59-240 — Oct. 19, 2015

A few notes in preparation for MT #1

① Mean free path equations

$$\lambda = \frac{kT}{\sqrt{2}\sigma p}$$

is the correct equation, and is included on the Eq. Sheet #1.

In the 10th Ed, this is given as:

$$\lambda = \frac{kT}{\sigma p}$$

, which is incorrect, as is the associated derivation.

② Different types of processes

For heating, cooling, expansion and compression, we learned that for an isothermal process:

$\Delta T = 0$, $\Delta U = 0$, $q = -w$

Some students are confused about other processes:

Ⓐ Phase transitions

PTs are isothermal ($\Delta T = 0$), as they occur at a fixed temperature.

(cont'd ⤵)

But $\Delta U \neq 0$, since energy flows in or out of the system to DRIVE the $\boxed{PT}$.

e.g., melt ice(s) [$H_2O(s)$] $\rightarrow$ $H_2O(\ell)$ at $p = 1$ bar

$\boxed{q > 0}$ (heating); $V_{(ice)} > V_{(water)}$, $\Delta V < 0$

$\therefore \boxed{w > 0}$ ($dw = -p_{ext}\, dV$)

$\therefore \boxed{\Delta U > 0}$ even though $\boxed{\Delta T = 0}$

(B) Reactions

Consider the combustion of benzene @ 298 K:

$$C_6H_6(\ell) + \tfrac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(\ell)$$

$\Delta_c H^\circ = -3267 \pm 20$ kJ mol^{-1}

Of course, a temperature change can result from this combustion, but one must define what medium this occurs in (e.g., water? calorimeter?) in which case we can use C_p or C (calorimeter constants) to figure out relationships btw. ΔT and $\Delta_c H^\circ$.

So, for a chemical reaction, since

$$H = U + nRT$$

then

$$\Delta H = \Delta U + \Delta n RT + nR\Delta T$$

ΔT has no meaning since Θ reactants → products

Δn: this is the diff in moles of gas molecules $n_{prod} - n_{react}$

so, ΔH and ΔU will be slightly different for rxns involving gases in different proportions on either side of the reaction equation.

e.g., for combustion of benzene,

$$\Delta n = 6 - 7.5 = -1.5$$

so, $\Delta U = \Delta H - \Delta n RT$ (ΔH: $\ominus$, $\Delta n RT$: $\ominus$)

For combustion of benzene

↳ Since $\Delta_c H \gg \Delta n RT$

$$\Delta U = \underset{-ve\ \#}{\text{large}} + \underset{+ve\ \#}{\text{small}} = \underset{-ve\ \#}{\text{large}}$$

so, $\Delta U, \Delta H < 0$, but $|\Delta H| > |\Delta U|$

or $\Delta H < \Delta U$