

YEAR 3 PHYSICAL FORMULA BOOKLET*

*Not all formulas may be covered, or even correct. Use at your own risk. We will not be liable for any stupid mistakes made in real life or in the exam. Like a factor of 10 in one of your electrochemical reactions could blow your lab up.



State fuhnction...

STATISTICAL THERMODYNAMICS

The weight of a molecular configuration (the number of complexions)

$$W = \frac{N!}{\prod_i n_i!}$$

Boltzmann probability distribution (also fractional population) in a general form including degeneracy of states:

$$p_i = \frac{N_i}{N} = \frac{g_i \cdot e^{-\frac{\epsilon_i}{kT}}}{\sum_j g_j \cdot e^{-\frac{\epsilon_j}{kT}}}$$

Definitions for molecular (q) and canonical (Q) partition functions and their importance in Statistical Thermodynamics. (ϵ_i – molecular energy; E_i – system (ensemble) energy). Be able to appreciate the difference between them. Be able to calculate them for simple models.

$$q = \sum_i g_i e^{-\frac{\epsilon_i}{kT}}$$

$$Q = \sum_i \Omega_i e^{-\frac{E_i}{kT}}$$

Appreciate the difference between canonical partition functions for distinguishable and indistinguishable particles:

$Q = q^N$ distinguishable particles

$Q = q^N / N!$ indistinguishable particles

(Remember that indistinguishability is accounted only once! (in $Q_{\text{trans}} = q_{\text{trans}}^N / N!$)

Understand the relation between thermodynamic functions and partition functions and how the former can be calculated from partition functions:

Total energy: $U = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N}$

Free energy: $A = -kT \ln Q$

Entropy: $S = k \ln Q + kT \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N}$

Be able to calculate their values for simple models.

The Boltzmann equation for entropy and its origin. Residual entropy

$$S = k \ln \Omega$$

Separation of partition functions for independent particles:

$$E_{total} = \varepsilon_1 + \varepsilon_2 + \dots + \varepsilon_N$$

$$Q_{total} = q_1 q_2 \dots q_N = q^N$$

Separation of partition functions for independent degrees of freedom of a particle:

$$\varepsilon_{total} = \varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{elec} + \dots$$

$$q_{total} = q_{trans} q_{rot} q_{vib} q_{elec} \dots$$

Appreciating the use of partition functions for finite (short polymer conformations, spin states, etc.) and infinite (long polymer configurations, vibrational and rotational states, etc.) discrete molecular states.

Appreciate the differences in associated heat capacities (C_v);

Be able to explain the behavior of C_v at the high- and low-T limits in each case.

Expression for translation partition function:

$$q_{trans} = \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} V$$

Expressions for vibrational partition function for a single vibration, characteristic vibrational temperature and associated fractional population:

$$q_{vib} = \frac{1}{1 - e^{-\left(\frac{hc\omega}{kT}\right)}}$$

$$\frac{N_n}{N} = \left(1 - e^{-\frac{\Theta_v}{T}} \right) e^{-\frac{n\Theta_v}{T}}$$

$$\Theta_v = \frac{hc\omega}{k}$$

Remember that a total vibrational function is a product of partition functions of individual vibrations of a molecule

$$q_{vib} = q_{vib1} q_{vib2} \dots q_{vibM}$$

M is either =3N-6 or =3N-5 (linear), N - total number of atoms in the molecule

High temperature approximation for q_{vib} :

$$q_{vib} = \frac{T}{\Theta_V}$$

Expressions for rotational partition function, characteristic rotational temperature and associated fractional population:

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

$$\frac{N_J}{N} = \frac{\Theta_R}{T} (2J + 1) e^{-\frac{\Theta_R J(J+1)}{kT}}$$

$$\Theta_R = \frac{hcB}{k}$$

High temperature approximation for q_{rot}

$$q_R = \frac{kT}{\sigma hcB}$$

The origin and the use of the symmetry number (σ)

Appreciate that electronic partition function is normally simply the ground state degeneracy:

$$q_e = g_0$$

Application of the classical equipartition of energy. Its use in the estimation of the heat capacities in the high-T limit.

$$\langle \varepsilon \rangle = \frac{1}{2kT}$$

Appreciate the algorithm for the calculation of the equilibrium constants for simple chemical reactions using partition functions of the reactants/products. See how different contributions can influence the equilibrium constant.

$$K_{eq} = \frac{\tilde{q}_C^c \tilde{q}_D^d}{\tilde{q}_A^a \tilde{q}_B^b}$$

for a gas type reaction : $aA + bB \rightarrow cC + dD$

Remember that $\tilde{q}_i = \frac{q_i}{N_A}$ in K_{eq}

Be familiar with the properties of the elementary Math functions (such as $\exp(x)$, $\ln(x)$, etc. Be able to use the rules for differentiation of elementary Math functions (incl. the chain rule).

The chain rule: For a function of $u(v(x))$: $\frac{\partial u}{\partial x} = \frac{\partial u}{\partial v} \frac{\partial v}{\partial x}$

Beer Lambert:

$$\log_{10} \frac{I_0}{I} = \epsilon cl = A$$

Oscillator Strengths

Oscillator strength, f , is related to fundamental molecular properties.

$$f = \frac{8\pi^2\nu_{if}m_e}{3he^2} \mu_{if}^2$$

μ_{if} is the (electric dipole) transition moment. It determines the effectiveness of a transition. The larger the magnitude, the stronger the transition and greater the magnitude of ϵ . If $\mu_{if} = 0$ then the transition should not occur at all (forbidden)

Transition Moments:

Rate at which photons absorbed $\Gamma = |\mu_{if}|^2 I(\nu_{if})$

$I(\nu_{if})$ is the intensity of light at the frequency corresponding to energy difference i and f .

Bras, kets and operators:

$$\langle \psi_a | \psi_b \rangle = \int_0^\infty \psi_a^* \psi_b d\tau$$

$$\mu_{if} = \langle \psi_i | \mu | \psi_f \rangle$$

Approximations and Selection Rules

- Only one electron excited during excitation
- Born-Oppenheimer to separate out nuclear interactions
- Electronic wavefunctions products of orbital and spin wavefunctions

$$\mu_{if} = \langle \psi_i | \mu | \psi_f \rangle = \langle \chi_i | \chi_f \rangle \langle \phi_i | \mu | \phi_f \rangle \langle S_i | S_f \rangle$$

Nuclear Overlap Selection Rule

$$|\langle \chi_i | \chi_f \rangle|^2 \neq 0$$

Spin Selection Rule

$$\Delta S = 0$$

Symmetry Selection Rule

Transitions can only occur if there is a change in parity

i.e.	$u \leftrightarrow g$		ALLOWED
	$u \leftrightarrow u$	&	$g \leftrightarrow g$
			FORBIDDEN

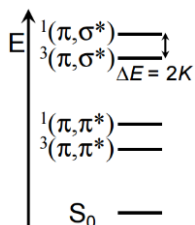
State Classifications and MO Diagrams

K: Exchange repulsion

$$E_{\text{triplet}} = J - K$$

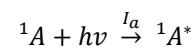
$$E_{\text{singlet}} = J + K$$

$$\Delta E_{S-T} = 2K$$

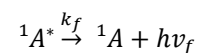


Quantum Yields and Luminescent Lifetimes

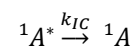
$$\phi = \frac{\text{number of moles of product produced (s}^{-1} \text{ m}^{-3}\text{)}}{\text{number of einsteins of light absorbed (s}^{-1} \text{ m}^{-3}\text{)}}$$



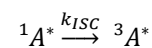
Excitation during initial photon absorption



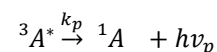
Fluorescence



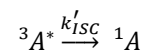
Internal Conversion



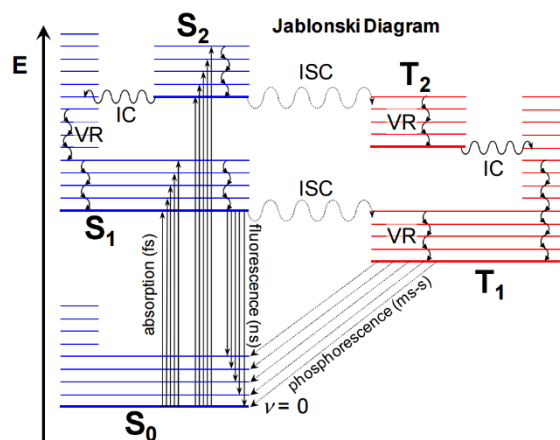
Inter System Crossing



Phosphorescence



Inter System Crossing to ground state



First Order Reactions & Exponential Decay

$$\frac{d[R]}{dt} = -k[R] \quad \rightarrow \rightarrow \rightarrow \quad [R] = [R]_0 e^{-kT}$$

$$[R] = [R]_0 e^{-\frac{t}{\tau}} \quad \tau = \frac{1}{k}$$

Fluorescence Lifetimes

$$I_f = I_f^0 e^{-\frac{t}{\tau_f}} \quad \frac{1}{k_f} \neq \tau = \frac{1}{k_\Sigma}$$

k_f is only related to fluorescence, but can also undergo Internal Conversion and Inter System Crossing

Quantum Yield for Fluorescence

$$\phi_f = \frac{\text{fluorescent photons emitted } (s^{-1} m^{-3})}{\text{photons absorbed } (s^{-1} m^{-3})} = \frac{k_f}{k_\Sigma}$$

Quantum Yield for Phosphorescence

$$\phi_p = \frac{k_{ISC}}{k_\Sigma} \frac{k_p}{(k_p + k'_{ISC})}$$

Quenching and the Stern – Volmer

$$\frac{\phi_f^0}{\phi_f} = \frac{k_\Sigma + k_Q[Q]}{k_\Sigma} = 1 + \frac{k_Q}{k_\Sigma}[Q] \quad \text{or} \quad \frac{\phi_f^0}{\phi_f} = 1 + \tau_f k_Q[Q]$$

Experimental Techniques

Comparing fluorescent yields from a sample to a reference sample

$$\frac{\phi_f}{\phi_{ref}} = \frac{n^2}{n_{ref}^2} \frac{A}{A_{ref}}$$

ELECTROCHEMISTRY

General Nernst Equation

$$E_{cell} = E_{cell}^0 - \frac{RT}{F} \ln \left(\frac{\prod_j a_{pj}^{v_j}}{\prod_i a_{pi}^{v_i}} \right)$$

Gibbs Free Energy

$$\Delta G^0 = -nFE^0$$

$$E^0 = \frac{RT}{F} \ln K$$

Faradaic Current

$$i_{ox} = nAFj$$

$$v = \frac{i}{nFA}$$

$$j = k^0[X]_s$$

$[X]_s$ = Surface concentration of ion of interest at electrode

Butler-Volmer Equation (You need to know how to derive – it's really long)

$$i = i_0 \left(\frac{[Red]_s}{[Red]_{bulk}} e^{\left(\frac{(1-\alpha)F}{RT} \eta\right)} - \frac{[Ox]_s}{[Ox]_{bulk}} e^{-\frac{\alpha F}{RT} \eta} \right)$$

If mass transport is fast then it reduces to

$$i = i_0 \left(e^{\left(\frac{(1-\alpha)F}{RT} \eta\right)} - e^{-\frac{\alpha F}{RT} \eta} \right)$$

$$i_0 = k^0 FA [Ox]_{bulk}^{(1-\alpha)} [Red]_{bulk}^{\alpha}$$

Tafel Analysis

$$\ln|-i_{red}| = \ln i_0 - \frac{\alpha F}{RT} \eta$$

$$\ln|-i_{ox}| = \ln i_0 - \frac{\beta F}{RT} \eta$$

$$\text{where } \beta = 1 - \alpha$$

Diffusion

Fick's First Law

$$j_{diff} = -Dx \frac{d[X]}{dx}$$

Fick's Second Law

$$\frac{\partial[X]}{\partial T} = D \frac{\partial^2[X]}{\partial x^2}$$

Current

$$i_l = \frac{DFA[X]_{bulk}}{\delta}$$

$$\delta = \sqrt{2Dt}$$

Stoke-Einstein Equation

$$D = \frac{k_B T}{6\pi\eta r}$$

Convection

$$\frac{d[X]}{dt} = -v_x \frac{d[X]}{dx}$$

Migration

$$j_{mig,x} \propto \mu_x [X] \frac{d\phi}{dx}$$

μ_x : Ionic mobility of X

Cottrell Equation

$$|i| = \frac{nFAD^{\frac{1}{2}}[A]_{bulk}}{\pi^{\frac{1}{2}}t^{\frac{1}{2}}}$$

Randell Sevcik Equation

Reversible Limit

$$i_p = 2.69 \cdot 10^5 AD^{\frac{1}{2}}C_{bulk}v^{\frac{1}{2}}$$

Irreversible Limit

$$i_p = 2.99 \cdot 10^5 \sqrt{\alpha} AD^{\frac{1}{2}}C_{bulk}v^{\frac{1}{2}}$$

α : charge transfer coefficient

Diagnostic Criteria:

Reversible Limit	$ E_p - E_{1/2} = 2.218 \frac{RT}{F}$	
Irrversible Limit	$ E_p - E_{1/2} = 1.857 \frac{RT}{\alpha F}$	Reduction
Irrversible Limit	$ E_p - E_{1/2} = 1.857 \frac{RT}{\beta F}$	Oxidation

where $\beta = 1 - \alpha$

EC Reaction

$$K_{EC} = \frac{k_{EC} RT}{v F}$$
$$\frac{\partial E_p}{\partial \log v} = \frac{2.303 RT}{2F}$$

EC' Reaction

$$K_{CAT} = \frac{k_{CAT} [Z] RT}{v F}$$

Microelectrodes

Fick's Second Law

$$\frac{dC}{dt} = D \left(\frac{\partial^2 C}{dr^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right)$$

Cottrell Equation

Spherical Electrode $i_{ss} = 4\pi r_e D F C_{bulk}$

Hemispherical Electrode $i_{ss} = 2\pi r_e D F C_{bulk}$

PHOTOPHYSICS

How far do atoms move during a vibration?

$$\langle x^2 \rangle = \frac{h}{8\pi^2nc\tilde{\nu}}$$

Absorption of Light

$$I = \frac{1}{2}c\varepsilon_0E^2$$

Fermi's Rule

$$\Gamma = \frac{2\pi}{\hbar} |\mathcal{K}_{int}|^2 \rho$$

Beer Lambert

$$-\frac{dI}{dz} = \alpha IC$$

$$I = I_0 e^{-\alpha z C}$$

$$I = I_0 10^{-\varepsilon z C} \quad \varepsilon = \frac{\alpha}{2.303}$$

$$A = -\log_{10} T$$

Chiral Molecules

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c}$$

Dissymmetry Factor

$$g = \frac{\varepsilon^L - \varepsilon^R}{\frac{1}{2}(\varepsilon^L + \varepsilon^R)}$$

Optical Polarization

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} = \frac{2P}{3 - P}$$

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

$$P = \frac{3 \cos^2 \alpha - 1}{3 + \cos^2 \alpha}$$

Forster Theory

$$k_{RET} = \frac{3\kappa^2}{2} \frac{1}{\tau_{A^*}} \left(\frac{R_0}{R}\right)^6$$

Two Photon Absorption

$$\frac{n}{V} = \frac{I\lambda}{hc^2}$$
$$-\frac{dI}{dz} = \beta I^2 C$$

Doppler-Free Spectroscopy

$$\Delta E = hv'_k + hv'_{-k} = 2hv$$

Higher Order Processes

$$\Delta E = m h \nu$$

Intensity depends on I^m where I is irradiance

DIFFRACTION

X-ray diffraction

Distances between planes

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Glancing angles

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)$$

Bragg Equation

$$2d_{hkl} \sin \theta = n\lambda$$

Laue Equation

$$a(\cos \alpha - \cos \alpha_0) = h\lambda$$

Intensities

$$f = 2\pi \int \rho(r) \frac{\sin kr}{kr} r^2 dr \quad k = \frac{4\pi}{\lambda} \sin \theta$$

Structure Factor

$$F_{hkl} = \sum f_i e^{i\phi_{hkl}(j)} \quad \phi_{hkl}(j) = 2\pi(hx + ky + lz)$$

Fourier Synthesis

Phase Problem

$$\rho(r) = \frac{1}{V} \sum F_{hkl} e^{-2\pi i(hx + ky + lz)}$$

Structure Refinement

R factor

$$R = \frac{\sum |F_0| - |F_c|}{F_0}$$