EXAM 1

Physical constants/conversion factors

1 N = 1 kg m s^{-2}
1 J = 1 N m = 1 kg m^2 s^{-2}
1 bar = 10^5 N m^{-2}
1 atm = 101325 N m^{-2}
1 bar = 750.06 Torr
1 cal = 4.184 J
1 C = 1 A s, 1 V = 1 J C^{-1}, 1 Ω = 1 V A^{-1}
R = 8.3145 J K^{-1} mol^{-1} = 0.08315 (L atm) (mol K)$^{-1}$
N_A = 6.022136*10^{23} mol^{-1}
1 L = 0.001 m^3
k = 1.38*10^{-23} J/K, kN = Rn
10 L bar = 1 kJ

Laws of thermodynamics

0th law – If A and B are in thermal equilibrium and B and C are in thermal equilibrium, then A and C are in thermal equilibrium. Defines Kelvin scale.
1st law – U is conserved. $dw + dq = dU$
2nd law – defines entropy and dir of time. $\Delta S = \int \frac{dq_{rev}}{T}$
3rd law – absolute scale. S → 0 as T → 0 for pure crystal.

Open: mass and energy can transfer
Closed: only energy, not mass
Isolated: neither energy nor mass

Extensive: depend on size of system (n, m, V)
Intensive: independent of size (T, p, V_{bar})

pV = nRT

van der Waals: $(p + \frac{a}{\overline{V}^2})(\overline{V} - b) = RT$

$w = F \cdot \ell$, also $w = \int_{\ell_i}^{\ell_f} k\ell \cdot d\ell = \frac{1}{2}k(\ell_f^2 - \ell_i^2)$

Expansion work: $w = -(p_{ext}A)\ell = -p_{ext}\Delta V$
Surface work: $dw = \gamma_{ext} dA$ (where γ_{ext} is surf tens in J/m^2)
Electrostatic work: $dw = Vde$
If heat enters system, it is positive
If system does work on surroundings, w < 0
If surroundings do work on system, w > 0
$\oint dw$ may be, but is not neccesarily 0
$dq = C_{path} dT$, $C_p > C_v$
$\oint dw + dq = 0 = dU$, so
$\Delta U = \int_1^2 dU = U_2 - U_1 = q + w$

Isothermal gas expansion

1. if p_{ext} = 0, $w = -p_{ext}\Delta V = 0$, ΔU=q
2. if $p_{ext}=p_2$, $w = -p_2 \Delta V$
3. if p_{ext}=p (reversible), $w = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$

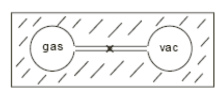
$$-\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln\frac{V_2}{V_1} = nRT \ln\frac{p_2}{p_1}$$

$$dU = C_{path} dT - p_{ext} dV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Constraints:

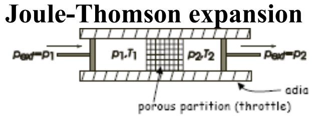
reversible -- $dU = dq_{rev} - p_{ext} dV$
isolated -- $dq = dw = \Delta U = 0$
adiabatic -- $dq = 0 \Rightarrow dU = dw$
constant V -- $dw = 0 \Rightarrow dU = dq_V = C_V dt$
$dU = C_V dT - C_V \eta_J dV$
for ideal gas, ΔU=0 for any isoT exp/comp
also for isoT, ΔH = ΔU + nRΔT = 0
for ideal gas, η_J=0

Joule free expansion



q = 0 (adiabatic), w = 0 (p_{ext} = 0)
isothermal, so ΔU, ΔH are 0
A constant internal energy process.

Joule-Thomson expansion



q = 0 (adiabatic), w = ΔU = -Δ(pV). ΔH = 0.
A constant enthalpy process.

Enthalpy

$H \equiv U + pV$, $\Delta H = q_p$ for reversible const P process

$\left(\frac{\partial H}{\partial T}\right)_p = Cp$, $dH = C_p dT - C_p \mu_{JT} dp$

For an ideal gas $\overline{C}_p = \overline{C}_V + R$, $C_v \Delta T = C_p \Delta T + p\Delta V$

For an ideal gas $dU = \overline{C}_V dT$, $dH = \overline{C}_p dT$

Reversible Adiabatic Expansion/Compression

Monatomic IG: $\overline{C}_V = \frac{3}{2}R$, $\overline{C}_p = \frac{5}{2}R$, $\frac{C_p}{C_V} \equiv \gamma = \frac{5}{3}$

$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$ and $\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma}$

Adiabatic expansion, gas cools
Adiabatic compression, gas heats up

Irreversible Adiabatic Expansion/Compression

$$T_2(C_V + R) = T_1\left(C_V + \frac{P_2}{P_1}R\right)$$ where $p_{ext}=p_2$

$(-w_{rev}) > (-w_{irrev})$ – less work recovered from irrev process

Cycles

ΔU, ΔH are state functions

dq, dw are not state functions

Thermochemistry

$$\Delta H_{rx} = \sum_i \nu_i \Delta H_f^\circ(\text{products}) - \sum_i \nu_i \Delta H_f^\circ(\text{reactants})$$

$\Delta H_{rx} < 0$, $q_p < 0$, exothermic; $\Delta H_{rx} > 0$, $q_p > 0$, endothermic

ΔH_{rx} is the ΔH for isothermal reaction at constant p

ΔH_f is the ΔH for the creation of 1 mole of compound

Calorimetry

$$\Delta H_{rx}(T_1) = -\int_{T_1}^{T_2} C_p(\text{Prod+Cal})dT \quad \text{(for constant P)}$$

$$\Delta H_{rx}(T_1) = -\int_{T_1}^{T_2} C_V(\text{prod+cal})dT + RT_1\Delta n_{gas} \quad \text{(const V)}$$

$$\Delta H_{rx}(T_2) = \Delta H_{rx}(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$$

$$\Delta U_{rxn} = \Delta H_{rxn} - \Delta pV = \Delta H_{rxn} - \Delta n_{gas}RT$$

Entropy

$$\oint \frac{dq_{rev}}{T} = 0, \quad \oint \frac{dq_{irrev}}{T} < 0$$

$$\int \frac{dq_{rev}}{T} = \int dS$$

$$\varepsilon = 1 + \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

for isolated systems, ΔS > 0 – spontaneous, irreversible, ΔS = 0, reversible (or equilibrium)

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dq_{rev}}{T}$$

Entropy – Joule expansion of IG

$$\Delta S_{back} = \int \frac{dq_{rev}}{T} = -\int \frac{dw}{T} = \int_{V_1}^{V_2} \frac{RdV}{V} = R\ln\left(\frac{V_2}{V_1}\right)$$

Entropy – Reversible expansion of IG

$$\Delta S = \int \frac{dq_{rev}}{T} = \int pdV = \frac{1}{T}\int_{V_1}^{V_2} \frac{RTdV}{V} = R\ln\left(\frac{p_1}{p_2}\right)$$

Entropy – Mixing of IGs at constant T, p

$$\Delta S_{mix} = -\int \frac{dq_{rev}}{T} = -nR[X_A \ln X_A + X_B \ln X_B]$$

where $X_A = \frac{n_A}{n_{tot}} = \frac{V_A}{V_{tot}}$

Entropy – Heating/cooling at constant V

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V dT}{T} = C_V \ln\frac{T_2}{T_1}$$

Entropy – Heating/cooling at constant p

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p dT}{T} = C_p \ln\frac{T_2}{T_1}$$

Entropy – Reversible phase change at constant T, p

$$\Delta S_{vap} = \frac{q_p^{vap}}{T_b} = \frac{\Delta H_{vap}}{T_b}$$

Entropy – Irreversible phase change at constant T, p

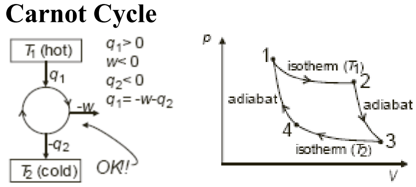
$$\Delta S = \frac{-\Delta H_{fus}}{T} + \int_{T_1}^{T_{fus}} \Delta C_p \frac{dT}{T} = [C_p(\ell) - C_p(s)]\ln\frac{T_{fus}}{T_1}$$

Surroundings and Universe (if T, p surroundings constant)

$$\Delta S_{surr} = \frac{\Delta H_{sys}}{T}, \quad \Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr}$$

if reversible, $\Delta S_{univ} = 0$

Carnot Cycle



Step	
1→2	$\Delta U = 0 = q_1 + w_1 = \int_1^2 pdV = RT_1 \ln\frac{V_2}{V_1}$
2→3	$\Delta U = w_1' = C_v(T_2 - T_1)$
3→4	$\Delta U = 0 = -w_1 = \int_4^3 pdV = RT_2 \ln\frac{V_4}{V_3}$
4→1	$\Delta U = w_2' = C_v(T_1 - T_2)$

$$\frac{q_2}{q_1} = \frac{T_2 \ln(V_4/V_3)}{T_1 \ln(V_2/V_1)}, \quad \frac{T_1}{T_2} = \left(\frac{V_4}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1}$$

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = \oint \frac{dq_{rev}}{T} = 0$$

Fundamental Equations

$dU = TdS - pdV$ (valid for any closed system, rev/irrev)

$dH = TdS + Vdp$

Generally, $dU + p_{ext}dV - T_{surr}dS < 0$

Helmholtz free energy: $A = U - TS$

Under constant $T=T_{surr}$, constant V, dA<0 spontaneous

Gibbs free energy: $G = H - TS = A + pV$

Under constant $T=T_{surr}$ and $p=p_{ext}$, dG<0 spontaneous

EXAM 2

Fundamental Equations

true for closed systems, pV work only

$$dU = TdS - pdV \Rightarrow U = H - pV$$

$$dH = TdS + Vdp \Rightarrow H = G + TS$$

$$dA = -SdT - pdV \Rightarrow A = U - TS$$

$$dG = -SdT + pdV \Rightarrow G = U - ST + pV$$

$$d\mu = -SdT + Vdp$$

at constant T, $\left(\frac{\partial \mu}{\partial p}\right)_T = \overline{V}$

at constant p, $\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$ et cetera!

For ideal gas

$$\overline{G}(T, p_2) = \overline{G}(T, p_1) + \int_{P_1}^{P_2} \frac{RT}{p} dp$$

$$\overline{S}(T, p) = \overline{S}^\circ(T) - R \ln \frac{p}{p^\circ}$$

For liquid/solid, V is small, so G(T) only

Define $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j=1}} = \overline{G}_i$

$$G = \sum_i n_i \overline{G}_i = \sum_i \mu_i n_i$$

but also partial H partial n, partial A partial n…
in each case keeping constant the nat var of the function.

For open systems

$$dU = Tds - pdV + \sum_i \mu_i dn_i$$

$$dH = Tds + Vdp + \sum_i \mu_i dn_i$$

$$dA = -SdT - pdV + \sum_i \mu_i dn_i$$

$$dG = -SdT + pdV + \sum_i \mu_i dn_i$$

Chemical potential at equilibrium is the same everywhere in a system.

$\mu_A(\text{mix}, T, p_{tot}) = \mu_A(\text{pure}, T, p_{tot}) + RT \ln X_A$

(note that mole fraction < 1, so $\mu_{mix} < \mu_{pure}$

This is due to entropy of mixing.

$$\mu(T, p) = \mu^\circ(T) + RT \ln \frac{p}{p^\circ}$$

$$\Delta G^\circ = \mu_g^\circ - \mu_\ell^\circ = -RT \ln \frac{p}{p^\circ} \text{ (change in state)}$$

$$\Delta G_{mix}^\circ = RT(X_A \ln X_A + X_B \ln X_B)$$

$$K_p = \frac{p_C^{\nu_c} p_D^{\nu_D}}{p_A^{\nu_A} p_B^{\nu_B}} = p^{\Delta\nu} \frac{X_C^{\nu_c} X_D^{\nu_D}}{X_A^{\nu_A} X_B^{\nu_B}} = e^{\frac{-\Delta G^\circ}{RT}}$$

Making ICE charts

Write initial # moles
Write change – must balance stoichiometrically
Solve for x, plug x back into change in moles

Quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

For solutions:

$$K_{eq} = \frac{[C]^{\nu_C}[D]^{\nu_D}}{[A]^{\nu_A}[B]^{\nu_B}} = e^{\frac{-\Delta G^\circ}{RT}}$$

also, $\mu_A(T, p, [A]) = \mu_A^\circ(T, p) + RT \ln[A]$

$$\frac{d \ln K(T)}{dT} = \frac{\Delta H^\circ(T)}{RT^2}, \; \Delta G^\circ = RT \ln K_p$$

$$\ln K(T_2) = \ln K(T_1) + \int_{T_1}^{T_2} \frac{\Delta H^\circ(T_1) + \Delta C_p(T_2 - T_1)}{RT^2} dT$$

or, if ΔH° assumed independent of T and ΔC_p negligible,

$$\ln K(T_2) \approx \ln K(T_1) + \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

ΔH°(T)	T_2_T_1	$K_p(T_2)$_$K_p(T_1)$	Equil shifts	_thermic
negative	>	<	reactants	exo
positive	>	>	products	endo

Heterogeneous equilibria – equilibrium constant includes only gases, but ΔG° includes all products and reactants.

Most stable compound at (T,p) has lowest (most negative) molar G_f

Function	What is kept constant?	Greater than/less than
dU	S, V, n_i	≤ 0
dA	T, V, n_i	≤ 0
dH	S, P, n_i	≤ 0
dG	T, P, n_i	≤ 0

Boltzmann equation

$S = k \ln \Omega$ where Ω is multiplicity (# poss. states)

$$S = -k \sum_{i=1}^{t} p_i \ln p_i$$

$$\Omega = \frac{N!}{n_1! \times n_2! \times \ldots n_i!} \text{ (general case; } n_i = \text{degeneracy)}$$

"number of ways to mix up N things with degeneracies"
if no degeneracy, then just N!

$$\Omega(k,N)=\binom{N}{k}=\frac{N!}{k!(N-k)!}$$ (binomial case, $N=n_{tot}$)

"number of ways to pick k things from N objects"
N^k "sequence of k items, each with N deg free"
maximizing Ω maximizes S

$$p_A=\frac{n_A}{N},\ \langle\varepsilon\rangle=\sum_{all}\varepsilon_i p_i$$

Stirling's approximation

$$n!\approx\left(\frac{n}{e}\right)^n,\ \ln n!=n\ln n-n,\ \ln n^x=x\ln n$$

Boltzmann distribution law

$$p_j^*=Q^{-1}\exp\left(-\frac{E_j}{kT}\right),\ Q\equiv\sum_j^t\exp\left(-\frac{E_j}{kT}\right)$$

relative populations: $\frac{p_i^*}{p_j^*}=\exp\left(\frac{-(E_i-E_j)}{kT}\right)$

As $T\to\infty$ or $E_j\to 0$, all states accessible
As $T\to 0$ or $E_j\to\infty$, only ground state accessible

More on the Partition Function

$$Q_{sys}=\prod_i q_i$$

For N independent, distinguishable particles, $Q=q^N$

For N independent, indistinguishable particles, $Q=\frac{q^N}{N!}$

$$\beta=\frac{1}{kT},\ \langle E\rangle=\frac{U}{N},\text{ so } U=kT^2\left(\frac{\partial\ln Q}{\partial T}\right)$$

$$S=k\ln Q+\frac{U}{T},\ A=-kT\ln Q$$

$$\mu=-kT\left(\frac{\partial\ln Q}{\partial N}\right)_{T,V},\ P=kT\left(\frac{\partial\ln Q}{\partial V}\right)_{T,N}$$

Absolute Entropy

$$\overline{S}(p,T)=\overline{S}^\circ(T)-R\ln\frac{p}{p^\circ}$$

At the given reference pressure, S°(T)=

$$\overline{S}^\circ(0K)+\int_0^{T_m}\frac{\overline{C}_p(s)dT}{T}+\frac{\Delta\overline{H}_{fus}}{T_m}+\int_{T_m}^{T_b}\frac{\overline{C}_p(\ell)dT}{T}+\frac{\Delta\overline{H}_{vap}}{T_b}+\int_{T_b}^{T}\frac{\overline{C}_p(g)dT}{T}$$

Integrate to whatever temperature desired (and adjust phase changes accordingly)
For every chemically homogeneous substance in a pure crystalline state, as $T\to 0$ K, $S\to 0$.

Phase Equilibria

$$\left(\frac{dp}{dT}\right)_{coexist}=\left[\frac{\overline{S}_\beta-\overline{S}_\alpha}{\overline{V}_\beta-\overline{V}_\alpha}\right]=\left(\frac{\Delta S}{\Delta V}\right)_{\alpha\to\beta}=\left(\frac{\Delta H}{T\Delta V}\right)_{\alpha\to\beta}$$

$$\Delta p\cong\frac{\Delta H_{fus}}{\Delta V_{fus}}\cdot\frac{\Delta T_m}{T_m}$$ (for melting point increase)

Clausius-Clapeyron:

$$\left(\frac{d\ln p}{dT}\right)\approx\frac{\Delta\overline{H}}{RT^2}\Rightarrow\ln\frac{p_2}{p_1}=\frac{\Delta\overline{H}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$\Delta H_{sub}=\Delta H_{vap}-\Delta H_{fus}$ (watch signs!!)

$$\Delta V_{fus}=\frac{1}{\rho_\ell}-\frac{1}{\rho_s}$$

EXAM 3

liquid mole fraction – x_A
gas mole fraction – y_A
F = C – P + 2

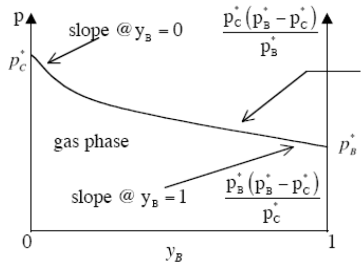
Raoult's Law ($x_A \rightarrow 1$)

$$p_A = p_A^* x_A = p_A^*(1-x_B)$$

$$y_C = \frac{x_C p_C^*}{p_B^* + (p_C^* - p_B^*)x_C}$$

$$x_C = \frac{y_C p_B^*}{p_C^* + (p_B^* - p_C^*)y_C}$$

$$p = \frac{p_B^* p_C^*}{p_C^* + (p_B^* - p_C^*)y_C} = \frac{x_C p_C^*}{y_C}$$



Constructing T-x diagrams
1. Use Clausius-Clapeyron
2. p = 1 atm = 1.013 bar
3. $\ln p/p_0 = \frac{\Delta H_{vap}}{RT} + C$
4. Use Raoult's Law

If A is more volatile than B, then $T_A^* < T_B^*$
temp at which pure A has vapor pressure = p

$$x_A = \frac{p - p_B^*}{p_A^* - p_B^*},\; y_B = \frac{x_B p_B^*}{p}$$

For an ideal solution,

$$\mu_i(\ell, T, p) = \mu_i^*(\ell, T, p) + RT\ln x_i$$

In non-ideal solutions, calculate $\Delta u = 2u_{AB} - (u_{AA} + u_{BB})$
if $\Delta u > 0$: positive deviation. like associates with like. p > Raoult. Most common.
if $\Delta u < 0$: negative deviation. mixing favored. p < Raoult.
If there is a minimum on coexistence curves, then dew line and bubble line touch – azeotrope.

Henry's Law ($x_A \rightarrow 0$)

$p_A = x_A K_A$ where K is empirical constant
for positive deviations, K > p star
for negative deviations, K < p star

Important terms:
Mole fraction
Molality – m_B = (moles solute)/(**kg** solvent) = $n_B/(n_A M_A)$
Molarity – $\check{c} = n_B/V$

Colligative Properties

1. Vapor pressure lowering: $\Delta p_A = p_A - p_A^* = -x_B p_A^*$
2. Boiling point elevation: $\Delta T_b = T_b - T_b^* = K_b m_B$
   where $K_b = \frac{M_A R (T_b^*)^2}{\Delta H_{vap}}$
3. Freezing point depression: $\Delta T_f = T_f - T_f^* = -K_f m_B$
   where $K_f = \frac{M_A R (T_f^*)^2}{\Delta H_{freezing}}$
4. Osmotic pressure: $\pi = RT\tilde{c}_B$ (and $\pi V = RTn_B$)
   also $\pi = \rho g h$

Rate of reaction if aA + bB → cC + dD

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt} = k\prod_{i=1}^{N} C_i^{\gamma_i}$$

$t_{1/2}$ is the time at which $[A]_t = 0.5[A]_0$

Zero order reaction (A → products)

$[A]_t = [A]_0 - kt$ and $t_{1/2} = [A]_0/2k$

First order reaction (A → products)

$$[A]_t = [A]_0 e^{-kt},\; \ln[A]_t = -kt + \ln[A]_0,\; t_{1/2} = \frac{\ln 2}{k}$$

Second order reaction (2A → products)

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + (2)kt,\; t_{1/2} = \frac{1}{2k[A]_0}$$

Second order reaction (A + B → products)

$$kt = \frac{1}{[A]_0 - [B]_0}\ln\frac{[A]_t[B]_0}{[A]_0[B]_t}$$

special case i: $[A]_0=[B]_0$. Then $\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$, $[A]_t=[B]t$

special case ii: $[B]_0 << [A]_0$. Then $[A]_t \approx [A]_0$, $[B]_t = [B]_0 e^{-k't}$
(since [A] is ~constant, $k' = [A]_0 k$, and $d[B]/dt = k'[B]$)

Parallel first-order reactions

$C \xleftarrow{k_2} A \xrightarrow{k_1} B$ (bucket with two holes)

$$[A]_t = [A]_0 e^{-(k_1+k_2)t},\; [B]_t = \frac{k_1[A]_0}{k_1+k_2}(1 - e^{-(k_1+k_2)t}),$$

$$[C]_t = \frac{k_2[A]_0}{k_1+k_2}(1 - e^{-(k_1+k_2)t})$$

Branching ratio: $[B]/[C] = k_1/k_2$ at all t

$$[B]_\infty = [A]_0 \frac{k_1}{k_1+k_2} \text{ and } [C]_\infty = [A]_0 \frac{k_2}{k_1+k_2}$$

Parallel first- and second-order reactions

$$A \xrightarrow{k_1} B,\ 2A \xrightarrow{k_2} C$$

$$[A]_t = \frac{k_1[A]_0}{e^{k_1 t}(k_1 + 2k_2[A]_0) - 2k_2[A]_0}$$

Limiting cases:

i) $k_2[A]_0 << k_1$, then $[A]_t = [A]_0 e^{-kt}$

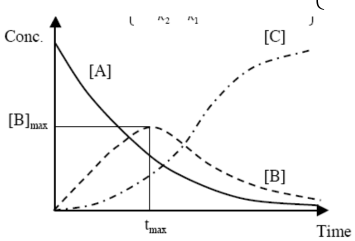
ii) $k_2[A]_0 >> k_1$, then $\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2k_2 t$

Consecutive reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$[A]_t = [A]_0 e^{-kt},\ [B]_t = \frac{k_1[A]_0}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$

$$[C]_t = [A]_0 - [A] - [B] = \left\{1 - \frac{1}{k_2 - k_1}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t})\right\}$$



t_{max} at $d[B]/dt = 0$

After [B] reaches [B]max, it's as if [B] isn't there at all

$$t_B^{max} = \frac{\ln(k_1/k_2)}{k_1 - k_2},\ [B]_{max} = \frac{k_1}{k_2}[A]_0 e^{-k_1 t_B^{max}}$$

Special cases:

i) $k_1 = k_2$. $t_B^{max} = \frac{1}{k_2}$, $[B]_{max} = \frac{[A]_0}{e}$

ii) $k_1 >> k_2$. $[A]_t = [A]_0 e^{-k_1 t}$, $[B]_t \approx [A]_0 e^{-k_2 t}$,

$[C]_t \approx [A]_0(1 - e^{-k_2 t})$. Looks like $A \xrightarrow{k_2} C$.

iii) $k_1 << k_2$. $[A]_t = [A]_0 e^{-k_1 t}$, $[C]_t \approx [A]_0(1 - e^{-k_1 t})$

Looks like $A \xrightarrow{k_1} C$ (A → B is RDS.)

First-order reversible reactions

$$A \xleftarrow{k_{-1}} B,\ A \xrightarrow{k_1} B$$

$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}} = e^{-(\Delta G^\circ/RT)} = \frac{k_1}{k_{-1}}$$

$$[B]_t = [B]_0 + ([A]_0 - [A]_t)$$

$$[A]_{eq} = \frac{k_{-1}}{k_1 + k_{-1}}([B]_0 + [A]_0)$$

$$[A]_t - [A]_{eq} = ([A]_0 - [A]_{eq})e^{-(k_1 + k_{-1})t}$$

$$k_{obs} = k_1 + k_{-1}$$

Higher-order reversible reactions

$$A + B \xrightarrow{k_1} C,\ A + B \xleftarrow{k_{-1}} C$$

1)Flooding.

If $[B]_t = [B]_0$ at all times, $\frac{d[A]}{dt} = -k_1'[A] + k_{-1}[C]$

where $k_1' = k_1[B]_0$, and

$$[A]_t - [A]_{eq} = ([A]_0 - [A]_{eq})e^{-(k_1' + k_{-1})t}$$

plot $k_1[B]_0 + k_{-1} \equiv k_{obs}$ vs $[B]_0$ to get individual k values (k_{obs} from slope of $\ln|A_t - A_{eq}|$ vs. t)

2) Steady State Approximation

$A \overset{k_1}{\longleftrightarrow} B \xrightarrow{k_2} C$ (valid only after B builds to ss value, when $k_2 >> k_1$ – B is small but not zero)

Assume $\frac{d[B]}{dt} = 0$, so $[B]_{ss} = \frac{k_1[A]}{k_{-1} + k_2}$

$[A]_t = [A]_0 e^{-k't}$ where $k' = \frac{k_1 k_2}{k_{-1} + k_2}$ ($A \xrightarrow{k'} C$)

3) Pre-Equilibrium Approximation

$A \overset{k_1}{\longleftrightarrow} B \xrightarrow{k_2} C$ (valid when when $k_2 << k_1 + k_{-1}$ – B is formed faster than it is destroyed)

Assume $\frac{k_1}{k_{-1}} \approx \frac{[B]}{[A]}$, so $\frac{d[C]}{dt} = \frac{k_1 k_2}{k_{-1}}[A]$

$[A]_t = [A]_0 e^{-k't}$ where $k' = \frac{k_1 k_2}{k_{-1}}$ ($A \xrightarrow{k'} C$)

EXAM 4

Free radical chain length: rate of product formation/rate of initial radical formation

Explosions happen when concentration of reactive intermediates becomes large (SS approx fails)

$$k(T) = e^{-\Delta H^\circ/RT} e^{\Delta S^\circ/R} = Ae^{-E_a/RT}$$

$$\ln k = -\frac{E_a}{RT} + \ln A$$

As T increases, collisions happen more frequently and harder. Pre-exponential constant is not highly dept on T

Ea – Joules/mol. A – conc^n-1/second

N molecules, 3N-6 internal coordinates

Transition state is the highest energy point on the minimum energy path

$$\Delta H_{rxn} = E_a(for) - E_a(rev)$$

Catalysis

Catalysis can work by ↓E_a (enthalpy) or ↑A (entropy)

For example, blocking active site is entropic, changing charge on active site is enthalpic

Catalysts change only rate. K_{eq}, ΔH, ΔS, ΔG unchanged

$$A + B \xrightarrow{k_1} 2B$$

at t_{infl}, $\frac{d^2[B]}{dt^2} = 0$. So $t_{infl} = \frac{\ln([A]_0/[B]_0)}{k_1([A]_0+[B]_0)}$

because $[A]_0 + [B]_0 - 2[B] = 0$.

$$[B]_{t_{inf}} = \frac{[A]_0 + [B]_0}{2}$$

i) very early time, $kt([A]_0+[B]_0) \ll 1$.

$$[B] = \frac{[B]_0}{1-kt[A]_0} \approx [B]_0(1-kt[A]_0)$$

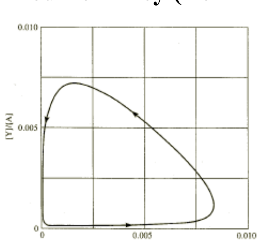
ii) early time, $e^{kt([A]_0+[B]_0)} \ll [A]_0/[B]_0$

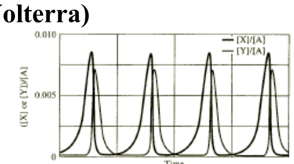
$$[B] \approx \frac{[B]_0([A]_0+[B]_0)}{[A]_0} e^{kt([A]_0+[B]_0)}$$

iii) late time, $e^{kt([A]_0+[B]_0)} \ll [A]_0/[B]_0$

$[B] = [A]_0 + [B]_0$

Predator-Prey (Lotka-Volterra)





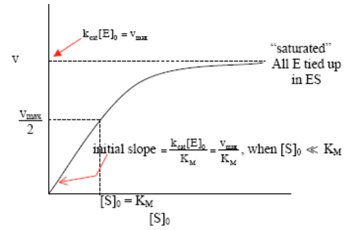
A = duck food, X = ducks, Y = wolves

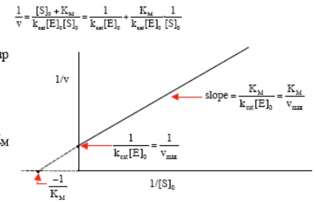
Michaelis-Menten

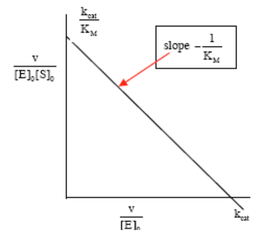
$$[ES]_{ss} = \frac{[E]_0[S]}{[S] + \frac{k_{-1}+k_2}{k_1}}, \quad [E]_0 = [E] + [ES]$$

$$\frac{dP}{dt} = k_2[ES]_{ss} = \frac{k_{cat}[E]_0[S]}{[S]+K_m}$$

K_m units: concentration







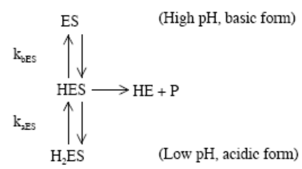
$k_2 = k_{cat}$ = turnover number

max # product molecules / # enzyme molecules

If an enzyme works on two S, producing two products, the ratio will be

$$\frac{(k_{cat}/K_m)_A[S_A]}{(k_{cat}/K_m)_B[S_B]} = \frac{v_A}{v_B}$$

For inhibition, $v = \frac{k_2[S][E]_0}{1+\frac{[S]}{K_S}+\frac{[I]}{K_I}}$ where $K_S = \frac{k_2+k_{-1}}{k_1}$



$$\frac{dP}{dt} = \frac{k[E]_0}{1+\frac{K_B}{[H^+]}+\frac{[H^+]}{K_A}}$$

Useful Catalysis Parameters

$$\frac{1}{v} = \frac{K_m}{v_{max}}\frac{1}{[S]} + \frac{1}{v_{max}}$$

$$\frac{d[P]}{dt} = \frac{k_{cat}}{K_m}[E]_0[S] \text{ when [S]<<Km}$$

$$\frac{d[P]}{dt} = k_{cat}[E]_0 \text{ when [S]>>Km}$$

Chemical Oscillations

Occur with two autocatalytic steps

Get a deviation δ above and below $[B]_{ss}$ and $[C]_{ss}$