

Chem 101 Lecture 9b Winter, 2010

Admin: administer student survey

Last time: we discussed calculations of ΔH_{rxn} by means of:

- 1) use of ΔH_f°
- 2) use of bond enthalpy
- 3) use of Hess's Law

Today:

- (0) First Law of Thermodynamics
- (1) ΔH and intermolecular interactions
- (2) introduction to electromagnetic radiation.
- (3) discussion of group quiz

Lecture:

(0) first law of thermodynamics:
(equivalent to conservation of energy):

$$\Delta E = q + w$$

where ΔE = change in the internal energy of system

q = heat added to system

w = work done on the system (many forms of work but for now, we concentrate only on mechanical work: work resulting from the expansion or contraction of a gas)

$$w = -p\Delta V \quad (p = \text{pressure}, \Delta V = \text{change in volume})$$

2 cases:

a) $\Delta V \neq 0$ in a reaction:

$$\text{so } \Delta E = q + w \text{ where } q \neq \Delta E$$

If we measure heat by constant pressure calorimetry:

$$-q_{\text{calorimetry}} = q_p = \Delta H \neq \Delta E$$

b) $\Delta V = 0$ in a reaction:

$$\text{so } \Delta E = q + w = q + 0 = q$$

(i) if $\Delta V = 0$ for a reaction then,

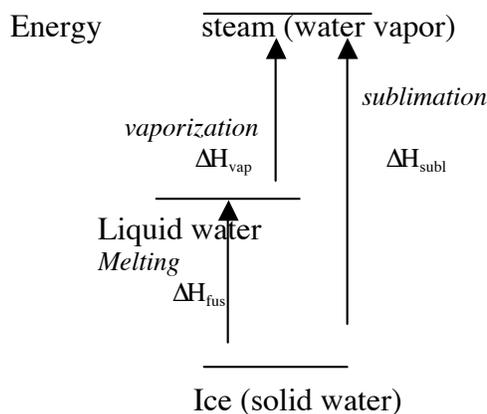
$$\Delta E = q_p + 0 = q_p = -q_{\text{calorimetry,P}}$$

(i) if $\Delta V \neq 0$ but we measure q by constant volume calorimetry (i.e. "bomb calorimetry"): then

$$-q_{\text{calorimetry}} = q_v = \Delta E \quad \text{and not } \Delta H$$

(1) **When substances interact through intermolecular interactions, energy is involved.**

Separating molecules of water in ice:



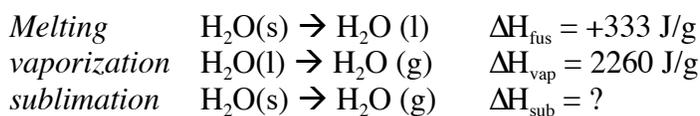
If the enthalpy of fusion ΔH_{fus} is 333 J/g

And the enthalpy of vaporization, ΔH_{vap} is 2260 J/g

What is the enthalpy of sublimation, ΔH_{subl} , for H_2O ?

$$\Delta H_{\text{subl}} = ???$$

Another way to write it:



How about $\Delta H_{\text{freezing}} = ?$, $\Delta H_{\text{condensation}} = ?$

Another example:



Net ionic:



What is $\Delta H^\circ_f(\text{Mg}^{2+}(\text{aq})) = ?$ if $\Delta H^\circ_f(\text{H}^+(\text{aq})) = 0$

$$\Delta H^\circ_1 = \Delta H^\circ_f(\text{Mg}^{2+}(\text{aq})) + 0 - 0 - 0$$

What is $\Delta H^\circ_f(\text{MgO}(\text{s})) = ?$ If $\Delta H^\circ_f(\text{H}_2\text{O}(\text{l})) = -286 \text{ J/mol}$

$$\begin{aligned}\Delta H^{\circ}_2 &= \Delta H_f^{\circ}(\text{Mg}^{2+}(\text{aq})) + \Delta H_f^{\circ}(\text{H}_2\text{O}(\text{l})) - \\ &\Delta H_f^{\circ}(\text{MgO}(\text{s})) - 2\Delta H_f^{\circ}(\text{H}^+(\text{aq})) = \\ &= \Delta H^{\circ}_1 - 286 - \Delta H_f^{\circ}(\text{MgO}(\text{s})) - 0.\end{aligned}$$

(2) Chapter 7 Electron configuration and the Periodic table

In this chapter, we look into the atom's electron structure. We start by looking at the behavior of electrons as they change their energy.

Nature of light:

Another form of energy

-starting point for quantum mechanics

-starting point for understanding the atom.

-a form of electromagnetic radiation

-speed, $c = 186,000 \text{ miles/sec} = 3.00 \times 10^8 \text{ m/s}$

it has a "wave property"

for any wave:

wavelength \times frequency = speed

or:

$\lambda \nu = c$ where λ = wavelength (m),

ν = frequency (s^{-1} or 1/sec or hertz)

see figure. Page 274

Planck:

Analyzed the black-body problem in

physics: Came up with revolutionary

concept: Light energy = discrete packets:

quanta

$E = h \nu$ where h = Planck's

constant = $6.63 \times 10^{-34} \text{ Js}$

As frequency goes up, E increases

But we can rearrange E expression

Since $E = h \nu$ and $\lambda \nu = c$

Therefore:

$$E = hc / \lambda$$

This is shown in the photoelectric effect:

Einstein showed that photons travelled in packets

3) Discussion of the group quiz

1) Suppose you react 50.0mls of 2.0 M HCl with 50.0mLs of 1.0M NaOH in a calorimeter containing 100. mLs of water at 20.0°C and the temperature rises to 25.0°C, what is the $\Delta H^\circ_{\text{rxn}}$ (in kJ/mol) for the neutralization reaction:



Solution: We know that in calorimetry, we use:

$$q_{\text{cal}} = mC_p(T_f - T_i)$$

Where m = total mass of the solution

$$= 100 \text{ g (water)} + 50 \text{ g HCl solution} + 50 \text{ g NaOH solution} = 200 \text{ g}$$

We assume them to have the properties of pure water.

$$\text{So : } q_{\text{cal}} = (200\text{g})(4.18\text{J/g}^\circ\text{C})(25^\circ\text{C} - 20^\circ\text{C}) = 4180 \text{ J}$$

$$\text{Since } q_p = -q_{\text{cal}} = \Delta H = -4180 \text{ J}$$

But to get $\Delta H^\circ_{\text{rxn}}$ we need #moles H^+ involved:

$$\text{i.e. } \Delta H^\circ_{\text{rxn}} = -4180 \text{ J} / (\text{\#moles } \text{H}^+ \text{ reacted})$$

the reaction is:



$$\text{\#moles: } .100 \text{ mol} \quad 0.050 \text{ mol}$$

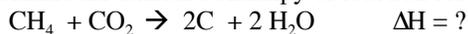
(where # moles = MV = 2.0M(0.0500L) = 0.100 moles etc.)

we note that NaOH = limiting reagent

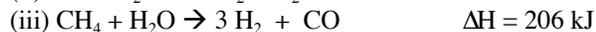
and only 0.050 mol HCl = 0.050 mol H^+ actually reacts.

$$\text{So, we have } \Delta H^\circ_{\text{rxn}} = -4180 \text{ J} / 0.050 \text{ mol} = 8.36 \times 10^4 \text{ J/mol}$$

2) Determine the standard enthalpy of reaction for the following equation



from the following given standard enthalpies of reaction:



solution:

we want to get the reaction, $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{C} + 2\text{H}_2\text{O}$ by adding the 3 given equations, (i), (ii) and (iii).

From inspection:

We see that (i) has the C on the left side and to utilize

it we need to reverse and double it: $-2 \times \text{(i)}$

We also see that (ii) has CO_2 on the right side and

thus we need to reverse it.

Finally, we see that (iii) is ok the way it is. So we

$$\text{have: } \Delta H_{\text{rxn}} = -2 \times \Delta H_{\text{i}} - \Delta H_{\text{ii}} + \Delta H_{\text{iii}}$$

$$= -2(131) - (-41) + (206) = -15 \text{ kJ/mole}$$