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):
\[ S = k_BlnW \quad \text{Where } k_B = 1.38 \times 10^{-23} \]

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:
\[ G = G^* + RTln \left( \frac{P}{1atm} \right) \]

Calculating change in G* through equilibrium constant:
\[ \Delta G^* = -RTlnK_p \]

Other weird functions I don’t understand but need to try and learn to at least have a small shot of getting a first:
\[ \frac{\partial (\Delta G)}{\partial T} = -\frac{\Delta H}{T^2} \]
\[ \frac{\partial lnK_p}{\partial T} = \frac{\Delta H^*}{RT^2} \]
\[ ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H^*}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]
Topic 1: Single component mixtures

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

\[ dG = (\mu_2 - \mu_1)dn \]
\[ dG = 0 \text{ if } \mu_1 = \mu_2 \]
\[ \left(\frac{dG_m}{dT}\right)_p = \left(\frac{d\mu}{dT}\right)_p = -S_m \]
\[ \left(\frac{dG_m}{dP}\right)_T = \left(\frac{d\mu}{dP}\right)_T = V_m \quad V_m > 0 \]

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

\[ P_T = P_A + P_B \]
\[ P_T = \chi_A P_A^* + \chi_B P_B^* \]

Dalton’s Law

\[ \chi_A = \frac{P_A}{P_T} = \frac{x_A P_A^*}{P_A^* + (P_A^* - P_B^*) x_A} \quad \chi_B = 1 - \chi_A \]

\[ P_T = \frac{P_A^* P_B^*}{P_A^* + (P_B^* - P_A^*) \chi_A} \]

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

\[ \Delta T_b = T_b - T_b^* = \left( \frac{RT_b}{\Delta H_{\text{vap}}} \right) x_{\text{solute}} \]

Lowering of a freezing point

\[ \Delta T_f = T_f - T_f^* = \left( \frac{RT_f^*}{\Delta H_{\text{freeze}}} \right) x_{\text{solute}} \]

Lowering of vapour pressure

\[ \Delta P = x_{\text{solute}} P_{\text{solvent}}^* \]

Dilute solution approximation

\[ \Delta T_b = K_b m_{\text{solute}} \quad \Delta T_f = K_f m_{\text{solute}} \]

\[ \frac{M_{\text{solute}}}{M_{\text{solvent}}} = \frac{K_f \text{mass}_{\text{solute}}}{K_b \text{mass}_{\text{solvent}}} \]

Osmotic Pressure

\[ \pi = \frac{RT}{(V_m)_{\text{solvent}}} x_{\text{solvent}} \]

\[ \pi = RT c_{\text{solute}} \]

\[ c_{\text{solute}} = \frac{c'}{M_{\text{solute}}} \]
Lecture 1

The steady state approximation (SSA)

\[
\frac{d}{dt} [I] = \ldots = 0
\]

Lecture 2

The Lindemann mechanism and the SSA

\[
rate = \frac{d[P]}{dt} = k_2[A \cdot] = \frac{k_2k_1[M]}{k_{-1}[M] + k_2[A]}
\]

Activation Energies

\[
k_{\infty} = \frac{k_2k_1}{k_{-1}} = \frac{A_1A_2}{A_{-1}} e^{\frac{E_{a_1} + E_{a_2} - E_{a_0}}{R_{a_0}}}
\]

Lecture 3

**SSA vs. QEA**

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

**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 = \[
\frac{d[C]}{dt} = \frac{k_2k_1}{k_{-1} + k_2}[A]
\]

**QEA**

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

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

Rate = \[
\frac{d[C]}{dt} = \frac{k_2k_1}{k_{-1}}[A]
\]

Lecture 4

\[
\frac{d[M]}{dt} = k_p \left( \frac{2k_1}{k_2} \right)^{\frac{1}{2}} [M][I]^{\frac{1}{2}}
\]

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

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

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

\[ \tau_{\text{pert}} \ll \frac{1}{k_{\text{fast}}} \]

Diffusion Controlled Reactions in Solution

\[ A + B \rightarrow C \quad -\frac{d[A]}{dt} = k_0[A][B] \]

\[ k_D = 4\pi LD_{AB}d_{AD} \]

\[ k_D = \frac{8RT}{3\eta} \]

\[ k_{\text{obs}} = \frac{k_d k_r}{k_d + k_r} \]

\[ k_D^l = 4\pi LD_{AB}d_{\text{eff}} \]

\[ d_{\text{eff}} = d_{AB} \left( \frac{\delta}{e^{\delta - 1}} \right) \]

\[ \delta = \frac{z_A^2 e^2}{4\pi \varepsilon_0 \varepsilon_r d_{AB} k_BT} \]

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

Activation Controlled Reactions and Transition State Theory

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

\[ K^\ddagger = \frac{k_B}{k_d} \quad K^\ddagger = \frac{k_BT}{\hbar} \quad \text{so} \quad k_{\text{TST}} = k\frac{k_BT}{\hbar\varepsilon_0} K^\ddagger \]

\[ k_{\text{TST}} = k\frac{k_BT}{\hbar\varepsilon_0} e^{\left( \frac{\Delta S^\ddagger}{R} \right)} e^{-\left( \frac{\Delta H^\ddagger}{RT} \right)} \]

\[ A = k\frac{k_BT}{\hbar\varepsilon_0} e^{\left( \frac{\Delta S^\ddagger}{R} \right)} \quad \Delta G_{ES}^\ddagger = \frac{Z_A^2 e^2 L}{4\pi \varepsilon_0 \varepsilon_r d_{AB}} \quad \ln k_{\text{TST}}^\ddagger = \ln k_{\text{TST}} - \frac{Z_A^2 e^2}{4\pi \varepsilon_0 \varepsilon_r d_{AB} k_BT} \left( \frac{1}{T} \right) \]

\[ \Delta S_{ES}^\ddagger = -C_P Z_A Z_B e^2 L \]

\[ \log \left( \frac{k_{TST}^{\text{DHY}}}{k_{TST}^\ddagger} \right) = 2AZ_A Z_B \sqrt{T} \]
**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

\[ \gamma = \frac{F_x}{2L} \text{ or for ring } \gamma = \frac{F_x}{2 \pi r} \]

Laplace Equation

\[ \Delta P = \frac{2 \gamma}{r} \]

\[ P_{\text{capillary}} = \frac{\gamma}{r} \]

Kelvin Equation

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

\[ \frac{P_{\text{vap}}}{P_{\text{vap}}^0} = e^{\frac{V_m 2 \gamma}{RT r}} \]

Gibbs absorption equation

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

Micelle equation

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

Area per molecule adsorbed

\[ a_2 = \frac{1}{f_2 N_{\text{AV}}} \]

**Solid Gas Surface**

Langmuir Isotherm for Chemisorption

\[ \theta = \frac{K \theta_A}{1 + K \theta_A} \]

\[ \theta = \frac{V}{V_{\text{mon}}} \]

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

\[ \text{Rate} = k P \theta_A \quad \theta_A = \frac{KP_A}{1 + KP_A} \]

BET Model

\[ \theta_A = \frac{V}{V_{\text{mon}}} = \frac{c z}{(1 - z) (1 + (c - 1) z)} \]

\[ c = e^{\frac{\Delta H_l - \Delta H_l}{RT}} \quad z = \frac{P}{P^*} \quad P^* = P_{\text{vap}} \]