (similar for other phase transitions)

Joule-Thomson coefficient: $\mu_{J-T} = \left(\frac{\partial T}{\partial P} \right)_H$

First and Second Laws Combined – Free Energies

Gibbs energy (definition) $G \equiv H - TS$ Helmholtz energy (definition) $A \equiv U - TS$

Process at const. T, V: spontaneous process if $dA < 0$; equilibrium if $dA = 0$

Process at const. T, p: spontaneous process if $dG < 0$; equilibrium if $dG = 0$

Gibbs equations: for $U = U(V,S)$: $dU = -pdV + TdS$

for $H = H(p,S)$: $dH = Vdp + TdS$

for $A = A(V,T)$: $dA = -pdV - SdT$

for $G = G(p,T)$: $dG = Vdp - SdT$

Maxwell's relations: $\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V$ $\left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p$

$\left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$ $\left(\frac{\partial V}{\partial T} \right)_p = - \left(\frac{\partial S}{\partial p} \right)_T$

Gibbs-Helmholtz equation: $-\frac{\Delta H}{T^2} = \left[\frac{\partial}{\partial T} \left(\frac{\Delta G}{T} \right) \right]_p$

Thermochemistry – equilibrium constant: $\ln K = -\frac{\Delta G_R}{RT}$

Chemical Potential

Chemical potential of component i (definition) $\mu_i \equiv \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}}$ (similarly for multi-phase systems)

Gibbs energy for an open system: $dG = -SdT + Vdp + \sum_i \mu_i dn_i$ (Gibbs equation)

Material equilibrium condition: $\sum_i \mu_i dn_i = 0$

Phase equilibrium condition: $\mu_i^\beta = \mu_i^\delta$

Phase Diagrams

Phase rule: $F = C - P + 2$

Units, Constants

Pressure: Pa = kg m⁻¹ s⁻²

1 atm = 1.01325 x 10⁵ Pa;

1 Torr = 133.322 Pa; 1 bar = 10⁵ Pa

Energy: J = kg m² s⁻²; 1 cal = 4.184 J

Temperature: T / K = θ / °C + 273.15

Avogadro's number: $N_0 = 6.02214 \times 10^{23}$ mol⁻¹

Ideal gas constant: $R = 8.3145101$ J mol⁻¹ K⁻¹ = 0.0820578 atm L K⁻¹ mol⁻¹