

**Lecture 1**

Entropy change when heat is supplied, assuming temperature is constant:

$$\Delta S = \frac{q_{rev}}{T}$$

Entropy change through change in temperature, assuming heat capacity remains constant with temperature:

$$\Delta S = C \ln\left(\frac{T_2}{T_1}\right)$$

**Lecture 2**

Entropy change through change in volume, assuming constant temperature and pressure:

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$$

Entropy change through change in pressure, assuming constant temperature and volume:

$$\Delta S = nR \ln\left(\frac{P_1}{P_2}\right)$$

Entropy change at a state function:

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{vap}}$$

Trouton's Rule:

$$\Delta S_{vap} \approx 85 \text{ JK}^{-1} \text{ mol}^{-1}$$

**Lecture 3**

Entropy of a crystal with a set number of microstates (W):

$$S = k_B \ln W \quad \text{Where } k_B = 1.38 \times 10^{-23}$$

**Lecture 4**

Entropy of surroundings in an isolated system:

$$\Delta S_{surr} = -\frac{\Delta H}{T}$$

$$\Delta S_{tot} = \Delta S + \Delta S_{surr}$$

**Lecture 5**

Gibbs free energy definition:

$$G = H - TS$$

Calculating G through G standard at different pressures:

$$G = G^\circ + RT \ln\left(\frac{P}{1 \text{ atm}}\right)$$

Calculating change in  $G^\circ$  through equilibrium constant:

$$\Delta G^\circ = -RT \ln K_p$$

Other weird functions I don't understand but need to try and learn to at least have a small shot of getting a first:

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

$$\left( \frac{\partial \ln K_p}{\partial T} \right) = \frac{\Delta H^\circ}{RT^2}$$

$$\ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

**Topic 1: Single component mixtures**

For a one-component system, chemical potential is equivalent to molar Gibbs energy

$$dG = (\mu_2 - \mu_1)dn$$

$$dG = 0 \quad \text{if} \quad \mu_1 = \mu_2$$

$$\left(\frac{dG_m}{dT}\right)_p = \left(\frac{d\mu}{dT}\right)_p = -S_m$$

$$\left(\frac{dG_m}{dP}\right)_T = \left(\frac{d\mu}{dP}\right)_T = V_m \quad V_m > 0$$

Clapeyron Equation

$$\left(\frac{dP}{dT}\right)_x = \frac{\Delta S_x}{\Delta V_x}$$

Gradient of phase coexistence lines for plastic crystals

$$\Delta S_x = \frac{\Delta H_x}{T}$$

Clausius Clapeyron Equation

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

**Topic 2: Thermodynamics of liquid mixtures**

Raoult's Law

$$P_T = P_A + P_B$$

$$P_T = x_A P_A^* + x_B P_B^*$$

Dalton's Law

$$y_A = \frac{P_A}{P_T} = \frac{x_A P_A^*}{P_B^* + (P_A^* - P_B^*)x_A} \quad y_B = 1 - y_A$$

$$P_T = \frac{P_A^* P_B^*}{P_A^* + (P_B^* - P_A^*)y_A}$$

**Topic 3: Thermodynamics of non-ideal liquid mixtures**

**Derivations from ideality (Raoult's Law) are defined with reference to pressure-composition diagrams and the sign of  $\Delta H_{mix}$**

Henry's Law

$$P_A = X_B K_B$$

**Topic 4: Two and Three component mixtures**

Gibbs phase rule

$$F = C - P + 2$$

**Topic 5: Colligative Properties**

Elevation of a boiling point

$$\Delta T_b = T_b - T_b^* = \left( \frac{RT_b^{*2}}{\Delta H_{vap}} \right) x_{solute}$$

Lowering of a freezing point

$$\Delta T_f = T_f - T_f^* = \left( \frac{RT_f^{*2}}{\Delta H_{freeze}} \right) x_{solute}$$

Lowering of vapour pressure

$$\Delta P = x_{solute} P_{solvent}^*$$

Dilute solution approximation

$$\Delta T_b = K_b m_{solute} \quad \Delta T_f = K_f m_{solute}$$

$$MM_{solute} = \frac{K_f mass_{solute}}{K_b mass_{solvent}}$$

Osmotic Pressure

$$\pi = \frac{RT}{(V_m)_{solvent}} x_{solvent}$$

$$\pi = RT c_{solute}$$

$$c_{solute} = \frac{c'}{MM_{solute}}$$

**Lecture 1**

The steady state approximation (SSA)

$$\frac{d}{dt}[I] = \dots = 0$$

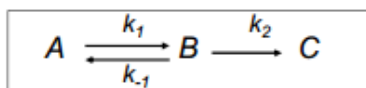
**Lecture 2**

The Lindemann mechanism and the SSA

$$\text{rate} = \frac{d[P]}{dt} = k_2[A^*] = \frac{k_2 k_1 [M]}{k_{-1}[M] + k_2} [A]$$

Activation Energies

$$k_\infty = \frac{k_2 k_1}{k_{-1}} = \frac{A_1 A_2}{A_{-1}} e^{-\frac{E_{a1} + E_{a2} - E_{a-1}}{Rt}}$$

**Lecture 3****SSA vs. QEA**

- [B] – short lived intermediate
- The rate law for [C] ?

$$\text{Rate} = \frac{d[C]}{dt} = k_2[B]$$

**SSA**

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] + k_2[B] = 0$$

$$[B] = \frac{k_1}{k_{-1} + k_2} [A]$$

$$\text{Rate} = \frac{d[C]}{dt} = \frac{k_2 k_1}{k_{-1} + k_2} [A]$$

**QEA**

$$\frac{[B]}{[A]} = \frac{k_1}{k_{-1}} = K_{eq}$$

$$[B] = \frac{k_1}{k_{-1}} [A]$$

$$\text{Rate} = \frac{d[C]}{dt} = \frac{k_2 k_1}{k_{-1}} [A]$$

**Lecture 4**

$$-\frac{d[M]}{dt} = k_p \left( \frac{2k_t}{k_t} \right)^{\frac{1}{2}} [M][I]^{\frac{1}{2}}$$

$$v = \frac{\text{number of monomer units consumed}}{\text{number of activated centres produced}}$$

$$v = \frac{\text{rate of propagation of chains}}{\text{rate of production of radicals}}$$

$$\langle n \rangle = 2v = 2k[M][I]^{\frac{1}{2}}$$

**Relaxation Kinetics**

$$\tau_{pert} \ll \frac{1}{k_{fast}}$$

**Diffusion Controlled Reactions in Solution**

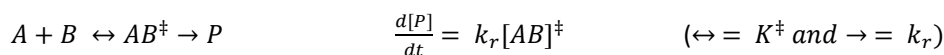
$$k_D = 4\pi L D_{AB} d_{AD}$$

$$k_D = \frac{8RT}{3\eta}$$

$$k_{OBS} = \frac{k_D k_r}{k_D + k_r}$$

$$k_D^I = 4\pi L D_{AB} d_{eff} \quad d_{eff} = d_{AB} \left( \frac{\delta}{e^{\delta} - 1} \right) \quad \delta = \frac{Z_A Z_B e^2}{4\pi \epsilon_0 \epsilon_r d_{AB} k_B T}$$

$$\tau_E \approx \frac{d_{AB}^2}{6D_{AB}}$$

**Activation Controlled Reactions and Transition State Theory**

$$K^\ddagger = \frac{k_D}{k_{-D}} \quad K^\ddagger = \frac{k_B T}{h} \quad \text{so} \quad k_{TST} = \kappa \frac{k_B T}{h C_0} K^\ddagger$$

$$k_{TST} = \kappa \frac{k_B T}{h C_0} e^{\left(\frac{\Delta S^\ddagger}{R}\right)} e^{-\left(\frac{\Delta H^\ddagger}{RT}\right)}$$

$$A = e \kappa \frac{k_B T}{h C_0} e^{\left(\frac{\Delta S^\ddagger}{R}\right)} \quad \Delta G_{ES}^\ddagger = \frac{Z_A Z_B e^2 L}{4\pi \epsilon_0 \epsilon_r d_{AB}} \quad \ln k_{TST}^I = \ln k_{TST} - \frac{Z_A Z_B e^2}{4\pi \epsilon_0 d_{AB} k_B T} \left( \frac{1}{\epsilon_r} \right)$$

$$\Delta S_{ES}^\ddagger = -\frac{C_s Z_A Z_B e^2 L}{4\pi \epsilon_0 \epsilon_r d_{AB}}$$

$$\log \left( \frac{k_{TST}^{(DH)}}{k_{TST}^I} \right) = 2AZ_A Z_B \sqrt{I}$$

**Introduction**

$$\Delta G = \Delta A \cdot \gamma$$

$$\Delta A = \left( \frac{V \text{ (volume of bigger surface area)}}{v \text{ (volume of smaller surface area)}} \right) a$$

**Liquid Gas Surface**

Surface tension as Force per unit length

$$\gamma = \frac{F_x}{2L} \quad \text{or for ring} \quad \gamma = \frac{F_x}{2 \times 2\pi r}$$

Laplace Equation

$$\Delta P = \frac{2\gamma}{r}$$

$$P_{\text{capillary}} = \frac{\gamma}{r}$$

Kelvin Equation

$$\ln \left( \frac{P_{\text{vap}}}{P_{\text{vap}}^0} \right) = \frac{V_m}{RT} \frac{2\gamma}{r}$$

$$\frac{P_{\text{vap}}}{P_{\text{vap}}^0} = e^{\left( \frac{V_m 2\gamma}{RT r} \right)}$$

Gibbs absorption equation

$$\Gamma = - \frac{1}{RT} \frac{d\gamma}{d \ln c} \quad (\text{for ionic solution: half the result as both ions count})$$

Micelle equation

$$\Delta G_{\text{micelle}} = RT \ln x_{\text{CMC}}$$

Area per molecule adsorbed

$$a_2 = \frac{1}{\Gamma_2 N_{\text{AV}}}$$

**Solid Gas Surface**

Langmuir Isotherm for Chemisorption

$$\theta = \frac{KP}{1 + KP}$$

$$\theta = \frac{V}{V_{\text{mon}}}$$

Linear representation to determine  $V_{\text{mon}}$ 

$$\frac{P}{V} = \frac{1}{KV_{\text{mon}}} + \frac{P}{V_{\text{mon}}}$$

Unimolecular

$$\text{Rate} = k\theta_A \quad \theta_A = \frac{KP_A}{1 + KP_A}$$

Bimolecular

$$\text{Rate} = kP_B\theta_A \quad \theta_A = \frac{KP_A}{1 + KP_A}$$

BET Model

$$\theta_A = \frac{V}{V_{\text{mon}}} = \frac{cz}{(1-z)\{1+(c-1)z\}} \quad c = e^{-\left(\frac{\Delta H_1 - \Delta H_L}{RT}\right)} \quad z = \frac{P}{P^*} \quad P^* = P_{\text{vap}}$$