Thermodynamics

**oops!!
caught with
no flesh on...**

<u>**Summary**</u> **of material
in FIRST YEAR lectures**
(skeleton notes)

WARNING

<u>**You**</u> **must put
'flesh' on these
'bare bones'**
(...**not everything is covered**)

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— Thermochemistry: Bare Bones —

Heat (energy transferred due to ΔT)

$$q = n \times C_p \times \Delta T$$

where n = amount, C_p = heat capacity, ΔT = temperature change

and for a calorimeter

$$q = q_{contents} + q_{calorimeter}$$
$$= (n \times C_p \times \Delta T) + (C_{calorimeter} \times \Delta T)$$

Heat out: q < 0;   Heat in: q > 0
    (*by definition*)

Work (at constant pressure)

$$w = -p\Delta V$$
$$= -\Delta n_{gas} RT$$

(negative for expansion)
(assuming Ideal Gas Equation)

First Law of Thermodynamics
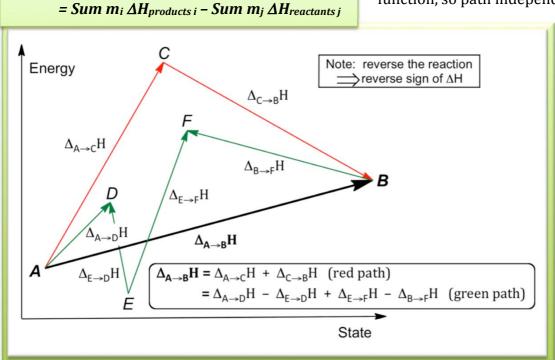
$$\Delta U = q + w$$

(state function ➔ path independent)

Enthalpy (Heat of Reaction at constant P)

$$\Delta H = \Delta U + pV = q_p$$
$$= H_{final} - H_{initial}$$
$$= Sum\ m_i\ \Delta H_{products\ i} - Sum\ m_j\ \Delta H_{reactants\ j}$$

Hess's Law: enthalpy is a state function, so path independent

Be able to use tabulated *standard** enthalpies to calculate $\Delta_r H°$:

- Enthalpy (heat) of formation, $\Delta_f H°$
- Enthalpy (heat) of combustion, $\Delta_c H°$
- Bond Enthalpy (energy), $\Delta_{X-Y} H°$
- Enthalpy of melting or vaporisation, Heat capacity *etc.*

*<u>Standard</u> states: P = 1.0 bar, pure (unmixed) substances or 1.0 mol L^{-1} solutions at the specified temperature

Second Law of Thermodynamics

ΔS (universe) > 0 for a spontaneous process

where **S = entropy, increases as disorder increases**

Third Law of Thermodynamics

S (pure crystal) → constant value as T → 0 K

Define S° (pure crystal) = 0 at T = 0 K

so can calc. S° at any T

$S° = Sum\ m_i\ \Delta S°_{products\ i} - Sum\ m_j\ \Delta S°_{reactants\ j}$

Gibbs Free Energy

$\Delta_r G = \Delta_r H - T\Delta_r S$
$= Sum\ m_i\ \Delta G_{products\ i} - Sum\ m_j\ \Delta G_{reactants\ j}$

$\Delta G = -T\ \Delta S\ (universe)$

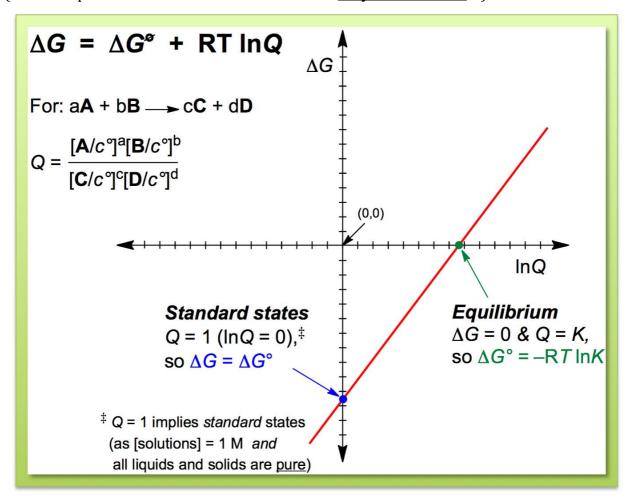*so...* $\Delta G < 0$ implies process (reaction) is **spontaneous**
$\Delta G > 0$ implies process (reaction) is **<u>non</u>-spontaneous**

At equilibrium:
$\Delta_r G = 0$
and $\Delta_r G° = \Delta_r H° - T\Delta_r S° = -RT\ lnK$ *(≠ 0)*

... and a little <u>extra</u> (not examinable, but it may help)
(to clear up confusion between ΔG and $\Delta G°$ -- <u>**they are different!!**</u>)

$$\Delta G = \Delta G^{\varnothing} + RT \ln Q$$

For: $a\mathbf{A} + b\mathbf{B} \longrightarrow c\mathbf{C} + d\mathbf{D}$

$$Q = \frac{[\mathbf{A}/c°]^a[\mathbf{B}/c°]^b}{[\mathbf{C}/c°]^c[\mathbf{D}/c°]^d}$$

ΔG

$(0,0)$

$\ln Q$

Standard states
$Q = 1 \ (\ln Q = 0),^{\ddagger}$
so $\Delta G = \Delta G°$

Equilibrium
$\Delta G = 0$ & $Q = K$,
so $\Delta G° = -RT \ln K$

‡ $Q = 1$ implies *standard* states
(as [solutions] = 1 M *and*
all liquids and solids are <u>pure</u>)

How should I study for this topic?

THINK CRITICALLY!!

Not available for this course

Ask yourself: <u>Do I understand</u> everything presented? Can I do all the problems... from lectures, worksheets & tutes?

Try to <u>understand</u> the material... (use the syllabus & lectures as a guide)

Attend lectures, do worksheets...

Read lecture notes & textbook ...

Do some more problems ...
(from tutorials, textbook & sample exams)

Do some <u>more</u> problems ...

repeat till you <u>understand</u> it all!!