

Physical Chemistry Formula Booklet



Courses

		Pages
1C24	Energetics & Spectroscopy	1-33
	In-depth revision material and equations	
	Completed	
2C2Y	Physical Chemistry I	34-41
	Important Equations (Formula pages)	
	Completed	
3C21	Physical Chemistry II	42 ...
	Important Equations (Formula pages)	
	Not Completed	

Last Updated: 05/05/2015

*Formula like this are important in
1C24: Energetics and Spectroscopy*

1C24: ENERGETICS AND SPECTROSCOPY

GASES AND KINETICS

Boyle's Law

The pressure of a fixed amount of gas is inversely proportional to its volume at constant temperature

$$P \propto \frac{1}{V}$$

Pressure

$$P = \frac{F}{A}$$

$$P_1V_1 = P_2V_2$$

Charles's Law

The volume of a fixed amount of gas depends linearly on the temperature at a constant pressure

$$V \propto T$$

Temperature

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Avagadro's Principle

Equal volumes of gas contain the same number of molecules at a given temperature and pressure

$$V \propto n$$

STP / SATP

STP: Standard Temperature and Pressure

0 °C / 273.15 K and 1 atm

22.414 dm³ mol⁻¹

SATP: Standard Ambient Temperature and Pressure

25 °C / 298.15 K and 1 bar (10⁵ Pa or 0.987 atm)

24.789 dm³ mol⁻¹

The Ideal Gas Equation of State

$$PV = nRT$$

R: Gas Constant: 8.314 J K⁻¹ mol⁻¹

Validity of the Ideal Gas Concept

- Non-interacting point particles
- Breaks down at high pressure

Dalton's Law

The total pressure exerted by a gaseous mixture is equal to the sum of the partial pressures of each individual component in a gas mixture

$$P_T = P_1 + P_2 + \dots$$

$$P_T = \sum_{i=1}^n P_i$$

Partial Pressure

The partial pressure P_i of the gas i is defined as:

$$P_i = x_i P_T$$

Where x_i is the mole fraction of the gas:

$$x_i = \frac{n_i}{n_T}$$

$$\sum_{i=1}^n x_i = 1$$

SI units

Quantity	SI Units	Base Units
Pressure	Pascals (Pa or Nm^{-2})	$\text{kg m}^{-1} \text{s}^{-2}$
Volume	Cubic metres (m^3)	m^3
Temperature	Kelvin (K)	K ($0\text{K} = -273.15\text{ }^\circ\text{C}$)
Energy	Joules (J)	$\text{kg m}^2 \text{s}^{-2}$

The Kinetic Model of Gases

Three assumptions:

1. Gas consists of molecules in constant random motion.
2. The size of molecules is negligible compared to the dimensions of the container and average distance between collisions.
3. The only way that the molecules interact with each other is by collisions.

The Pressure of a Gas

Gas molecules exert a steady pressure on the walls of a container by collision and transfer of their momentum. On the basis of this, the pressure exerted by a gas of molar mass M in a volume V is:

$$P = \frac{nMc^2}{3V}$$

The temperature dependent rms speed can be obtained by comparison of the gas pressure with the gas law:

$$c = \left(\frac{3RT}{M}\right)^{\frac{1}{2}}$$

Maxwell Distribution of Speeds

$$f(v) = 4\pi \left(\frac{M}{2\pi RT}\right) v^2 e^{-\frac{Mv^2}{2RT}}$$

$f(v)$ = distribution of speeds

v = speed

Limits to Maxwell Distribution

As $v \rightarrow \text{Infinity}$

$$e^{-\frac{Mv^2}{2RT}} \rightarrow e^{-\text{infinity}} \rightarrow 0 \quad \text{and} \quad v^2 \rightarrow \text{infinity}$$

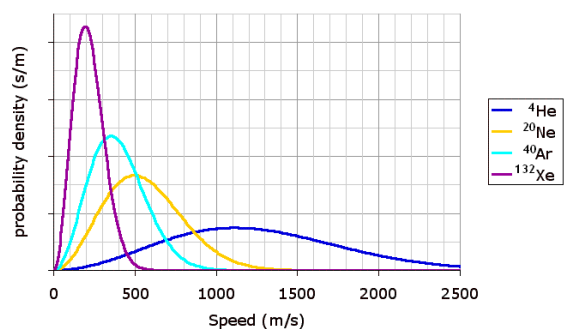
Therefore $f(v) \rightarrow 0$

$V \rightarrow 0$	$f(v) \rightarrow 0$
$T \rightarrow 0$	$f(v) \rightarrow 0$
$T \rightarrow \text{infinity}$	$f(v) \rightarrow \text{small}$
$M \rightarrow \text{small}$	$f(v) \rightarrow \text{large}$
$M \rightarrow \text{large}$	$f(v) \rightarrow \text{small}$

All of these can be explained through simple chemical observation

- Includes a decaying exponential function. Therefore the fraction of molecules with very high speeds is small (if $v \rightarrow \text{large}$, $f(v) \rightarrow 0$)
- $f(v)$ must go to zero when M is large for the same reasons
- $T = \text{high}$, exponential factor approaches 1. Therefore a greater fraction of molecules have high speeds at high temperatures
- The factor v^2 multiplies the exponential. Therefore $f(v)$ approaches 0 as v approaches 0. Therefore the fraction of molecules with low speeds is small

Maxwell-Boltzmann Molecular Speed Distribution for Noble Gases



Molecular Collisions

Mean Free Path (λ) The average distance that a molecule travels between collisions

$$\lambda = \frac{RT}{\sqrt{2N_A\sigma P}}$$

Collision frequency (z) The average rate of collisions made by one molecule

$$z = \frac{\sqrt{2}N_A\sigma cP}{RT}$$

Time of flight ($1/z$) The average time that a molecule spends in flight between two collisions, and is the inverse of collision frequency ($1/z$)

The Collision Cross – Section (σ)

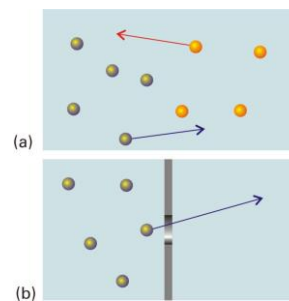
The target area presented by one molecule to another

$$\sigma = \pi d^2$$

Diffusion and Effusion

Diffusion The process by which the molecules of different substances mingle with each other by random motion along a concentration gradient

Effusion The process where individual molecules flow through a hole without collisions between molecules



Graham's Law

The rate of effusion of a gas is inversely proportional to the square root of its molar mass at a given pressure and temperature:

$$R_{Effusion} \propto \frac{1}{M^{\frac{1}{2}}}$$

at constant pressure and temperature

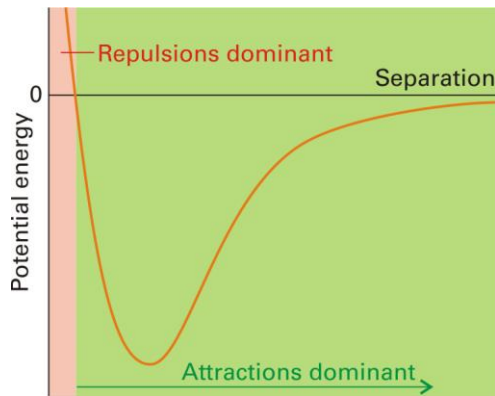
Real Gases

The assumptions made for ideal gases are only true when the *mean free path* is greater than the *collision cross section* (ie $\lambda \gg d$)

Otherwise, molecular interactions have to be taken into account.

$$E_T = KE + PE$$

Molecular Interactions



Intermolecular interactions give rise to potential energy that contributes to the total energy of the gas.

Attractions lower the overall energy.

Repulsions increase the overall energy.

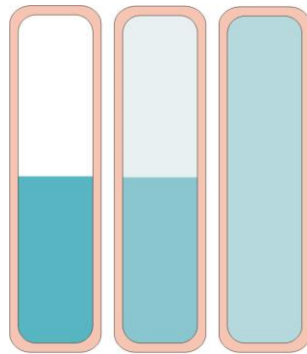
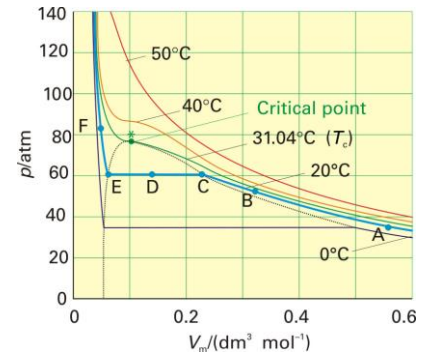
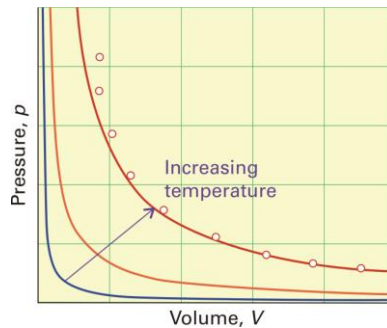
Consequently intermolecular interactions affect the bulk properties of a gas.

Isotherms (PV-plots) differ from Boyle's Law once potential energy terms become important

Isotherms and Critical Temperature

A gas cannot be condensed to a liquid by the application of pressure unless the temperature is below the critical temperature!

The critical point is the temperature at which thermal energies overcome cohesive energies of the molecules (condensed phases can't form)



The Compression Factor

The compression factor is the ratio of the actual molar volume of a gas to the molar volume of a perfect gas

$$Z = \frac{V_n}{V_m^{ideal}}$$

Or

$$Z = \frac{V_m}{RT/P} = \frac{PV_n}{RT}$$

$Z > 1$ Molar volume of the real gas is greater than that of an ideal gas

Repulsive forces dominate

$Z < 1$ Molar volume of the real gas is smaller than that of an ideal gas

Attractive forces dominate

$Z \rightarrow 1$ The gas behaves more ideally

The Virial Equation of State

A deviation of Z can be used to construct an empirical equation of state:

$$Z = 1 + \frac{B}{V_n} + \frac{C}{V_n^2} + \dots$$

The coefficients B, C , are called virial coefficients.

Combination of Z with the ideal gas law results in the virial equation of state:

$$P = \frac{nRT}{V} \left(1 + \frac{nB}{V} + \frac{n^2C}{V^2} + \dots \right)$$

The Van der Waals E.o.S

Step 1 The **repulsive** interactions (b) between two molecules hamper them to approach each other. Therefore, the actual volume molecules can travel is reduced to some extent.

$$P = \frac{nRT}{V - nb}$$

Step 2 The **attractive interactions** (a) between molecules reduce the pressure exerted by the gas (proportional to sq. of concentration):

$$P = \frac{nRT}{V - nb} - a \left(\frac{n}{V} \right)^2$$

or

$$\left(p + \frac{an^2}{V^2} \right) (V - nb) = nRT \quad \text{Van der Waals Equation}$$

CHEMICAL KINETICS

The Beer-Lambert Law

$$\log \frac{I_0}{I} = \epsilon cl$$

$$I = I_0 10^{-\epsilon cl}$$

The exponent is called **absorbance**

$$A = \epsilon cl$$

Reaction Rate

The rate of a chemical reaction can be defined as amount of a reactant (or product) which vanishes (is produced) within a certain time:

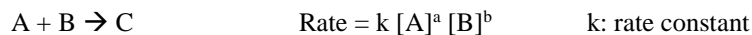
$$\text{rate} = \frac{dc}{dt} = \frac{[\Delta c]}{\Delta t}$$

Example for a *Generalized* Chemical Reaction



$$\text{Rate} = \frac{d[D]}{dt} = \frac{1}{3} \times \frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2} \times \frac{d[B]}{dt}$$

Rate Laws



The rate constant is **independent of the concentration** of the species, but is **dependent** on the temperature!

YOU NEED TO BE ABLE TO WORK OUT THE UNITS OF RATE CONSTANTS

$$\text{Rate} = k[A] \quad s^{-1}$$

$$\text{Rate} = k[A]^2 \quad \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$\text{Rate} = k[A][B][C] \quad \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

$$\text{Rate} = k[A]^{-1} \quad \text{dm}^{-6} \text{ mol}^2 \text{ s}^{-1}$$

Reaction Order

The power to which the concentration is raised in the rate law is the **reaction order**

$$\text{Rate} = k[A]^2 \quad \text{There is **second-order** in A.}$$

The overall order of a reaction is the sum of all the orders of all the components

Rate Law	Individual Orders	Overall Order
Rate = k[A]	[A]: First order	First Order
Rate = k[A] ²	[A]: Second order	Second Order
Rate = k[A][B][C]	[A]: First order, [B]: First order, [C]: First order	Third Order

Important Point: The rate law is established experimentally and cannot in general be inferred from the chemical equation of the reaction. However it can be derived if the elementary steps are known.

The Isolation Method

The determination of the rate law is simplified by the isolation method, in which all the reactants except one are present in large excess. This in effect allows us to focus on a single reactant because we can assume that the concentration on the other reactants are constant. The dependence of the rate on each of the reactants can be found by isolating each of them in turn.

Example

If reactant B is in large excess, it is a good approximation to take its concentration as constant throughout the reaction.

$$\text{Rate} = k[A]^a[B]^b \quad \text{becomes} \quad \text{Rate} = k'[A]^a \quad k' = k[B]_0^b$$

By approximating [B] by its initial value [B]₀ (*k'* is the effective rate constant)

The Method of Initial Rates

The instantaneous rate is measured at the beginning of the reactions for several different initial concentrations. The initial rate is estimated by calculating the linear function of the logarithmic rate law.

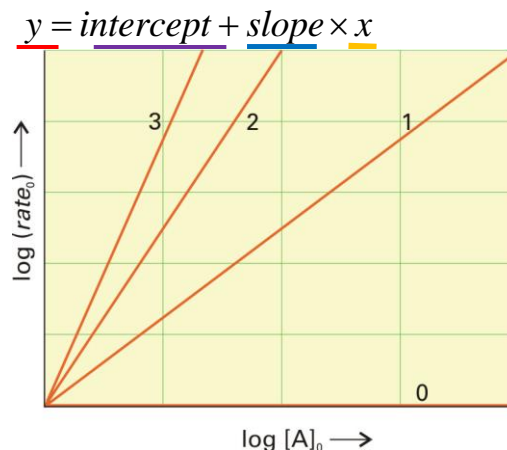
$$r = k'[A]^a \rightarrow r_0 = k'[A]_0^a$$

$$\log r_0 = \log k' + a \log [A]_0$$

r_0 is the initial rate of the reaction

$[A]_0$ is the initial concentration

THE GRADIENT OF THE SLOPE TELLS YOU THE REACTION ORDER



Integration of Rate Equations

First Order

$$\begin{aligned} -\frac{d[A]}{dt} &= k[A] && \rightarrow && -\frac{d[A]}{[A]} = k dt \\ -\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} &= \int_0^t k dt && \rightarrow && -\ln([A]) \Big|_{[A]_0}^{[A]} = kt \Big|_0^t \\ -\ln([A] - [A]_0) &= k(t - 0) && \rightarrow && \ln([A]_0 - [A]) = kt \end{aligned}$$

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

$$[A] = [A]_0 e^{-kt}$$

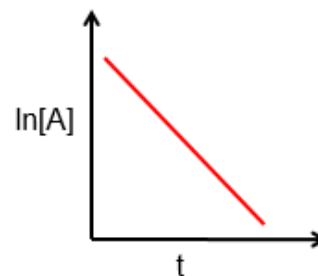
Analysing First Order Reactions

$$\ln[A] = \ln[A]_0 - kt$$

Plot of $\ln [A]$ against t

Slope: $-k$

Intercept: $\ln[A]_0$



If the reaction is first order, plotting the data in this way will result in a straight line. If the data do not give a straight line – *the reaction is not first-order!*

Second Order

$$-\frac{d[A]}{dt} = k[A]^2 \quad \rightarrow \quad \frac{1}{[A]} - \frac{1}{[A]_0} = kt \quad \rightarrow \quad [A] = \frac{[A]_0}{1 + kt[A]_0}$$

YOU NEED TO KNOW HOW TO DERIVE THESE EQUATIONS. IT IS SIMILAR TO THAT ABOVE AND THE ANSWER IS IN A TUTORIAL

Analysing Second Order Reactions

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt \quad \frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Plot of $1/[A]$ against t

Slope: k

Intercept: $1/[A]_0$

Half Lives

The half-life of a reaction is the time it takes for the concentration of a reactant to fall to half its initial value.

First Order $t = t_{1/2}$ $t_{1/2} = \frac{\ln 2}{k}$

Temperature Dependence

Arrhenius found experimentally, that $\ln k$ is inversely proportional to the temperature in most reactions:

$$k = Ae^{-\frac{E_a}{Rt}}$$

$$\ln k = \text{intercept} + \text{slope} \times \frac{1}{T}$$

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

Plot of $\ln k$ against $1/T$

Intercept: $\ln A$

Slope: $-E_a / R$

Collision Theory

In collision theory, reaction occurs when two molecules of sufficient kinetic energy collide.

Introduces an activation barrier E_a

Pre-exponential factor (A) The constant of proportionality between concentration and the collision rate of reactants

$$A = \sigma \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}} N_A^2 \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

Activation Energy (E_a) The minimum kinetic energy required for a collision to result in reaction

The Steric Factor

A steric factor $0 < P < 1$ should be included into the pre-exponential factor (A) to account for the relative orientation of the reactants

Transition State Theory (More in Year 2C2Y)

In the transition state theory, reactions can occur when two molecules form an **activated complex**

Reaction Equilibrium

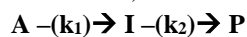
$$K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k}{k'}$$

$K \gg 1$ The forward rate constant is bigger than the reverse rate constant

$K \ll 1$ The reverse rate constant is bigger than the forward rate constant

Consecutive Reactions

Many reactions produce intermediates, which then lead into products.



$$A \rightarrow I \quad \frac{d[I]}{dt} = k_1[A]$$

$$I \rightarrow P \quad \frac{d[P]}{dt} = k_2[I]$$

I reaches maximum concentration at:

$$t = \frac{1}{k_1 - k_2} \ln\left(\frac{k_1}{k_2}\right)$$

Unimolecular Reactions

These only involve single molecules and can include molecules “shaking” themselves apart or nuclear decay.



The decay of A is proportional to its concentration.

Therefore the rate can be denoted as

$$-\frac{d[A]}{dt} = k[A]$$

And we can conclude that a unimolecular reaction is first order

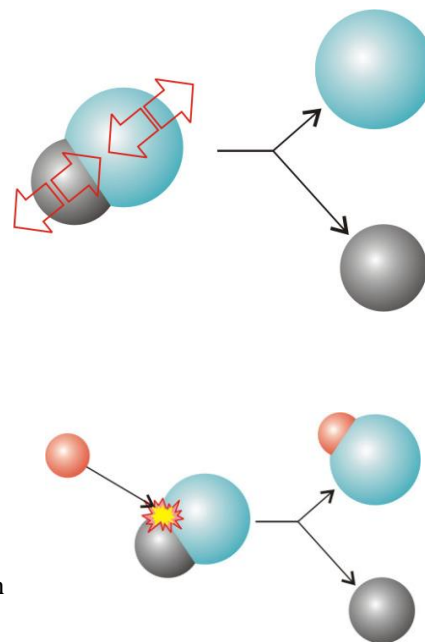
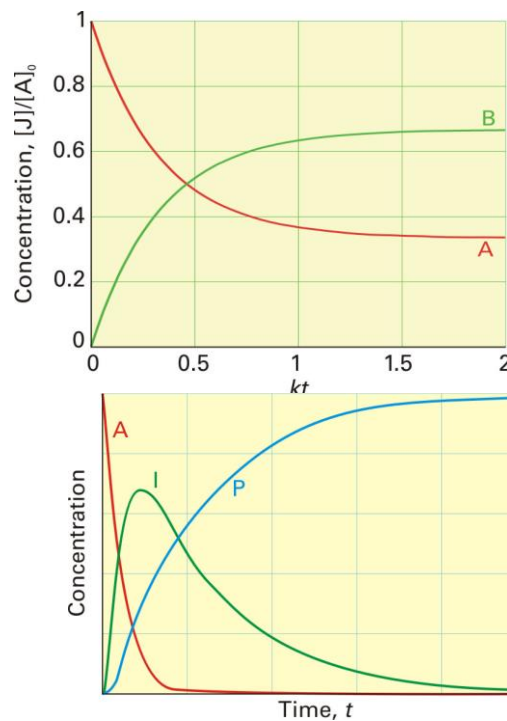
Bimolecular Reactions

These involve two molecules colliding and generally exchanging energy and atoms.



The rate of a bimolecular reaction is proportional to the rate at which the reactants meet (collision frequency)

$$-\frac{d[A]}{dt} = k[A][B] \quad \text{Bimolecular reactions are second order}$$



THERMODYNAMICS

Systems

System A system is the portion of the physical work being studied.

Universe System and Surroundings

System Wall Boundary between system and its surroundings

Adiabatic Wall Heat cannot pass through the system wall (Thermally isolated or insulated)

Diathermal Wall Heat can pass through the wall

Thermal Contact Two systems connected by a diathermal wall

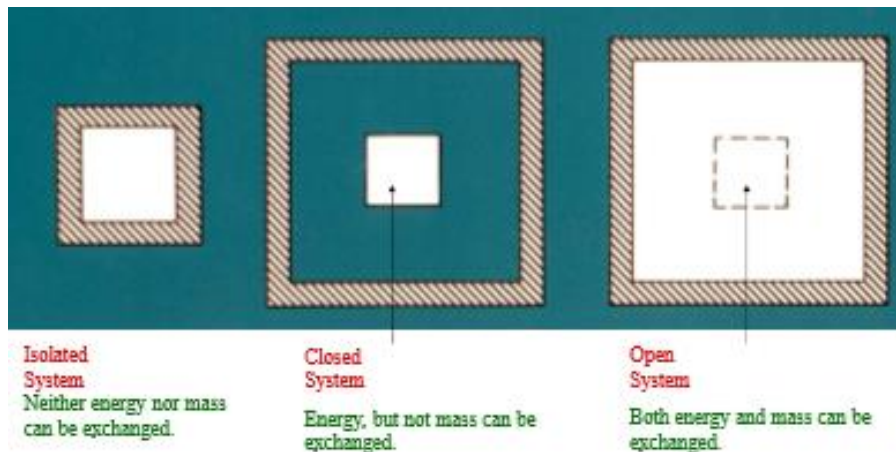
Isolated System Cannot exchange mass or energy with its surroundings

The wall of an isolated system must be adiabatic

Closed System Can exchange energy, but not mass, with its surroundings

The energy exchange may be mechanical (associated with a volume change) or thermal (associated with heat transfer through a diathermal wall)

Open System Can exchange both mass and energy with its surroundings



State Functions

State functions are independent of the manner in which the change is made (path of the process)

VOLUME ALTITUDE MONEY...

State Functions – Money

I have £100 in my bank account £100 (We are students, we wish! Ha!)

I withdrew £50 £50

I could have added £100 £200

Then withdrew £150 £50

The state (money in the account) is the same at the end, but the path taken is different.

ENTHALPY is a state function (Hess's cycles)

State Functions / Thermodynamic Variables

Thermodynamic variables The observable macroscopic variables of a system (P, V, and T)

They are used to describe an equilibrium state of the system, they are known as state variables

Extensive Variables Depend on the size of the system (e.g. mass, volume, entropy, magnetic moment)

Intensive Variables Do not depend on the size of the system (e.g. pressure, temperature, magnetic field)

Specific Value An extensive value may be changed into an intensive variable, known as a **specific value**, by dividing it by a suitable extensive variable, such as mass, no. of moles, or no. of molecules.

Example: The specific heat is normally (heat capacity) / (mass)

Equilibrium States

Equilibrium State Is one in which the properties of the system do not change with time

Non-equilibrium state May contain intensive variables which vary in space and/or time

Equation of state A functional relationship between the state variables. E.g. if **P**, **V** and **T** are the state variables then the equation of state has the form **f(P,V,T)=0**

In 3-dimensional **P-V-T** space...

An equilibrium state is represented by a point

The equation of state is represented by a surface

Equations of State

$$PV = nRT$$

The ideal gas equation is our favourite (and simplest) equation of state

Heat and Work

Heat (q) and Work (w) are NOT state functions because their values depend on the specific *transition* (or path) between two equilibrium states.

If **heat** is provided **to a system** Energy of system **increases** **+ve**

If **heat** is escaped **from a system** Energy of system **decreases** **-ve**

If **work** is done **on the system** Energy of system **increases** **+ve**

If **work** is done **by the system** Energy of system **decreases** **-ve**

Thermodynamic Processes

Process The change from one equilibrium state to another

Quasi-static process Takes place so slowly that the system may be considered as passing through a succession of equilibrium states

Reversible process The direction can be reversed by an infinitesimal change of the variable

A process may be represented by a **path** (or line) on the equation of state surface

A reversible process is a quasi-static process in which no dissipative forces, such as friction, are present

A reversible change must be quasi-static – but a quasi-static process does not need to be reversible

Isobaric Process Pressure is constant

Isochoric Process Volume is constant

Isothermal Process Temperature is constant

Adiabatic Process No heat enters or leaves the system ($q=0$)

Isentropic Process Entropy is constant

Zeroth Law

Two bodies A and B are in thermal equilibrium. If C is in thermal equilibrium with B, then A and C are also in equilibrium.

If warm and cool objects are placed in thermal contact, energy, known as heat, flows from the WARM to the COLD object until thermal equilibrium is established

Zeroth Law of Thermodynamics

Two systems, separately in thermal equilibrium with a third system, are in thermal equilibrium with each other

The property which the three systems have in common is known as **temperature θ** .

$$\text{If } \theta_1 = \theta_2 \text{ and } \theta_2 = \theta_3, \text{ then } \theta_1 = \theta_3$$

The Kelvin Scale

Using **temperature θ** the kelvin scale was derived using Boyle's law.

$$T_K = T_C + 273.15$$

Work in a Gas

If you have a cylinder with cross sectional area **A**, then the force pushing a piston down a distance **d** would be...

$$P = F / A \quad w = Fd \quad w = pAd \quad = PV$$

$$w = P\Delta V_{gas}$$

Changes in Volume under constant Pressure

Under constant pressure, evolved gas does **work on the surroundings**.

WORK IS DONE BY THE SYSTEM onto the surroundings

ENERGY OF THE SYSTEM decreases

*If ΔV is positive (gas expands), work done **on the gas** $w = -P\Delta V$*

*If ΔV is negative (gas compressed), the work done **on the gas** is still $w = -P\Delta V$*

Why? Work done **on the gas** means that the energy of the gas has increased.

Changes in Volume not under constant pressure

Work against variable pressure

$$w = \sum_{V_1}^{V_2} P\Delta V \quad w = \int_{V_1}^{V_2} \frac{nRT}{V} dV = \int_{V_1}^{V_2} PdV \quad = nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$w = - \int_{V_1}^{V_2} PdV = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

Isobaric Constant pressure

$$W = P(V_2 - V_1)$$

Isothermal Constant temperature

Enthalpy

$$H = U + PV$$

PV and U are state functions, therefore Enthalpy (H) is also a state function.

When considering **only pressure and/or volume work**

$$\Delta H = q_p \text{ when all other work is 0}$$

q_p is the heat transferred (to or from the system) at constant pressure P.

Internal Energy and Enthalpy

Enthalpy can be measured directly, using calorimetry for example.

$$\Delta U = \Delta H - P\Delta V$$

Endothermic Absorbs heat from the surroundings. Feels cold. $\Delta H = +ve$

Exothermic Transfers heat to the surroundings. Feels hot. $\Delta H = -ve$

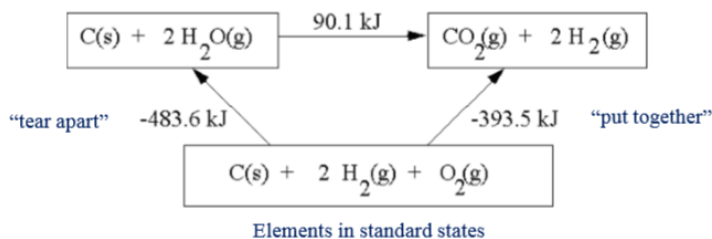
Hess's Law

If a reaction is carried out in a number of steps, ΔH for the overall reaction is the sum of ΔH for all the individual step.

Standard Molar Enthalpy Of an element is defined as **zero IN ITS MOST NATURAL STATE**.
This defines the zero on an energy scale.

This allows the state functions of ΔH and ΔU to be used to calculate enthalpies of reactions.

$$\Delta H_{\text{reaction}}^{\ominus} = \sum \Delta H_{\text{f}}^{\ominus}(\text{products}) - \sum \Delta H_{\text{f}}^{\ominus}(\text{reactants})$$



Heat Capacities

Heat capacities are quoted in different ways

Molar Heat Capacity The energy required to raise the temperature of **one mole** of substance by **one degree celcius**

Specific Heat Capacity The energy required to raise the temperature of **unit mass (usually 1kg)** of a substance by **one degree celcius**

(Unspecific) Heat Capacity The energy required to raise the temperature of a **given substance** by **one degree celcius**

Monatomic Gasses

For one mole of monatomic gas being heated at constant volume

$$\Delta U = 0 + q = C_{V,m}\Delta T$$

No work is being done on the gas, hence the 0 (replacement of w). $C_{V,m}$ is the molar heat capacity at constant volume. Multiply this number by the number of moles if it is different.

For a monoatomic gas, the molar heat capacity at constant volume is

$$C_{V,m} = \frac{3}{2}R$$

Instead of constant volume, let's try constant pressure

$$\Delta U = w + q = C_{P,m}\Delta T$$

For a monoatomic gas, the molar heat capacity at constant volume is

$$C_{P,m} = \frac{5}{2}R$$

$$C_{V,m} + R = C_{P,m}$$

BUT THE SPECIFIC HEAT CONSTANT IS NOT CONSTANT OVER TEMPERATURE

Step 1: Find heat capacity expressed as a polynomial

$$C_{P,m} = d + eT + fT^2$$

Step 2: Use the constants you have found into this equation

$$\Delta(\Delta H_m) = \Delta d + \Delta e \left(\frac{T_2^2 - T_1^2}{2} \right) - \Delta f \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

SPECTROSCOPY

Electronic Spectroscopy

Light and Its Interaction with Matter

Light can be a wave or a particle.

Snell's Law

$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$

The photoelectric effect creates the ideas of **photons**, an entity with wave and particle like properties

Properties of photons

Atoms are **polarized** in a static electric field (electrons to +ve, nucleus to -ve). This results in a **dipole moment**. The side of this dipole depends on the **polarizability**.

Energy is transferred from incident light to the molecule and induced oscillating dipole generated.

This is an **absorption**. The reverse is possible during relaxation and is called **emission**.

$$c = v\lambda$$

$$v = \frac{c}{n}$$

$$E = hv$$

$$h = 6.63 \times 10^{-34} \text{ Js} \quad c = 3 \times 10^8 \text{ m s}^{-1} \quad n > (\text{or equal to}) 1$$

All things have a **natural frequency** and only when the frequency of light matches that of the atom, the maximum amount of energy is transferred.

Spectroscopy and Spectrometers

A **spectrum** is a plot of intensity against function of frequency. Many instruments use **double beam** arrangements and the ratio of the two beams gives a **transmission spectrum** (I/I_0).

$$v = c\tilde{\nu} = \frac{c}{\lambda}$$

$$\tilde{\nu} = \frac{1}{\lambda} (\text{m}^{-1}) \quad 1\text{eV} = 806600 \text{ m}^{-1}$$

Energy Levels and the Electronic Structure of Atoms

Energy levels are **discrete** and **quantized**.

Rydberg Equation

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

R_H = Rydberg Constant = 109468 cm^{-1} for the hydrogen atom. n_1 is an integer for each series

1 Lyman

2 Balmer

n_2 takes the form $n_1+1, n_2 + 2, n_1 + 3 \dots$

As n_2 tends to infinity, the spacing between the levels get closer. When the lines converge ($\sim n=8$) the electron is removed from the effect of the nucleus and is **ionized**. The energy of the converged lines is the **ionization energy**. The **ionization potential** of an atom is the energy required to remove it from the ground state.

For the H atom, the orbitals of level n are of the same degeneracy.

Selection Rules

$$\Delta n = 1, 2, 3, \dots$$

$$\Delta l = \pm 1$$

$$m_s = \pm \frac{1}{2} \quad \Delta S = 0$$

Also **orbital overlap determines the transition strength**.



Vibrational Spectroscopy

Infrared Spectroscopy

Diatomic molecules can be seen as **molecular springs**

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

Selection Rules

Vibrations may only show up in the IR spectrum if the vibration concerned causes a change in the molecular dipole moment

Polyatomic molecules

NON LINEAR

3N - 6 Vibrational Modes

LINEAR

3N - 5 Vibrational Modes (e.g. diatomics: 3(2)-5=1)

NMR Spectroscopy

Nuclei possess spin, ^1H has spin $1/2$.

Multiplicity

$$\text{Number of energy levels} = 2I + 1$$

For H, $I = 1/2$, therefore $2(1/2)+1 = 2$ energy levels.

$$\Delta E = \frac{h\gamma}{2\pi} B$$

$$\nu = \frac{\gamma}{2\pi} B$$

γ is the **magnetogyric ratio**, for ^1H its $2.6752 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}$

The relationship between frequency and field is 42.577 MHz/T.

Shielding

Less shielded areas (less electron density) show higher frequency and high field.

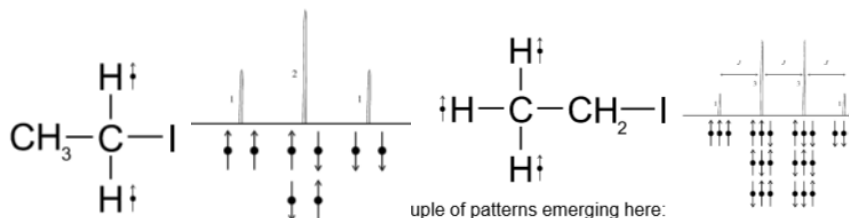
Chemical Shift Scale

Referenced to TMS. Chemical shift is defined as

$$\delta (\text{ppm}) = \frac{(v_{\text{sample}} - v_{\text{TMS}}) \text{Hz}}{\text{operating frequency MHz}}$$

Fine Structure

Is due to spin coupling in the same molecule to nearby atoms. 1-3 relationship.



n spins split the band into n + 1 peaks.

The gaps between the peaks are the same in this cases and is referred to as **coupling constant (J)**, which reflects the magnetic coupling between nuclei

The intensities match that as in Pascal's triangle and the number of spins can be obtained from the splitting pattern

<i>Number of spins (n)</i>	<i>number of peaks (n+1)</i>	<i>Intensities</i>
0	1-singlet	1
1	2-doublet	1 1
2	3-triplet	1 2 1
3	4-quartet	1 3 3 1
4	5-quintet	1 4 6 4 1
5	6-sextet	1 5 10 10 5 1
6	7-septet	1 6 15 20 15 6 1

Aromatics

For aromatics the **ring current** adds to the applied H nuclei and resonate are deshielded.

Conductivity and Mobility

Ohm's Law, Resistance and Conductance

Voltage	V	Measured in Volts
Current	I	Measured in Amps
Resistance	R	Measured in Ohms

$$\text{Ohms Law: } V = IR$$

Resistance is the extent to which a material resists the passage of electric current.

Conductance	G	Measured in Siemens
-------------	---	---------------------

Conductance is the extent to which a material allows the passage of an electric current.

$$G = \frac{1}{R} \quad \text{unit: Siemens } (S = \Omega^{-1})$$

Resistance of the load...

Depends on the length	R is proportional to l
Depends on the area	R is inversely proportional to A (double area, half resistance)

Resistivity and Conductivity

From the above relationships we can write

$$R = \frac{\rho l}{A}$$

Where rho is the resistivity constant of the material. Conductivity is the inverse

$$G = \frac{1}{R} = \frac{1A}{\rho l} = \kappa \frac{A}{l} \quad G = \kappa \frac{A}{l}$$

Where kappa is the conductivity

Units

Resistivity	ρ	$\Omega \text{ m}$
Conductivity	κ	S m^{-1}

Beware the use of millisiemens (ms) and centimetres (cm) etc...

Molar Conductivity

For the conductivity of a solution, the **cell constant is L/A**

If you have more ions in solution, you imply a higher conductivity. Therefore the molar conductivity (Λ_m) of a solute can be calculated.

$$\Lambda_m = \frac{\kappa}{c}$$

Where c is the concentration

Molar Conductivity Λ_m $\text{S mol}^{-1} \text{m}^{-1} \text{dm}^3$

As the concentration of ions increases, the conductivity will increase but the molar conductivity should remain constant.

Strong and Weak Electrolytes

STRONG ELECTROLYTES

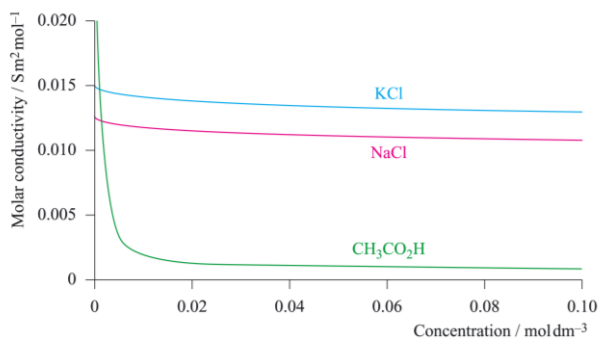
NaCl, KCl

Non-ideality, viscous drag between ions

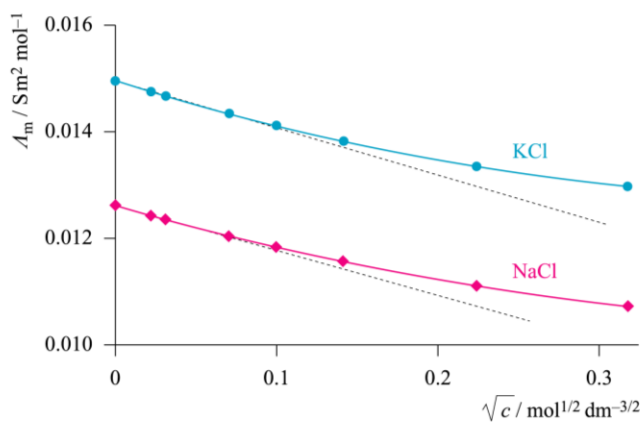
WEAK ELECTROLYTES

Carboxylic acids

Dissociation more complete at low concentration due to equilibrium



Kohlrausch's Law and Limiting Molar Conductivity



$$\Lambda_m = \Lambda_m^\infty - k\sqrt{c}$$

Holds at low concentrations. At infinite dilution (low concentration $0 < c^{1/2} < 0.1$) no ion may interact with any other ion.

Law of Independent Migration of Ions

He also found out...

$$\Lambda_m^\infty = \nu^+ \lambda^{\infty+} + \nu^- \lambda^{\infty-}$$

Where

Conductivity of compound Λ

Conductivity of individual ions λ

Number of anions (cations) per formula unit ν

Ostwald's Law of Dilution

$$K_a = \frac{c\alpha^2}{1-\alpha} \quad \text{and} \quad \alpha = \frac{\Lambda_m}{\Lambda_m^\infty}$$

Then...

$$K_a = \frac{c\Lambda_m^2}{\Lambda_m^\infty(\Lambda_m^\infty - \Lambda_m)}$$

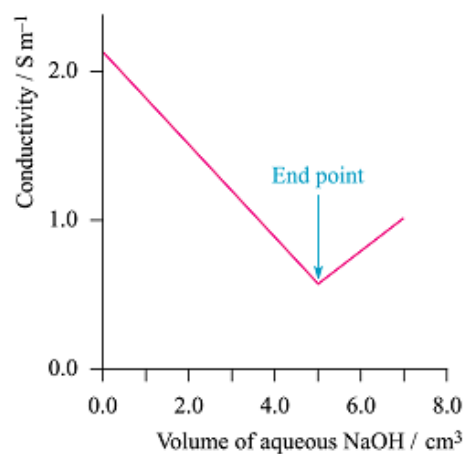
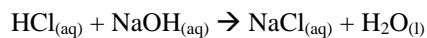
Rearrange to give linear form...

$$c\Lambda_m = \frac{K_a c \Lambda_m^{\infty 2}}{\Lambda_m} - K_a \Lambda_m^\infty$$

Now in linear form. Plot conductivity vs reciprocal of molar conductivity.

Conductometric Titrations

Monitor conductivity as solution is added



WEAK ACID / STRONG BASE

Conductivity starts low, rises as more acid reacts.

End point is where gradient changes

STRONG ACID / WEAK BASE

Conductivity starts high and begins to drop

End point is where gradient changes due to equilibrium

SPARINGLY SOLUBLE SALT

Insoluble salt formed

After end point soluble AgNO_3 is added to AgCl etc...

Ionic Mobility, Conductivity and Hydration

Why does H^+ appear to have an anomalous conductivity? And how mobile are ions in the solution.

$$F_E = zeE$$

Force on ion F_E

Electric Field E

Charge on electron e

Number of charges z

Eventually due to frictional forces...

$$u = \frac{s}{E} = \frac{ze}{6\pi\mu a}$$

Transport Number

Counter ions keep solution electrically neutral and there is no need to have two types of ion to carry the charge. Each ion carries a fraction of the total current, which is known as the transport number.

$$t_+ = \frac{v_+\lambda_+}{\Lambda_m^0}$$

Acids and Bases

Dissociation of Water



Since $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ are much smaller than $[\text{H}_2\text{O}]$, and the concentration of water is constant during dissociation, you can simplify the expression.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

K_w is constant for water and is $10^{-14} \text{ mol}^2 \text{ dm}^{-6}$. That means that pure water ($[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ mol dm}^{-3}$).

Therefore if $[\text{H}_3\text{O}^+] = 10^{-x} \text{ mol dm}^{-3}$ then $[\text{OH}^-] = 10^{-(14-x)}$

The pH Scale

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

pH	0	3	5	7	9	11	14
$[\text{H}_3\text{O}^+]$	10^{-0}	10^{-3}	10^{-5}	10^{-7}	10^{-9}	10^{-11}	10^{-14}
$[\text{OH}^-]$	10^{-14}	10^{-11}	10^{-9}	10^{-7}	10^{-5}	10^{-3}	10^{-0}
	Acidic			Neut	Basic		

Strong Acids and Bases

Strong acids and bases are ionic compounds that are completely dissociated in water (HNO_3 or NaOH)

Easy as can use above formula to work out, for acid "HA" at concentration $[\text{HA}] > 10^{-6} \text{ M}$ then substitute into pH formula.

e.g. HCl at 0.1 M has $\text{pH} = 1$.

For bases, $\text{pH} = 14 + \log_{10}[\text{B}]$

$$\text{pH} + \text{pOH} = \text{p}K_w \quad \text{p}K_a + \text{p}K_b = \text{p}K_w$$

Weak Acids and Bases

Not completely dissociated.

Let α = fraction of acid dissociated and c = concentration of acid as prepared

$$K_a = \frac{c\alpha^2}{1-\alpha} \quad pH = \frac{1}{2}(pc + pK_a) \quad p(x) = -\log_{10}(x)$$
$$K_b = \frac{\alpha^2 c}{(1-\alpha)} \quad pH = pK_w - \frac{1}{2}(pc + pK_b)$$

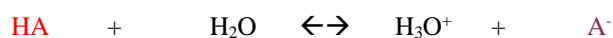
For example, an acid HA at 1 M. $c = 1$ M, therefore $pc = 0$.

$$pH = \frac{1}{2}(pc + pK_a) \rightarrow pH = \frac{1}{2} pK_a$$

So an acid with that concentration with a pK_a of 12 has pH 6. Etc...

Water is Amphiprotic

Meaning that it has the capacity to act as an acid or as a base.



ACID

CONJUGATE BASE

A^- behaves as a base. Strong acids give weak conjugate bases, whereas weak acids give strong conjugate bases.

Henderson Hasselbalch Equation

$$pK_a = pH + \log_{10} \left(\frac{[HA]}{[A^-]} \right) \quad \text{or when rearranged } pH = pK_a + \log_{10} \left(\frac{[A^-]}{[HA]} \right)$$

Buffers

A buffer is a solution that resists changes in pH.

Prepare a solution with $[HA] = [A^-]$

$$pK_a = pH + \log_{10} ([HA]/[A^-])$$

$$\log_{10}([HA]/[A^-]) = 0$$

$$pK_a = pH$$

HA acts as a sponge for OH^-

A^- acts as a sponge for H_3O^+

Example.

Take a weak acid $pK_a = 4$.

Use $[HA] = [A^-] = 0.05 \text{ M}$

The solution has pH 4 because $pH = pK_a$

Add the same volume of 0.01 M HCl

New ratio is $[A^-]/[HA] = (0.05 - 0.01) / (0.05 + 0.01)$

Change in $pH = \log_{10} 0.67 = -0.17$ (therefore goes to pH 3.83)

Note: Buffers have an effective pH range of $pK_a = \pm 1$.

Electrochemistry

Introduction to Electrochemistry

It's a method of understanding electron transfer reactions.

Half-Reactions

A way of understanding electrochemical reactions and are written as reduction reactions.

Electrons are always on left hand side for that reason.

Example. $Zn^{2+}_{(aq)} + 2 e^- \rightarrow Zn_{(s)}$ $Cu^{2+}_{(aq)} + 2 e^- \rightarrow Cu_{(s)}$

The difference between the two half reactions gives the redox reaction.

$Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

A redox couple is where oxidized and reduced components can be written as a redox couple.

Ox / Red is written as Zn^{2+} / Zn

Electrodes and Notation

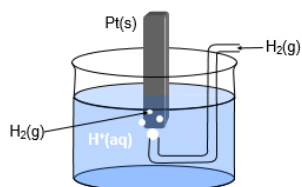
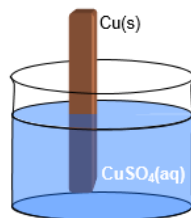
When considering a single electrode reaction convention:

- Phase boundaries are represented by vertical lines
- Write reduced species on LHS and oxidized on RHS Red | Ox
- Represent the reaction by a reduction half reaction

Types of Cell

Metal / Metal ion electrode

- Cu metal takes part in the cell reaction
- $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$
- $\text{Cu}(\text{s}) | \text{Cu}^{2+}(\text{aq})$

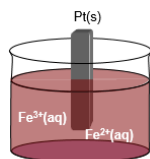
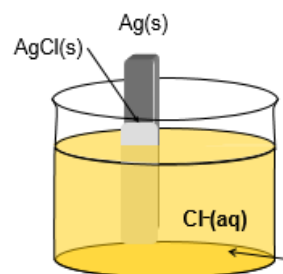


Hydrogen electrode

- Hydrogen electrode used as standard electrode
- Pt electrode does not take part in the reaction
- $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$
- $\text{Pt}(\text{s}) | \text{H}_2(\text{g}) | \text{H}^+(\text{aq})$

Insoluble Salt Electrode

- Metal electrode element covered by porous layer of its salt
- Normally NaCl or KCl solution
- $\text{AgCl}(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$
- $\text{Ag}(\text{s}) | \text{AgCl}(\text{s}) | \text{Cl}^-(\text{aq})$



Redox Electrode

- Pt electrode does not take part in reaction
- $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$
- $\text{Pt}(\text{s}) | \text{Fe}^{2+}(\text{aq}), \text{Fe}^{3+}(\text{aq})$

Galvanic Cells and Conventions

Measure potency as potential difference with respect to an arbitrary reference electrode

- Standard Temperature 298 K
- Standard Pressure 1 atm
- Standard Concentration 1 M
- Standard Electrode Hydrogen Electrode

An electrochemical (galvanic cell) comprises two electrodes which differ in potential

Electrochemical potential from individual standard electrode potentials

Cell	Reaction	Applications
Galvanic	Spontaneous Reaction	Batteries
Fuel	External Reactant Supplied	Higher power and longer life. Aerospace, electric cars..
Electrolytic	External Current Drives Reaction	Electroplating, Electrolysis, Al refining, Solar fuels?

Galvanic Cell Conventions

- Two electrode elements (metallic conductors) are immersed in an ionic conductor electrolyte (liquid or solid).
- Electrochemical cell involves flow of electrons arising from reduction and oxidation reactions at the electrodes

	LHS	RHS
Electrode	Anode	Cathode
Charge	Negative	Positive
Redox Reaction	Oxidation	Reduction

Note that the anode and cathode are in difference electrolytic cells

Standard Potential

Measure of potency of reduction reactions referenced to the standard hydrogen electrode

The more positive the E^0 the greater the affinity of the electrode to be reduced

Spontaneous cell reaction involves electron release (oxidation) on the LHS and reduction on the RHS

$$E^0_{(LHS)} < E^0_{(RHS)}$$

Type of Galvanic cells

Single electrolyte cell

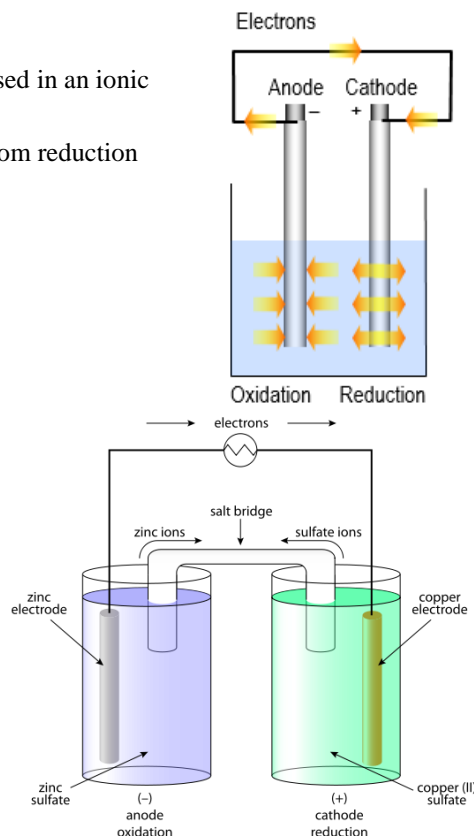
- Electrodes share a common electrolyte

Salt bridge cell

- Different electrolytes in separate compartments
- Electrically neutrality maintained by a salt bridge (salt solution in a gel)
- Bridge indicated by double vertical bar ||

Daniel cell

- Sulfate ions migrate through salt bridge
- Specific salt bridge cell consisting of Zn and Cu.
- $Zn_{(s)} | ZnSO_4(aq) || CuSO_4(aq) | Cu_{(s)}$



Measurement of Cell Potential

E^0 of the Zn electrode - 0.76 V

“ Cu electrode + 0.34 V

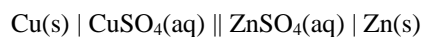
The more negative on the LHS is oxidation and the more positive on the RHS is reduction. This will give a spontaneous reaction reading $L \rightarrow R$.



$$E^0 (\text{cell}) = \text{RHS} - \text{LHS} = 0.34 - - 0.76 \text{ V} = 1.1 \text{ V}$$

On the other hand...

Imagine that, in an exceptional circumstance, the cell was the wrong way around.

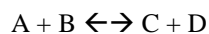


$$E^0 (\text{cell}) = \text{RHS} - \text{LHS} = -0.76 - 0.34 \text{ V} = - 1.1 \text{ V}$$

The negative sign indicates that the spontaneous reaction is the reverse of that written.

Nernst Equation

For a reversible reaction



$$Q = \frac{[C][D]}{[A][B]}$$

Concentrations include all components not in solid state. When Q and K are not equal the reaction can proceed

Condition	Direction
$Q > K$	Backwards
$Q = K$	No reaction
$Q < K$	Forwards

If E^0 is measured under nonstandard conditions we can apply the Nernst Equation

$$E = E^0 - \frac{RT}{nF} \ln Q$$

n Number of electrons transferred in cell reaction

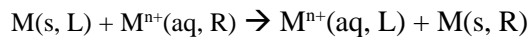
F Faraday constant

Concentration Cells

Cell with same electrode as anode and cathode under standard conditions have no potential difference. The driving force for these reactions is the concentration difference.



The cell reaction is ...



$$Q = \frac{[M^{n+}(R)]}{[M^{n+}(L)]} \quad E = E^0 - \frac{RT}{nF} \ln \frac{[M^{n+}(R)]}{[M^{n+}(L)]}$$

Note that for these cells $E^0 = 0$!

Gibbs Free Energy of Cell Reaction

Gibbs Free Energy (G) under standard conditions...

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

ΔG_m^0 Standard molar free energy of the reaction

Note that E^0 is positive so that ΔG_m^0 is negative

Also when not under standard conditions $\Delta G = -nFE$

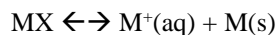
Equilibrium Constants from the Standard Cell Potential

At equilibrium $K = Q$, and therefore $E = 0$ V. The Nernst equation can be rearranged.

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

Solubility Constants from Cell Potentials

A sparingly soluble salt is governed by the equilibrium



K_s is the solubility constant or product

$$K_s = [M^+(aq)][X^-(aq)]$$

Note that the solubility of MX is given by $\text{SQRT}(K_s)$

END OF 1C24 FORMULA

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:

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

Lecture 2

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

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

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

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

Entropy change at a state function:

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

Trouton's Rule:

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

Lecture 3

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

$$S = k_B \ln W \quad \text{Where } k_B = 1.38 \times 10^{-23}$$

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:

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

Calculating change in G° through equilibrium constant:

$$\Delta G^\circ = -RT \ln K_p$$

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

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

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

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

THERMODYNAMICS II

Topic 1: Single component mixtures

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

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

$$dG = 0 \quad \text{if} \quad \mu_1 = \mu_2$$

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

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

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

$$P_T = P_A + P_B$$

$$P_T = x_A P_A^* + x_B P_B^*$$

Dalton's Law

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

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

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 ΔH_{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

$$\Delta T_b = T_b - T_b^* = \left(\frac{RT_b^{*2}}{\Delta H_{vap}} \right) x_{solute}$$

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

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

$$MM_{solute} = \frac{K_f \text{mass}_{solute}}{\Delta T_f \text{mass}_{solvent}}$$

Osmotic Pressure

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

$$\pi = RT c_{solute}$$

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

COMPLEX KINETICS

Lecture 1

The steady state approximation (SSA)

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

Lecture 2

The Lindemann mechanism and the SSA

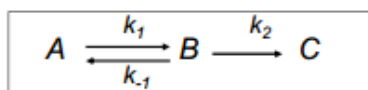
$$\text{rate} = \frac{d[P]}{dt} = k_2[A^*] = \frac{k_2 k_1 [M]}{k_{-1}[M] + k_2} [A]$$

Activation Energies

$$k_\infty = \frac{k_2 k_1}{k_{-1}} = \frac{A_1 A_2}{A_{-1}} e^{-\frac{E_{a1} + E_{a2} - E_{a-1}}{Rt}}$$

Lecture 3

SSA vs. QEA



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

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

SSA

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

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

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

QEA

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

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

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

Lecture 4

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

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

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

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

THEORIES OF CHEMICAL REACTIONS

Relaxation Kinetics

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

Diffusion Controlled Reactions in Solution



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

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

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

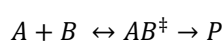
$$k_D^l = 4\pi L D_{AB} d_{eff}$$

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

$$\delta = \frac{Z_A Z_B e^2}{4\pi \epsilon_0 \epsilon_r d_{AB} k_B T}$$

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

Activation Controlled Reactions and Transition State Theory



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

$$K^\ddagger = \frac{k_D}{k_{-D}}$$

$$K^\ddagger = \frac{k_B T}{h}$$

$$\text{so } k_{TST} = \kappa \frac{k_B T}{h c_0} K^\ddagger$$

$$k_{TST} = \kappa \frac{k_B T}{h c_0} e^{\left(\frac{\Delta S^\ddagger}{R} \right)} e^{-\left(\frac{\Delta H^\ddagger}{RT} \right)}$$

$$A = e\kappa \frac{k_B T}{h c_0} e^{\left(\frac{\Delta S^\ddagger}{R}\right)} \quad \Delta G_{ES}^\ddagger = \frac{Z_A Z_B e^2 L}{4\pi\epsilon_0\epsilon_r d_{AB}} \quad \ln k_{TST}^I = \ln k_{TST} - \frac{Z_A Z_B e^2}{4\pi\epsilon_0 d_{AB} k_B T} \left(\frac{1}{\epsilon_r}\right)$$

$$\Delta S_{ES}^\ddagger = -\frac{C_s Z_A Z_B e^2 L}{4\pi\epsilon_0\epsilon_r d_{AB}}$$

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

SURFACE CHEMISTRY & HOMOGENEOUS CATALYSIS

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

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

Laplace Equation

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

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

Kelvin Equation

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

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

Gibbs absorption equation

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

Micelle equation

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

Area per molecule adsorbed

$$a_2 = \frac{1}{F_2 N_{AV}}$$

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

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

Bimolecular

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

BET Model

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

END OF 2C2Y FORMULA

3C21: PHYSICAL CHEMISTRY II

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.

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

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

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

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

The chain rule:

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

PHOTOCHEMISTRY AND PHOTOBIOLOGY

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

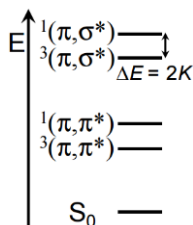
State Classifications and MO Diagrams

K: Exchange repulsion

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

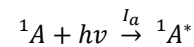
$$E_{\text{singlet}} = J + K$$

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

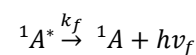


Quantum Yields and Luminescent Lifetimes

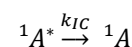
$$\phi = \frac{\text{number of moles of product produced } (s^{-1} m^{-3})}{\text{number of einsteins of light absorbed } (s^{-1} m^{-3})}$$



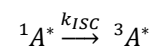
Excitation during initial photon absorption



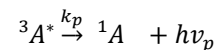
Fluorescence



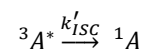
Internal Conversion



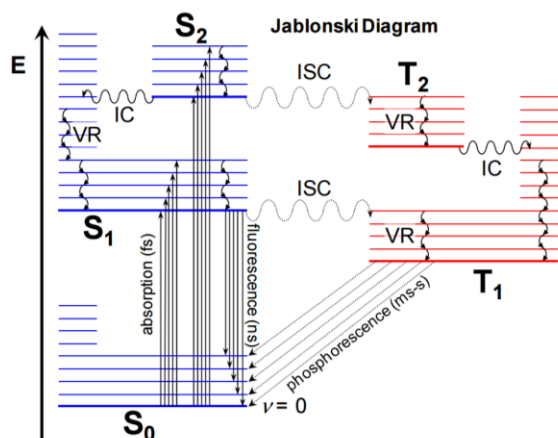
Inter System Crossing



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?

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

Absorption of Light

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

Fermi's Rule

$$\Gamma = \frac{2\pi}{\hbar} |\kappa_{int}|^2 \rho$$

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

$$\Delta E = mh\nu$$

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

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