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:

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

Lecture 2

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

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

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

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

Entropy change at a state function:

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

Trouton's Rule:

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

Lecture 3

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

$S = k_B lnW$ 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:

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

Calculating change in G° through equilibrium constant:

$$\Delta G^{\circ} = -RTlnK_p$$

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

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

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

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

Topic 1: Single component mixtures

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

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

$$dG = 0 \quad if \quad \mu_1 = \mu_2$$

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

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

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

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

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

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 ΔHmix

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

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

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

Osmotic Pressure

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

$$\pi = RTc_{solute}$$

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

Lecture 1

The steady state approximation (SSA)

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

Lecture 2

The Lindemann mechanism and the SSA

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

Activation Energies

$$k_\infty = \frac{k_2 k_1}{k_{-1}} = \frac{A_1 A_2}{A_{-1}} e^{-\frac{Ea_1 + Ea_2 - Ea_{-1}}{Rt}}$$

Lecture 3

SSA *vs.* QEA

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

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

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

SSA

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

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

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

QEA

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

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

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

Lecture 4

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

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

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

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

Relaxation Kinetics

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

Diffusion Controlled Reactions in Solution

$A + B \rightarrow C$ $\quad -\frac{d[A]}{dt} = k_D[A][B]$

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

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

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

$k_D^I = 4\pi L D_{AB} d_{eff}$ $\quad d_{eff} = d_{AB}\left(\frac{\delta}{e^{\delta}-1}\right)$ $\quad \delta = \frac{z_A z_B e^2}{4\pi\varepsilon_0\varepsilon_r d_{AB} k_B T}$

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

Activation Controlled Reactions and Transition State Theory

$A + B \leftrightarrow AB^{\ddagger} \rightarrow P$ $\quad \frac{d[P]}{dt} = k_r[AB]^{\ddagger}$ $\quad (\leftrightarrow = K^{\ddagger}\ and \rightarrow = k_r)$

$K^{\ddagger} = \frac{k_D}{k_{-D}}$ $\quad K^{\ddagger} = \frac{k_B T}{h}$ so $\quad k_{TST} = \kappa\frac{k_B T}{hC_0}K^{\ddagger}$

$$k_{TST} = \kappa\frac{k_B T}{hC_0} e^{\left(\frac{\Delta S^{\ddagger}}{R}\right)} e^{-\left(\frac{\Delta H^{\ddagger}}{RT}\right)}$$

$A = e\kappa\frac{k_B T}{hC_0} e^{\left(\frac{\Delta S^{\ddagger}}{R}\right)}$ $\quad \Delta G_{ES}^{\ddagger} = \frac{Z_A Z_B e^2 L}{4\pi\varepsilon_0\varepsilon_r d_{AB}}$ $\quad lnk_{TST}^I = lnk_{TST} - \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 d_{AB} k_B T}\left(\frac{1}{\varepsilon_r}\right)$

$$\Delta S_{ES}^{\ddagger} = -\frac{C_s Z_A Z_B e^2 L}{4\pi\varepsilon_0\varepsilon_r d_{AB}}$$

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

Introduction

$$\Delta \boldsymbol{G} = \Delta \boldsymbol{A} \cdot \gamma$$

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

Liquid Gas Surface

Surface tension as Force per unit length

$$\gamma = \frac{F_x}{2L} \qquad or\ for\ ring \qquad \gamma = \frac{F_x}{2x2\pi r}$$

Laplace Equation

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

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

Kelvin Equation

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

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

Gibbs absorption equation

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

Micelle equation

$$\Delta G_{micelle} = RTlnx_{CMC}$$

Area per molecule adsorbed

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

Solid Gas Surface

Langmuir Isotherm for Chemisorption

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

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

Linear representation to determine V_{mon}

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

Unimolecular

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

Bimolecular

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

BET Model

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