# P. Chem Cheatsheet

## QM

$H_{aa} = \int \phi_a^* \hat{H} \phi_a \, d\tau$ : Coulomb Integrals

$H_{ab} = H_{ba} = \langle \phi_a | \hat{H} | \phi_b \rangle = \langle \phi_b | \hat{H} | \phi_a \rangle$

Resonance Integrals

$S_{ab} = \langle \phi_a | \phi_b \rangle = \langle \phi_b | \phi_a \rangle = S_{ba}$ : overlap integrals

Total e⁻ energy: $E_{tot} = \sum_i n_i E_i$

e⁻ population $Q_k = \sum_i n_i c_{ik}^2$

Total charge $q_k = 1 - Q_k$

most positive ⇒ nucleophilic attack

Bond orders $P_{jk} = \sum_i n_i c_{ij} c_{ik}$

if smallest, bond length longest

## Spectroscopy

### Rotational Spectroscopy

$F(J) = BJ(J+1) - DJ^2(J+1)^2$

$B = \frac{h}{8\pi^2 I c}$

$D = \frac{4B^3}{\omega_e^2}$

$\Delta J = \pm 1$

$\frac{N_J}{N_0} = (2J+1) e^{-\frac{hcBJ(J+1)}{kT}}$

$J_{max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$

$\Delta \tilde{\nu} = 2B(J+1)$

### Vibrational spec

$\tilde{\nu} = G(v) = \omega_e(v+\frac{1}{2}) - \omega_e x_e (v+\frac{1}{2})^2$

$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

$V(x) = hc D_e (1 - e^{-ax})^2$

$a = \sqrt{\frac{\mu \omega_e^2}{hc D_e}}$

~~$\Delta v$~~

$\Delta v = \pm 1, \pm 2, \pm 3 \ldots$

$\frac{N_v}{N_0} = e^{-hc[G(v) - G(0)]/kT}$

$D_e = D_0 + \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e$

$D_e = \frac{\omega_e^2}{4\omega_e x_e}$

$V_{max} = \frac{\omega_e'}{2\omega_e x_e'} - 1$

### Vib-rot spec

| $\Delta J$ | −1 | 0 | +1 |
|---|---|---|---|
| | P | Q | R |

$\tilde{\nu}(v, J) = \omega_e(v+\frac{1}{2}) + \omega_e x_e (v+\frac{1}{2})^2 + B_v J(J+1)$

$B_v = B_e - \alpha_e(v + \frac{1}{2})$

### Electronic spectroscopy

$\Delta S = 0$

$\Delta \Lambda = 0, \pm 1$

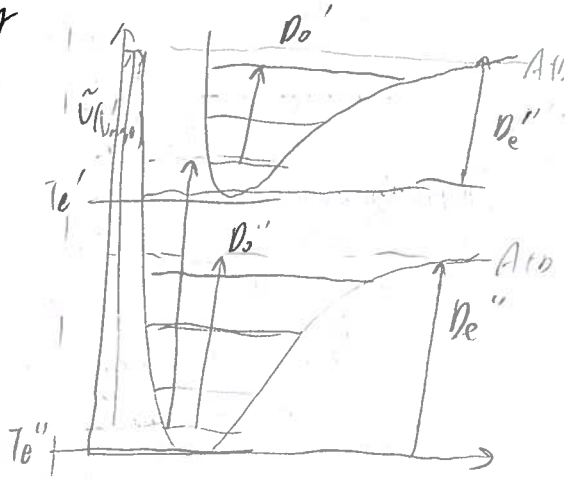
$g \leftrightarrow u$; $g \not\leftrightarrow g$; $u \not\leftrightarrow u$

$+ \leftrightarrow +$; $- \leftrightarrow -$; $+ \not\leftrightarrow -$

$\Delta \Sigma = 0$, $\Delta \Omega = 0, \pm 1$

$\Omega = |\Lambda + \Sigma|$

$^{2S+1}\Lambda^{\pm}_{g/u,\Omega}$




$\tilde{\nu}(v', v'') = T_e' - T_e''$
$+ \omega_e'(v'+\frac{1}{2}) - \omega_e x_e'(v'+\frac{1}{2})^2$
$- \omega_e''(v''-\frac{1}{2}) + \omega_e x_e''(v''-\frac{1}{2})^2$

# Statistical Mechanics

## Boltzmann Distribution

$$\frac{n_i}{n_j} = e^{\frac{-(\varepsilon_i - \varepsilon_j)}{kT}}$$

$$n_i = \frac{N e^{-\beta \varepsilon_i}}{q}$$

$$q = \sum_i e^{-\beta \varepsilon_i}$$

## Partition functions

$$q = \sum_i g_i e^{-\beta \varepsilon_i}$$

### Canonical ensemble

$$Q = \sum_i e^{-\beta E_i}$$

[$i$ : label of molecule]

$g_i$ = degeneracy

$$g_i = 2J+1$$

[solids]

independent & distinguishable : $Q = q^N$

independent & indistinguishable : $Q = \frac{q^N}{N!}$

[2 Bg]

### Translational:

$$q^T = \frac{V}{\Lambda^3}$$

$$\Lambda = \frac{h}{(2\pi m kT)^{\frac{1}{2}}}$$

### Rotational:

$$q^R = \sum_J (2J+1) e^{-\beta R hc J(J+1)}$$

$$q^R = \frac{kT}{hc\beta}$$

[linear non-symmetrical diatomic molecules]

$$q^R = \frac{kT}{\sigma hc\beta} \qquad \theta^R = \frac{hc\beta}{k} \qquad q^R = \frac{T}{\theta^R}$$

## Thermodynamic Functions

$$\langle \varepsilon \rangle = \varepsilon_{g.s} - \frac{1}{q}\left(\frac{\partial q}{\partial \beta}\right)_V$$

$$U = U(0) - \frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V$$

$$U - U(0) = -N\left(\frac{\partial \ln q}{\partial \beta}\right)_V$$

$$U - U(0) = NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V$$

$$U = U(0) - \left(\frac{\partial \ln Q}{\partial \beta}\right)_V$$

$$G(T) = G(0) - nRT \ln \frac{q}{N}$$

$$G(T) = G(0) - kT \ln Q + \underbrace{VkT\left(\frac{\partial \ln Q}{\partial V}\right)_T}_{p}$$

$$A = A(0) - kT \ln Q$$

$$H(T) = H(0) - \left(\frac{\partial \ln Q}{\partial \beta}\right)_V + kTV\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

### Heat capacity, Schotty Anomaly

$$C_V = \left(\frac{dU}{dT}\right)_N = \frac{N\varepsilon^2}{kT^2}\left[\frac{e^{\beta\varepsilon}}{(1+e^{\beta\varepsilon})^2}\right]$$

### Canonical Ensemble

$$\varepsilon_{tot}^{int} = E_i(N) = \varepsilon^T + \varepsilon^R + \varepsilon^V + \varepsilon^E + \varepsilon^{int}(N)$$

$$E_{tot} = N\langle \varepsilon_{tot} \rangle$$

## Entropy

$$S = k \ln W \qquad W = \frac{N!}{n_0! n_1! n_2! \cdots}$$

Interacting $S = \frac{U - U(0)}{T} + k \ln Q$

Independent & distinguishable $S = \frac{U - U(0)}{T} + Nk \ln q$

Independent & indistinguishable $S = \frac{U - U(0)}{T} + Nk \ln \frac{q e^1}{N}$

## Thermodynamics:

### Gibbs Energy

$$dG = dH - TdS$$
$$= Vdp - SdT$$

### State function

$$\mu = G_m = \frac{G}{n}$$

$$S_m = -\left(\frac{\partial \mu}{\partial T}\right)_p$$

$$V_m = \left(\frac{\partial \mu}{\partial p}\right)_T$$

$$d\mu = -S_m dT + V_m dp$$

### Gibbs Phase rule

$$F = C - P + 2$$

### Mole fraction

$$x_J = \frac{n_J}{n}$$

### Partial Molar Volume

$$V_J = \frac{\partial V}{\partial n_J}$$

$$V = V_A n_A + V_B n_B$$

### Partial Molar Gibbs energy

$$\mu_J = \frac{\partial G}{\partial n_J}$$

$$G_i = \mu_A n_A + \mu_B n_B$$

## Gibbs Energy for Binary systems

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B$$

### Mixing:

$$\Delta_{mix} G = nRT(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta_{mix} S = -nR(x_A \ln x_A + x_B \ln x_B)$$

### Chem potential of Ideal Liquids

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

$$\mu_A(g) = \mu^\circ_A(g) + RT \ln \frac{p_A}{p^\circ}$$

$$\mu_A(l) = \mu_A^*(l) + RT \ln \frac{p_A}{p_A^*}$$

w/o solute B

$$\mu_A^* = \mu^*(l) = \mu^\circ_A(g) = \mu^\circ + RT \ln \frac{p_A^*}{p^\circ}$$

w/ solute B

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}$$

ideal: $\mu_A(l) = \mu_A^*(l) + RT \ln x_A$

non-ideal: $\mu_A(l) = \mu_A^*(l) + RT \ln a_A$

Raoult's Law:

$p_A \approx x_A p_A^*$

rate of vapourisation

$k x_A$

rate of condensation

$k' p_A$

Lever rule:

$n_\alpha l_\alpha = n_\beta l_\beta$

Henry's Law

$p_B = x_B k_B$

Elevation of B.P.

$\Delta T = \frac{R T_b^2}{\Delta_{vap} H} x_B$

Depression of F.P.

$\Delta T = \frac{R T_f^2}{\Delta_{fus} H} x_B$

Van't Hoff eqn

$\Pi = [B] RT$

$\Pi = [J] RT (1 + B[J] + \dots)$

Excess functions

$G^E = \Delta_{mix} G^{real} - \Delta_{mix} G_i^{ideal}$
$= nRT(x_A \ln \gamma_A + x_B \ln \gamma_B)$

$S^E = \Delta_{mix} S^{real} - \Delta_{mix} S^{ideal}$
$= -G^E/T$

$H^E = \Delta_{mix} H^{real}$

$V^E = \Delta_{mix} V^{real}$

Extent of Rx

$d\xi = \frac{1}{\nu_J} dn_J$

Rx Gibb's Energy

$\Delta_r G_i = \frac{\partial G}{\partial \xi}$

Fugacity

$\mu = \mu^\circ + RT \ln\left(\frac{f}{p^\circ}\right)$

$f = p\phi$

Activity

$a_A = \frac{p_A}{p_A^*}$ $\gamma_A = \frac{p_A}{x_A p_A^*}$

$a_A = \gamma_A x_A$

$\mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A$

Vapour composition

$y_i = \frac{p_i}{p_{tot}}$

# Kinetics

Extent of Rx:

$\delta\xi = \frac{\delta n_Q}{\nu_Q}$

Rate:

$r = \frac{1}{\nu_Q} \frac{d[Q]}{dt}$

$r = k[A]^\alpha [B]^\beta$

order $= \alpha + \beta$

SSA if:

[M] is reactive

[A] is small - atom/free radical

after [M] maximise, after induction period

$\frac{d[M]}{dt} \approx 0$

Arhenius eqn

$k(T) = A \exp\left(-\frac{E_a}{RT}\right)$

$k_{theoretical} = \frac{\sigma_{AB} \langle s \rangle_{rel} N_A^2}{2} e^{-\frac{E_a}{RT}}$

Lindemann Rx
(Unimolecular Rx)

$A + M \rightarrow A^* + M \quad k_1$

$A^* + M \rightarrow A + M \quad k_{-1}$

$A^* \rightarrow P \quad k_2$

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

Rate of Heat Loss:

$Q = KS(T - T_s)$