

Notes for chem 101 lecture 7c

0) admin – Test 2 returned . Thu rec furloughs

March 4. Ave \pm sd = 95 ± 36 (highest = 155)

$63\% \pm 24\%$ (In Test 1 it was $54\% \pm 21$)

A significant improvement in general.

Last time: Energy and chemistry:

Today:

(1) measuring heat and heat capacity.

(2) heat accompanying phase changes

(3) 1st Law: $E = q + w$

(4) enthalpy: $q_p = \Delta H$, ΔH_f° ,

(5) calorimetry: $q_{cal} = -q_p$

(6) Use of ΔH_f° (standard enthalpy of formation)

Thermochemistry

0) In thermochemistry, we are interested in determining the change of energy of the form called "enthalpy". H. "heat content" of system. We can measure ΔH by calorimetry.

Heat transferred at constant pressure, $q_p = \Delta H$

1) Measuring the heat by its effect on the temperature (T) of a substance.

$$Q = mC_p\Delta T.$$

m= mass of substance (in g) ,

C_p = specific heat (J/g°C). (at constant pressure)

ΔT = change in temperature= $(T_f - T_i)^\circ C$,

Q= heat transferred (in J)

$C_p = 1.0 \text{ cal/g}^\circ C$ for water. $1 \text{ cal} = 4.18 \text{ J}$. (Joule is the SI unit of energy)

Example: How many joules of energy are needed to raise the temperature of 31.0 g water from 23° to $88^\circ C$?

$$Q = mC_p\Delta T = (31.0\text{g})(4.18\text{J/g}^\circ\text{C})(88-23)^\circ\text{C} = 8423 \text{ J} \\ = 8.42 \text{ kJ (note: 1kJ=1000J)}$$

2) Phase changes:

Heat transferred in changes of physical state (i.e. “phase changes”):

example: water \rightarrow ice



Occurs at the T_{freezing} which is also $T_{\text{melting}} = 0^\circ\text{C}$

So we can't use $Q = mC_p\Delta T$ since $\Delta T = 0!$

Instead, we use:

$$Q = m\Delta H_{\text{fusion}} \text{ where } \Delta H_{\text{fus}} = 333 \text{ J/g} \\ \text{(note: } \Delta H_{\text{fusion}} = -\Delta H_{\text{freezing}})$$

To freeze 20.0 g of water, we would need:

$$Q = (20.0\text{g})(-333\text{J/g}) = -6.66 \text{ kJ} \quad \text{“-“ means it loses heat. Exothermic.}$$

For boiling: (at $T_b = \text{boiling point} = 100^\circ\text{C}$)

$$\Delta H_{\text{vap}} = -\Delta H_{\text{condensation}} = 2260 \text{ J/g}$$

UNDERSTAND Graphs like Fig. 6.11 on page 193.

3) Calorimetry:

A technique used to measure heat, Q , by means of T changes. It is useful for determining the energetics of a reaction.

It uses $Q_{\text{cal}} = mC_p\Delta T$ where m usually mass of solution. Often we ignore the solutes (why?).

Example: Suppose we add 20.0 mL of 1.0M HCl to 20 mL of 1.0 M NaOH and the temp of the mixture increases from 20°C to 23°C , what is the energy of the neutralization reaction (per mol H^+ neutralized)?

$$Q = mC\Delta T : m = \text{mass of aqueous soln mixture, } \approx 20+20 = 40 \text{ g why? (note: density=1g/mL for water)}$$

$C = 4.18 \text{ J/g}^\circ\text{C}$ (assume same as water). $\Delta T = 23 - 20 = +3^\circ\text{C}$

$$Q_{\text{cal}} = (40)(4.18)(3) = 501.6 \text{ J}$$

The enthalpy is $\Delta H = q_p = -Q_{\text{cal}}$

$$\text{So, } q_p = -501.6 \text{ J} = \Delta H$$

(note that this is for neutralization of $(MV = .020\text{L} \times 1.0\text{mol/L} = .020 \text{ mol} = 20 \text{ mmol } \text{H}^+)$)

Per H^+ this would be:

$$- 501.6 \text{ J} / .020\text{mol} = -25,080 \text{ J/mol} = - 25.1 \text{ kJ/mol}$$

Let's go back and think of this example. This is a calorimetric example. It involves use of insulated container, heat released or absorbed is directly measured in the temp change of the water, no heat is lost or gained from the outside of the water since it is insulated.

In the above example, if that was the result of a chemical reaction occurring in the water, say:

$\text{A}(\text{aq}) + \text{B}(\text{aq}) \rightarrow \text{C}(\text{aq})$, we can think of the system as the moles (or ions) of the solute, A, B and C and the water as the surroundings.

The reaction of A, B and C don't involve water directly. so, if we can determine how much heat was gained by the water (by measuring how much it heated up), then we can determine how much heat was given off by the reaction.

$$q_{\text{calorimeter}} = -\Delta H.$$

(4) heat of Formation

suppose that $\text{A} + 2\text{B} \rightarrow 3\text{C}$ is a balanced equation then ΔH for this equation is:

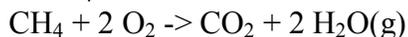
$$\Delta H_{\text{rxn}} = 3 \Delta H_f^\circ(\text{C}) - \Delta H_f^\circ(\text{A}) - 2 \Delta H_f^\circ(\text{B})$$

where ΔH_f° = "standard enthalpy of formation"
obtained from the appendix J

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

What is the enthalpy of the following reaction?

a) Calculate the enthalpy for the complete combustion of methane: CH_4 :



$$\text{solution: } \Delta H_{\text{rxn}} = \Delta H_f(\text{CO}_2) + 2\Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{CH}_4) - 2\Delta H_f(\text{O}_2) = -394 - 2(242) - (-75) - (0) = -561 \text{ kJ/mol}$$

In general, if we can find the heats of fusion on a table, we are able to get the ΔH_{rxn} .

(2) Let's recall how to get ΔH :

a) by BE: $\Delta E \approx \Delta H$ (whenever there is no work like pV work)

$$\text{so, } \Delta H \approx \sum \text{BE}(\text{broken}) - \sum \text{BE}(\text{formed})$$

In your book, they write it as: $\Delta H \approx \sum \text{BE}(\text{rxt}) - \sum \text{BE}(\text{prod})$

b) by calorimetry (2 ways: q_p and q_v). this is the direct experimental way. If there is not any expansion, $q_v \approx q_p$. In any case, $q_p = \Delta H$

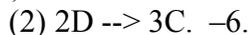
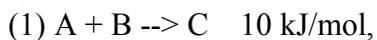
c) by ΔH_f° 's.

d) A fourth way?

(4) Hess' Law says that we can treat a reaction as if it were done in a multi step process, as long as the final reaction is the one we want:

What is ΔH for: $3\text{A} + 3\text{B} \rightarrow 2\text{D}$?

Say we knew the ff:



See if we can add the 2 in such a way as to end up with the equation we want:

Try: $3 \times (1) - (2)$: $3(10) - (-6) = 36$! This is a quick intro to Hess' law

(5) A word or 2 about the general discussions we have had about pV work and ΔE .

Again: $\Delta E = q + w$. q and w are not state functions, but E is a state function.

q and w may vary depending on path of going from state 1 to state 2. We may be able to extract some work out of the system. So far we are only considering pV work in our discussion. In more complex systems there are other forms of work, such as chemical work, the work of synthesizing new complex molecules for example as occurs in living systems.

OK, looking at pV work: If we are dealing with a gas, we usually assume it is like an ideal gas.

So, $pV = nRT$. what is the work done by an ideal gas when it expands from V_1 to V_2 at constant pressure, p_0 ?

$w = p_0(V_2 - V_1)$. We can directly measure it by expressing units in SI. p in pascals and V in m^3 .

This can be also measured by measuring changes in n or T . E.g. in vaporization, n changes as gas is formed. so $p\Delta V = \Delta nRT$. here T is constant. (this is isothermal, isobaric expansion)

Or, there can be change in T but constant n and p : $p\Delta V = nR\Delta T$. depends on the conditions.

(6) Know that inter molec intrxns also give rise to ΔH changes. For example, just dissolving solid in a liquid can cause a net break and form'n of intermolec intrxns. This is what happens in the case of heat of solution

when a solid (ionic compd) dissolves, several steps occur.
 $\Delta H_{\text{lattice}} (+) + \Delta H_{\text{solvent}} (+) + \Delta H_{\text{solvation}} (-)$

compare with nonpolar substances dissolving in polar substances: here $\Delta H_{\text{solute}} (+) + \Delta H_{\text{water}} (+) + \Delta H_{\text{water-oil intx}} (-)$ = usually very positive and not favored much. too endothermic.

Others: heat of vaporization, heat of