

REVIEW

(1)

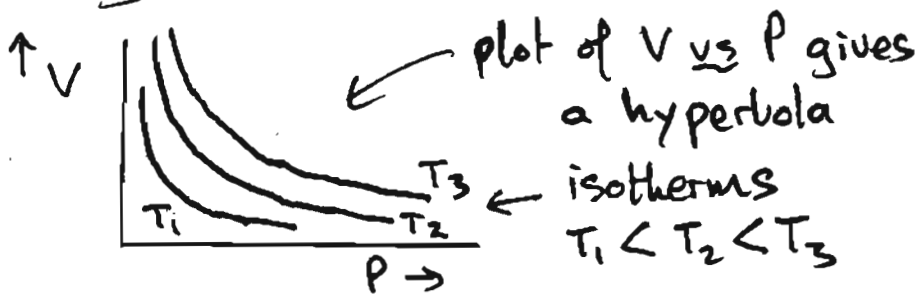
A. GAS LAWS

- relevant to atmospheric chemistry

a) Volume and pressure (const. T)

force/area i.e. Nm^{-2}

Boyles Law (1662)

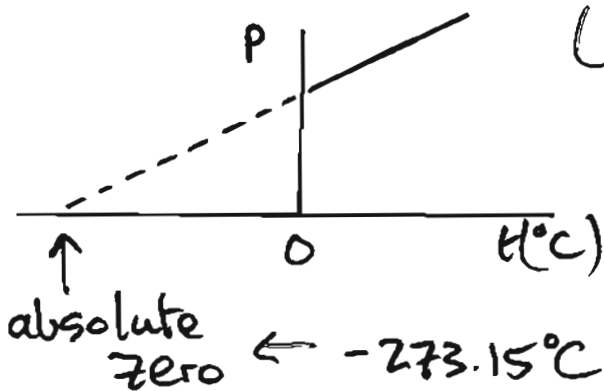


$$V \propto \frac{1}{P}$$

$$\text{i.e. } PV = \text{constant}$$

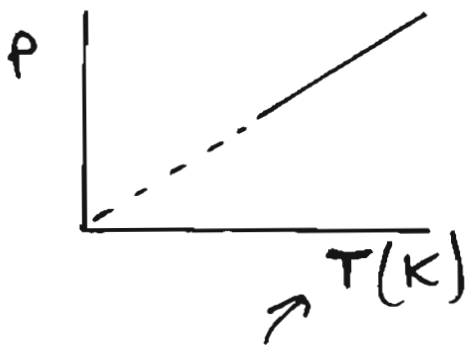
b) Pressure and temperature (const. V)

(Amontous 1702)



$$P \propto T$$

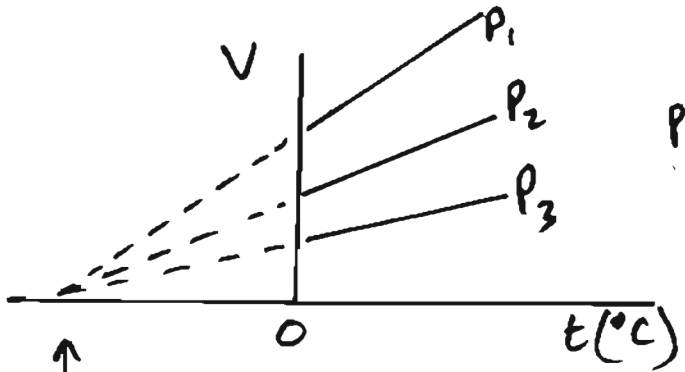
$$\text{i.e. } \frac{P}{T} = \text{constant}$$



thermodynamic temp.

c) Volume and temperature (const. P)

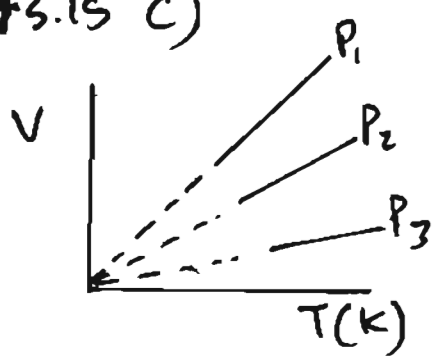
Charles law (1787) (also Gay-Lussac, 1802)



$P_1 < P_2 < P_3$

abs. zero
(-273.15 °C)

$V \propto T$



i.e. $\frac{V}{T} = \text{constant}$

d) Avogadro (1811)

At constant P and T

$V \propto n$

i.e. $\frac{V}{n} = \text{constant}$

n = no. of moles

→ one mole of all (ideal) gases at standard temperature and pressure (1 atm / 273.15 K) occupies 22.414 L.

e) Ideal gas law

③

Combining the gas law equations:

$$V \propto \frac{1}{P}; \quad V \propto T; \quad V \propto n$$

$\Rightarrow V \propto \frac{nT}{P}$; the proportionality const. is \underline{R} , the gas constant

$$\boxed{PV = nRT}$$

Since 1 mol of ideal gas occupies 22.414 L at STP,

then $R = \frac{PV}{nT} = \frac{(1 \text{ atm})(22.414 \text{ L})}{(1 \text{ mol})(273.15 \text{ K})} = \boxed{0.08206 \text{ LatmK}^{-1} \text{ mol}^{-1}}$

In SI units, $1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$

$$\therefore R = \frac{(1.01325 \times 10^5 \text{ Pa})(22.414 \times 10^{-3} \text{ m}^3)}{(1 \text{ mol})(273.15 \text{ K})}$$

$$R = 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} = \boxed{8.314 \text{ JK}^{-1} \text{ mol}^{-1}}$$

Note $\text{Pa} = \text{Nm}^{-2}$

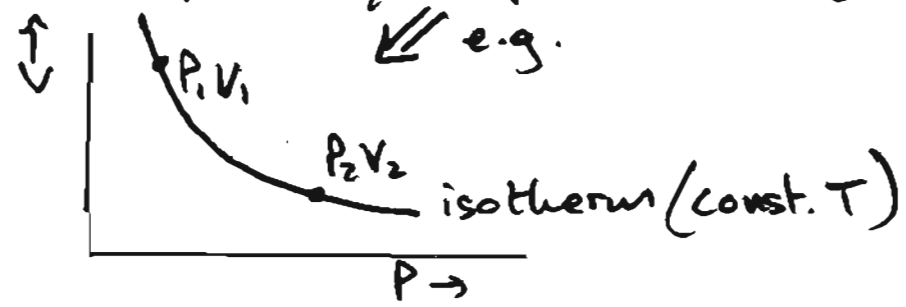
hence " Pa m^3 " = $\text{Nm}^{-2} \text{ m}^3 = \text{Nm}$
force \times distance

i.e. energy $\rightarrow \frac{\text{J}}{\text{mol}}$

f) Using the gas laws

$$\left. \begin{aligned}
 P_1 V_1 &= P_2 V_2 \quad (\text{const. } T) \\
 \frac{V_1}{T_1} &= \frac{V_2}{T_2} \quad (\text{const. } P) \\
 \frac{P_1}{T_1} &= \frac{P_2}{T_2} \quad (\text{const. } V)
 \end{aligned} \right\} \text{i.e. } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

- for example: start with press. P_1 and vol. V_1 and can get the pressure if gas is expanded/compressed to V_2



Note: when using $PV = nRT$

if P is in atm and V is in L, then use $R = 0.08206 \text{ LatmK}^{-1} \text{ mol}^{-1}$

if P is in Pa and V is in m^3 then use $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ (remember $1 \text{ L} = \text{dm}^3 = 10^{-3} \text{ m}^3$)

Hence: $1 \text{ L} \cdot \text{atm} = 101.325 \text{ Pa} \cdot \text{m}^3$ (joules)

g) Mixture of ideal gases.

(5)

- total press. is the sum of the P 's due to each gas

$$P_{\text{tot}} = P_1 + P_2 + P_3 + \dots + P_N = \sum_{i=1}^N P_i$$

← final value
← initial value

Dalton's Law of Partial Pressures ... each gas in a mixture exerts its own press. indep. of other gases in the mixture.

→ i.e. partial press. of gas i is ... $P_i = \frac{n_i RT}{V}$

no. of moles of i ← total vol.

Say we have: n_{O_2} moles of O_2
 n_{N_2} ——— N_2
 n_{CO_2} ——— CO_2

Total no. of moles, $n = n_{O_2} + n_{N_2} + n_{CO_2}$

and $P_{\text{tot}} = P_{O_2} + P_{N_2} + P_{CO_2}$ (Dalton)

and since $P_{O_2} = \frac{n_{O_2} RT}{V}$, $P_{N_2} = \dots$ etc.

$$\text{then } P_{\text{tot}} = \frac{n_{O_2} RT}{V} + \frac{n_{N_2} RT}{V} + \frac{n_{CO_2} RT}{V}$$

$$P_{\text{tot}} = \frac{RT}{V} (n_{O_2} + n_{N_2} + n_{CO_2}) = \boxed{\frac{RT}{V} \sum_{i=1}^N n_i}$$

Define mole fraction for a gas i

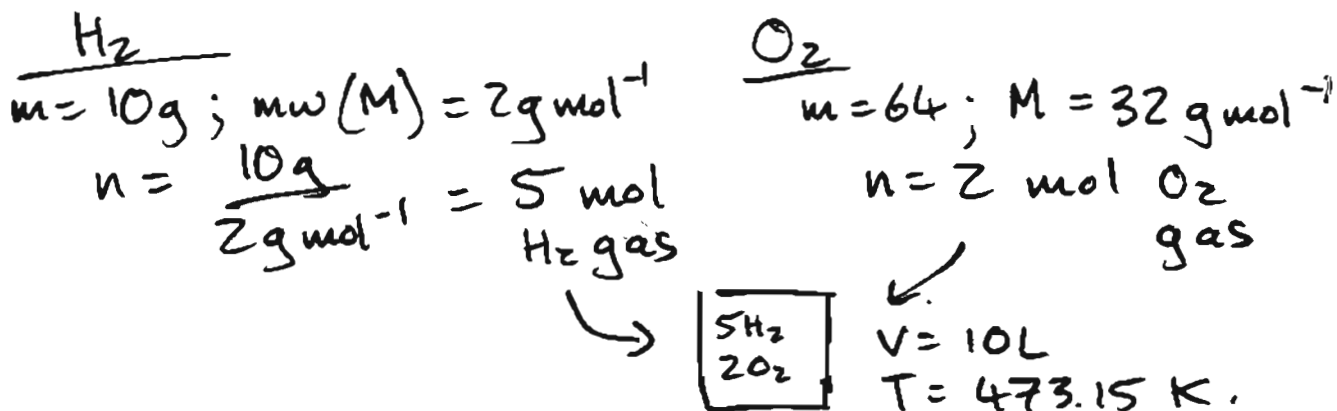
$$\boxed{x_i = \frac{n_i}{n}}$$

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

$$\text{and } \boxed{P_i = x_i P_{\text{tot}}}$$

← often written as P_T

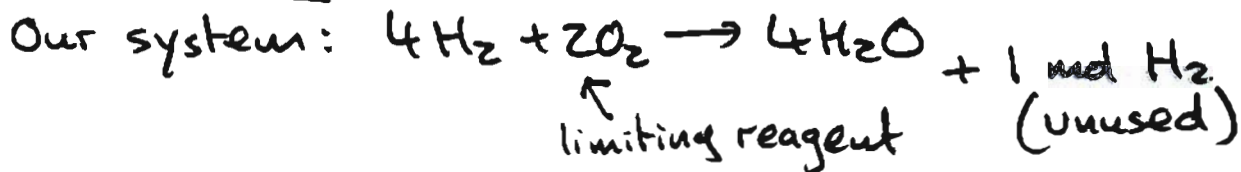
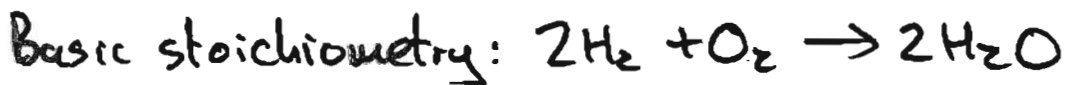
⑥
 Q If 10g H₂ and 64g O₂ are contained in a 10L flask at 200°C, calculate the total pressure of the mixture in atm.



$$P_T = \frac{RT}{V} \sum n_i = \frac{(0.0821 \text{ LatmK}^{-1} \text{ mol}^{-1})(473.15)}{10L} \sum (5+2) \text{ mol}$$

$$\Rightarrow \sim \underline{\underline{27.2 \text{ atm}}}$$

Let's say we spark this mixture - what's the final P in the flask?



Since T is 473.15K \gg 373.15K (b.p. H₂O)
 the product will be H₂O(g)

So $\sum n = 4 + 1 = 5$

$$P_T = \frac{(0.0821 \text{ LatmK}^{-1} \text{ mol}^{-1})(473.15 \text{ K})}{10L} \times 5 \text{ mol}$$

$$\Rightarrow \underline{\underline{19.4 \text{ atm}}}$$

h) Kinetic Theory of gases

Considers gases as particles zooming around in a box (can derive gas law this way)

Without proof:

(i) Average kinetic energy, $E_{av} = \frac{3}{2} RT \text{ mole}^{-1}$
 $(= \frac{3}{2} k_B T \text{ molec}^{-1})$

since $R = k_B N_A$ ← Avogadro no.
Boltzmann Const. $\approx 1.38 \times 10^{-23} \text{ JK}^{-1}$

(ii) Average speed (r.m.s.)

$v_{av} = \left(\frac{3RT}{M} \right)^{\frac{1}{2}}$
← molar mass

e.g. for N_2 (20°C) → 511 ms^{-1}
(~1100 mph)

(iii) Collisions

• mean free path, $\lambda = (3.1 \times 10^7 \text{ pm}^3 \cdot \text{atm} \cdot \text{K}^{-1}) \frac{T}{\sigma^2 P}$
e.g. N_2 (20°C, 1 atm) diam. of molec (pm) → $\sigma^2 P$

$\lambda \approx 6.6 \times 10^{-8} \text{ m}$ (≈ 175 molecular diameters)

• Divide $\frac{v_{av}}{\lambda}$ get an estimate of the no. of collisions (collision freq. z)
 $\approx 8 \times 10^9 \text{ collisions/sec}$

B. THERMODYNAMICS

(8)

- relationship between energy changes that occur in chemical or physical processes
- energy can be mechanical, electrical, heat, chemical, electromagnetic radiation... etc.
- can determine how much "work" is done; energy added or released
- tells us about the preferred direction by which a system will evolve
e.g. will the rx. go forward or not.
- can help us understand equilibria and equilibrium concentrations.

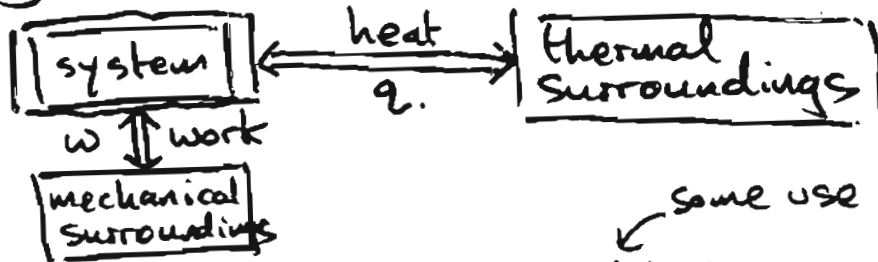
Note — not based on ideas of molecules or atoms, although a linkage between atomic/molecular properties and thermodynamics can be achieved using statistical methods

— it does not tell us about the rate of a process (how fast) domain of kinetics

(9)

a) 1st Law - energy is conserved

Can transfer energy in and out of a system either by heat (q) or work (w)



Can change the internal energy U by any combu. of q and w

i.e. $\Delta U = q + w$

some use E
 w and q are +ve when they tend to increase U of the sys., and -ve for a decrease in U .

(i) Work

Expansion or compression (imp. in gaseous systems)

... given by $w = -P\Delta V$

accounts for compression work being +ve (expansion is -ve)

(ii) Heat

- at const. V , $w = 0$, so $\Delta U = q$

- at const. P (more common, e.g. 1 atm),

the heat causes the volume to change, e.g. pushing back the atmosphere

so, $\Delta U = q - P\Delta V$

or, $q_p = \Delta U + P\Delta V$ - called ΔH , (enthalpy) 10

i.e. $q_p = \Delta H$
 ↑ heat at const. P
 ← heat change at const. P
 ... includes most biological processes.

So... we have, $\Delta H = \Delta U + P\Delta V$

For solids/liquids, ΔH and ΔU are v. similar (little vol. change)

For gases, the equ \underline{u} . can be written as:

$$\Delta H = \Delta U + \Delta nRT \quad \left(\begin{array}{l} \text{since} \\ \Delta(PV) = \Delta(nRT) \end{array} \right)$$

$$\Delta n = \# \text{ moles gaseous prods} - \# \text{ moles gaseous reactants}$$

It's a small correction; $\Delta nRT = [8.314 \text{ JK}^{-1} \text{ mol}^{-1}](298 \text{ K})$
 $\approx \underline{\underline{2.5 \text{ kJ mol}^{-1}}}$

b) Heat capacity, C_p :

Amount of heat required to raise the temp. of a substance by 1°C (or 1°K)

$$C_p = \frac{\Delta H}{\Delta T}$$

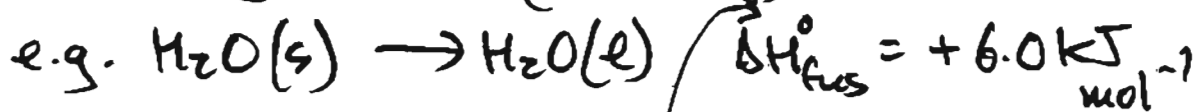
($\text{JK}^{-1} \text{ mol}^{-1}$)
units

Water has a very high heat capacity ($\sim 75 \text{ JK}^{-1} \text{ mol}^{-1}$)
 -- good for the planet/biological systems

c) Thermochemistry of change

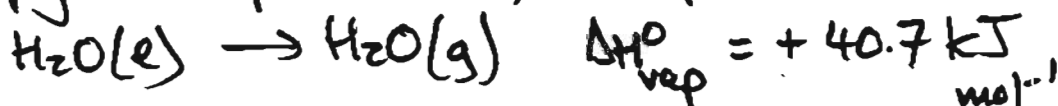
(1) Changes of physical state

(i) Enthalpy of fusion (melting), ΔH_{fus}



refers to a standard enthalpy change, pure materials at 1 atm, T is specified. Std. states for solutes is 1M.

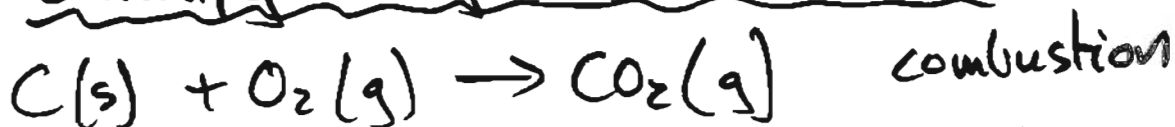
(ii) Enthalpy of vaporisation, ΔH_{vap}



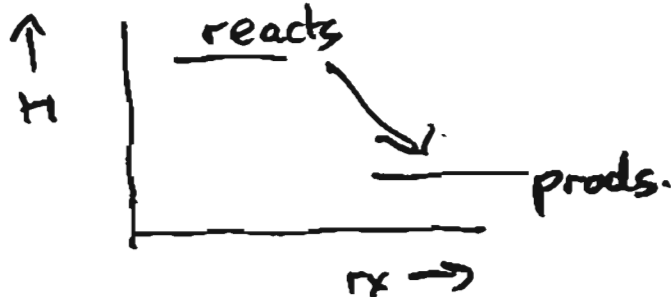
(iii) Enthalpy of sublimation, ΔH_{sub} (s \rightarrow g)

$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$ (enthalpy is a state function)

(2) Enthalpy changes for chemical rxns

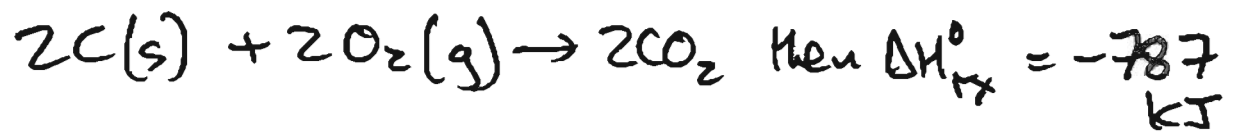


$\Delta H_{rxn}^\circ = -393.5 \text{ kJ}$
(exothermic)



i.e. downhill energetically.
...favourable

Note: ΔH is stoichiometric, i.e. if rx was,

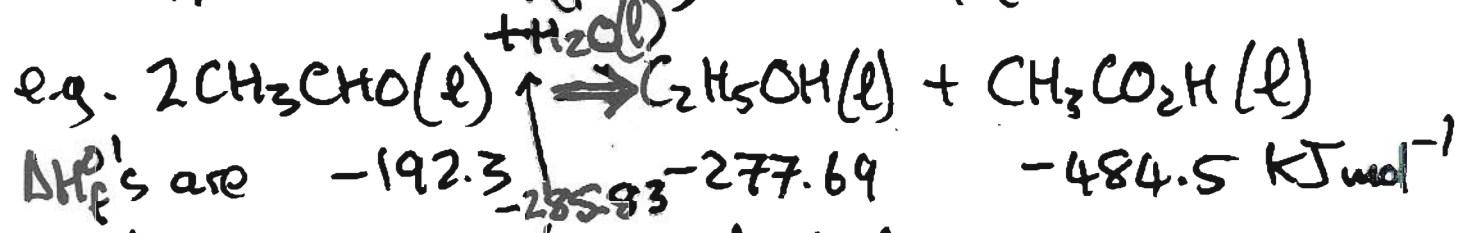


(3) Standard enthalpies of formation, ΔH_f°

- enthalpy change for forming 1 mol of compound in its standard state from its constituent elements in their std. states.

ΔH_f° values are tabulated and are very useful. e.g. can calc. ΔH° for any rx. if the ΔH_f° 's are known for the species involved in the rx.

$$\Delta H_{rx}^\circ = \sum \Delta H_f^\circ(\text{prods}) - \sum \Delta H_f^\circ(\text{reactants})$$



Using these values get $\Delta H_{rx}^\circ = \frac{-377.6 \text{ kJ}}{-91.76 \text{ kJ}}$

Note: - for pure elements in their most stable form, $\Delta H_f^\circ = 0$

- ↳ halogens, $F_2(g)$, $Cl_2(g)$, $Br_2(l)$, $I_2(s)$
- carbon (graphite), $\Delta H_f^\circ = 0$ (for diamond = 1.9 kJ mol^{-1})

In soln. we often have ion-pairs e.g. $Na^+(aq)$, $Cl^-(aq)$.

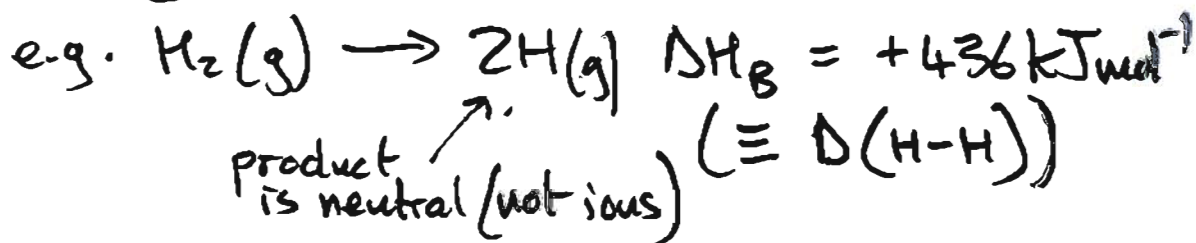
∴ define a reference; set $\Delta H_f^\circ(H^+(aq)) = 0$

(4) Hess' Law

Another way to get ΔH°_{rx} sum (cunningly) chosen equations (each with a known ΔH°_{rx}) to get the rx. you want.

(5) Bond energies in covalent molecules

- breaking bonds costs energy
- the bond dissociation energy (BDE, a +ve quantity) indicates the strength of a chemical bond (gas phase molecules)



Examples.

$$D(C-H) \approx \underline{412 \text{ kJ mol}^{-1}}$$

$$D(C \equiv N) \approx 891 \text{ (triple bond)}$$

$$D(C-Br) \approx 276$$

$$D(C-Cl) \approx 338$$

$$D(C-F) \approx 484$$

relevant to photodissociation of CFC's in the atmosphere

(6) Photon energies

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$$E = h\nu$$

← relevant to atmospheric chemistry

← frequency

Planck's const.
($6.626 \times 10^{-34} \text{ Js}$)

← wavelength

$$\text{so, } E = \frac{hc}{\lambda} \quad (\text{since } c = \lambda\nu)$$

speed of light ($2.998 \times 10^8 \text{ ms}^{-1}$)
 $\sim 3 \times 10^8 \text{ ms}^{-1}$

Light usually measured in:

wavelength λ (in metres)

frequency ν (in s^{-1} (Hertz, Hz))

From the above, short λ has higher E

$$\text{eg. } 200 \text{ nm} \rightarrow 993 \times 10^{-21} \text{ J} \rightarrow 598 \text{ kJ mol}^{-1}$$

(VUV)

$$50 \mu\text{m} \rightarrow \sim 4 \times 10^{-21} \text{ J} \rightarrow 2.40 \text{ kJ mol}^{-1}$$

(mid-IR)

Important in astrophysical/atmospheric rxns.

(7) Entropy S

- spontaneous processes are irreversible and lead to an increase in disorder

Altho' downhill energetic rxs (exothermic) are favoured, there is an additional factor, entropy, which can also enter into the discussion of whether or not rxs proceed.

$$\Delta S = \frac{q_{rev}}{T}$$

← heat supplied reversibly
← temp. at which energy transfer takes place

In any process, the total entropy of the universe must increase (2nd law of TD)

$$\Delta S_{total} > 0$$

(or univ.)

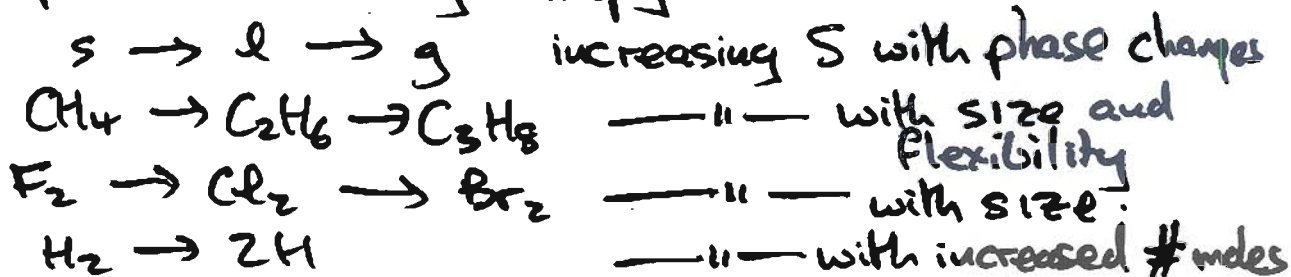
← 3rd Law of TD

At absolute zero (T=0K), S=0

note, we can define an absolute entropy (unlike U and H where only changes are measured)

hence Fabulated S values are always +ve

Examples of increasing entropy:



For reactions then: $\Delta S_{rx}^{\circ} = \sum S^{\circ}_{prods.} - \sum S^{\circ}_{reacts.}$

(8) Gibbs Free Energy

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... spontaneous processes tend to minimise energy and maximise disorder

e.g. \uparrow 2 gases mixing

e.g. ball rolling down a hill \uparrow

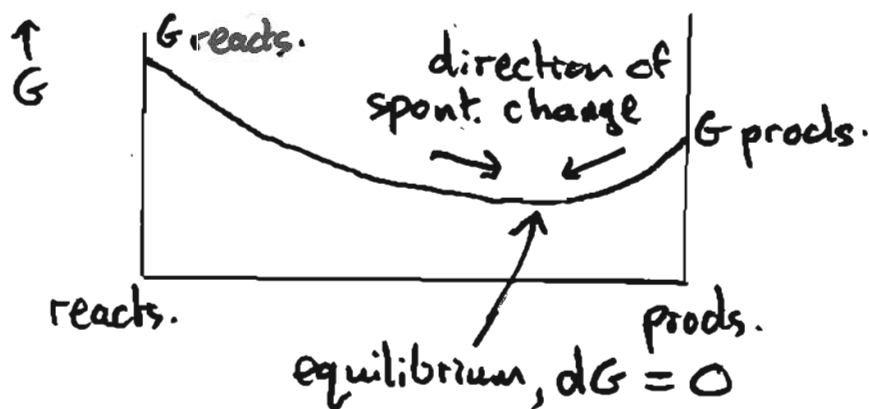
This balance is handled by a new term, the Gibbs free energy, G (and it gets us away from having to worry about $\Delta S_{\text{total}} (= \text{sys} + \text{surr})$)

$$\Delta G = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$$

these \uparrow can work together or compete, but the overall requirement for a rx. to go forward is that:

$$\Delta G \text{ is } -ve$$

i.e. toward lower free energy



i.e. when $\Delta G_{\text{rx}} = 0$, we are at equilibrium

ΔG_f° values are known (like ΔH_f° and S°)

$$\text{so, } \Delta G_{\text{rx}}^\circ = \sum \Delta G_f^\circ(\text{prods.}) - \sum \Delta G_f^\circ(\text{reacts.})$$

Note: ΔG_f° values are given at a particular temperature (298 K), so if we want ΔG_{rx}° at other temps we must use:

$$\Delta G_{rx}^\circ = \Delta H_{rx}^\circ - T_{\text{new}} \Delta S_{rx}^\circ \quad \left(\begin{array}{l} \text{assumes } \Delta H, \Delta S \\ \text{are indep. of} \\ T \text{ (not entirely} \\ \text{true)} \end{array} \right)$$

(9) Free energy and concentration

ΔG_f° values can give us ΔG_{rx}°

Problem: we rarely have standard conditions (1 atm, 1 M)

ΔG_{rx} must depend on concns

$$\Delta G_{rx} = \Delta G_{rx}^\circ + RT \ln Q$$

ΔG_{rx}° : std. conditions
 $RT \ln Q$: addnl. term to account for non-unit concns
 Q : rx. quotient
 eg. $\frac{[C]^c [D]^d}{[A]^a [B]^b}$
 for the rx, $aA + bB \rightarrow cC + dD$

(10) ΔG_{rx}° and K (equilibrium const.)

At equilib $\Delta G_{rx} = 0$

$$\therefore \Delta G_{rx}^\circ = -RT \ln K \quad \leftarrow \text{Wow!}$$

Note: K depends on T

we have $\left\{ \begin{array}{l} \Delta G_{rx}^\circ = \Delta H_{rx}^\circ - T \Delta S_{rx}^\circ \\ \Delta G_{rx}^\circ = -RT \ln K \end{array} \right\}$ combine $\Rightarrow \ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$

C. RATES OF REACTIONS (Kinetics)

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(1) A rx. goes forward if $\Delta G_{rx} < 0$ (and we can get the equilibrium position)

Kinetics tells us about:

⇒ rx. rates (how fast, slow)

⇒ factors which affect rx. rates, e.g. concn., T, etc

⇒ reaction mechanisms

- includes investigation of solvent effects, catalysts, effect of light, etc.

Each rx. is different. Hence the approach is:

Expts \longrightarrow Rate law (order and rate constant k) $\xrightarrow{\text{suggests}}$ mechanism

e.g. for the rx $A + 2B \rightarrow C$

Rate of rx. given by $-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{d[C]}{dt}$

The 'rate law' is of the form

$$\text{Rate} = k []^x []^y \dots$$

Units \nearrow
concn. per time
e.g. $M s^{-1}$

rate const. \nearrow

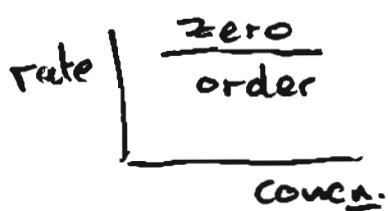
concn. raised to some power
(often integer) \uparrow

Need to do various expts. looking at the effect of concns. on the rate.

- hence get the rate law

(2) Rate and concentration

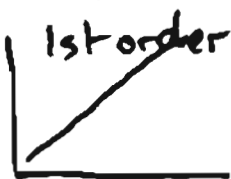
Typical rate/concn. plots



Rate = k
 e.g. $-\frac{d[A]}{dt}$

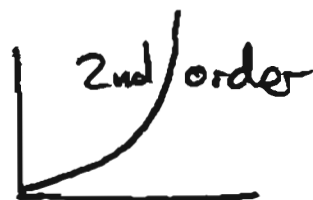
Units of k

zero
 $M s^{-1}$



Rate = $k[A]$

1st
 s^{-1}



Rate = $k[A]^2$
 or = $k[A][A]$

2nd
 $M^{-1} s^{-1}$

(3) Concentration and time

(i) Zero order rx. (rate indep. of concn.)

Rate = $-\frac{d[A]}{dt} = k$ ← differential form of the rate law

Separate variables $[A]$ and t and integrate between $[A]_2, [A]_1$ and t_2, t_1

$\Rightarrow [A]_1 - [A]_2 = k(t_2 - t_1)$

If $[A]_0 =$ concn. at $t=0$ (initial concn)

then $[A]_0 - [A] = kt$ or $[A] = [A]_0 - kt$

\uparrow concn. at a later time \uparrow initial concn.

(20)

(ii) First order rx.

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

$$\text{Integrate} \Rightarrow \boxed{\ln[A] = \ln[A]_0 - kt}$$

Note: $[A] = [A]_0 e^{-kt}$ concn. of A decreases exponentially

Radioactive decay is a 1st order process

Half life given by (substitute $[A] = \frac{[A]_0}{2}$)

$$\boxed{t_{1/2} = \frac{0.693}{k}} \quad \text{i.e. indep. of concn.}$$

(iii) 2nd order rx's.

$$\text{Class I} \quad -\frac{d[A]}{dt} = k[A]^2$$

$$\text{Class II} \quad -\frac{d[A]}{dt} = k[A][B]$$

integrate

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

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

Half life

$$t_{1/2} = \frac{1}{k[A]_0}$$

depends on initial concn.

Note: Class II can become Class I if their initial concns (A & B) are equal and they are used up at the same rate.

Differential rate law relates rate and concn (21)

$$\text{Rate} = \frac{-d[A]}{dt} = k_0$$

$$= k_1[A]$$

$$= k_2[A]^2$$

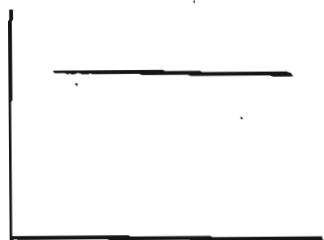
or $k_2[A][A]$

ZERO ORDER

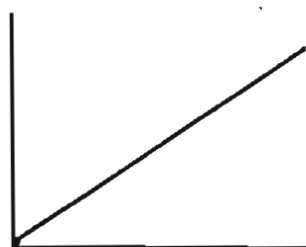
1st ORDER

2nd ORDER

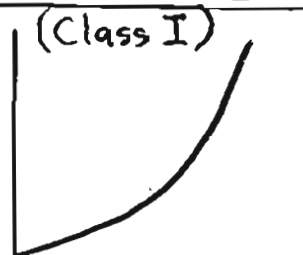
↑
rate



concn



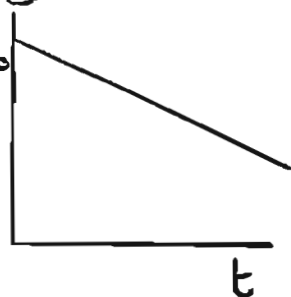
concn



concn

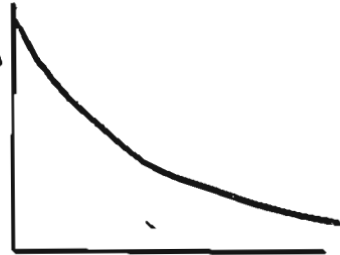
Integrated rate law relates concn and time

↑
[A]₀
concn



t

[A]₀



t

[A]₀



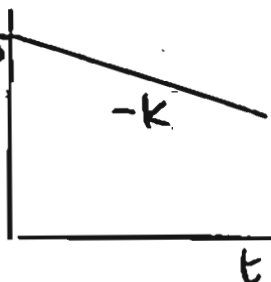
t

$$[A] = [A]_0 - k_0 t$$

$$\ln[A] = \ln[A]_0 - k_1 t$$

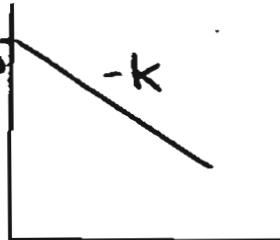
$$\frac{1}{[A]} = \frac{1}{[A]_0} + k_2 t$$

↑
[A]₀
concn



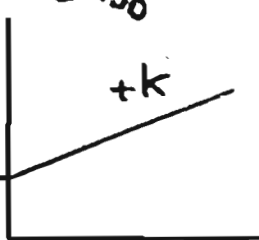
t

↑
ln[A]₀
ln[A]



-k

↑
1/A



+k

UNIT \$
M s⁻¹

OF k
s⁻¹

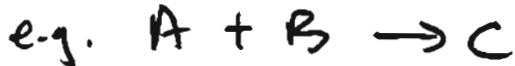
M⁻¹ s⁻¹

(4) Simplifying assumptions for rate laws

(22)

(i) Pseudo 1st (or higher) order

If a reagent is present in great excess, its concn is essentially constant during the rx.



Rate law, $-\frac{d[A]}{dt} = k[A][B]$

2nd order

- determined by expt.
Does not necessarily follow the stoichiometry

If [B] is in excess, [B] is constant and so,

$$-\frac{d[A]}{dt} = k_{obs}[A] \quad (\text{where } k_{obs} = k[B])$$

1st order

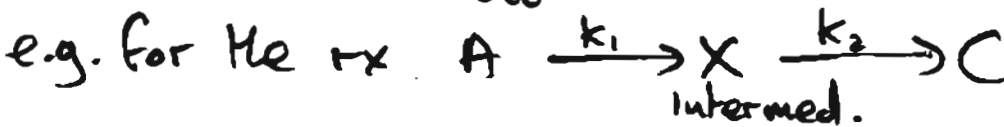
Pseudo-order often occurs in biochem. rxs where water is a reactant, but often in excess.

(ii) Steady state approximation

useful for complex rxs.

- based on assumption that during the rx., the concn of reactive intermediates are const. and small

i.e. $\frac{d[\text{intermed.}]}{dt} = 0$



k_1, k_2
1st order rate constants

(i) $-\frac{d[A]}{dt} = k_1[A]$

(ii) $\frac{d[X]}{dt} = k_1[A] - k_2[X]$

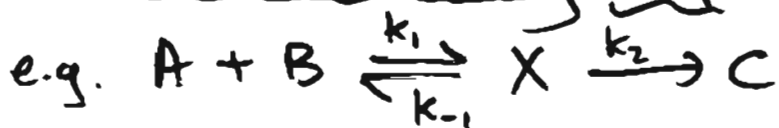
(iii) $\frac{d[C]}{dt} = k_2[X]$

← set this = 0 & solve.

Get $\frac{d[C]}{dt} = k_1[A]$

(iii) Rate determining step.

(23)



$$(i) -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_1[A][B] - k_{-1}[X]$$

$$(ii) \frac{d[X]}{dt} = k_1[A][B] - k_{-1}[X] - k_2[X] \leftarrow$$

$$(iii) \frac{d[C]}{dt} = k_2[X]$$

Assuming steady state approx, $\frac{d[X]}{dt} = 0$

Solving for $[X]$ and substituting into (iii) we get

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

If $k_2 \gg k_{-1}$ i.e. X goes rapidly to C, then the first step is rate determining

Hence the above becomes $\frac{d[C]}{dt} = k_1[A][B]$

However, if $k_2 \ll k_{-1}$ then we get

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

Since $\frac{k_1}{k_{-1}} = K \leftarrow$ equilibrium const for 1st step

(5) Temperature dependence of rx rates

Arrhenius (1869) found a general exponential increase in the rate with temperature

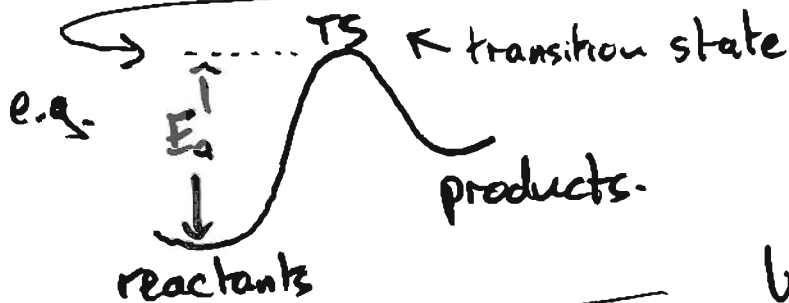
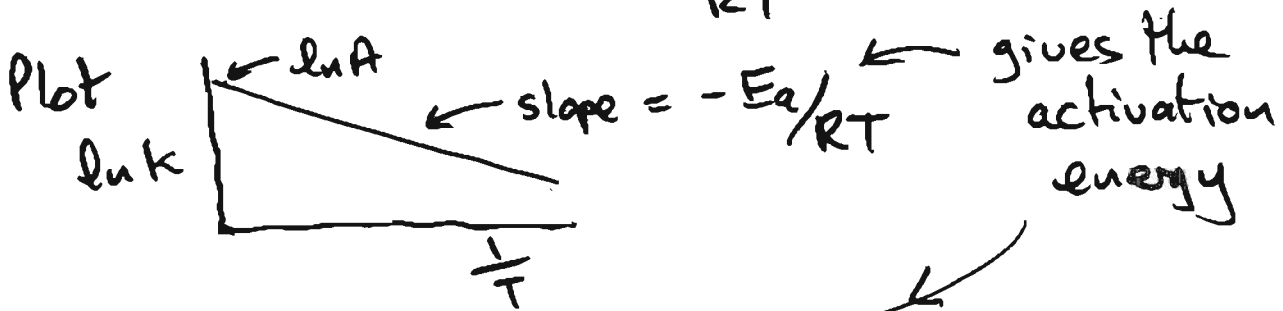
$$k = A e^{-E_a/RT}$$

rate const pre-exponential factor (NOT a reactant!!) activation energy

this term is to do with the collision frequency and an orientation factor

Re-writing the equation

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



Note: a catalyst can lower the barrier, i.e. smaller E_a

→ this happens in O_3 depletion $Cl\cdot$ (from CFC's) can catalyse the decomp.