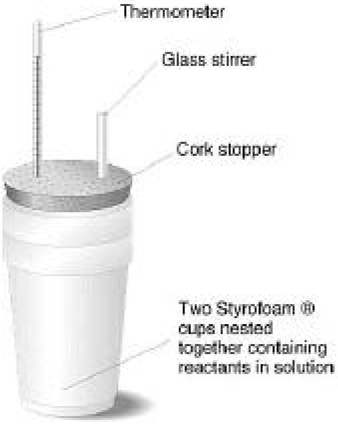
Announcements – 10/18/00

Constant-Pressure Calorimetry

- So-called “coffee-cup” calorimetry:



- Add reactants to cup
- Measure resulting temperature increase (or decrease)
- $q_{soln} = -q_{rxn}$
- <u>So</u>: $\Delta H = -q_{soln} = -m_{soln}(\text{sp heat})\Delta T$
- You will do this *this* week in lab!

How are ΔE and ΔH related?

- From the definition of Enthalpy:

$$\mathbf{\Delta H = \Delta E + P\Delta V}$$

-for an ideal gas: $\mathbf{P\Delta V = RT\Delta n}$

So:

$$\boxed{\mathbf{\underset{\overset{\uparrow}{q_p}}{\Delta H} = \underset{\overset{\uparrow}{q_v}}{\Delta E} + \underset{\overset{\nwarrow}{\text{PV work}}}{RT\Delta n}}}$$

Enthalpies of Reactions

- Enthalpy (H) is a *state function*, so all we need to know are the initial and final values for a reaction:

$$\Delta H_{rxn} = H\ (\text{products}) - H\ (\text{reactants})$$

Together with a balanced reaction expression, we have a ***thermochemical equation:***

$$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_20\ (g) \qquad \Delta H = -483.6\ kJ$$

Balanced, with physical states

Note sign: *exothermic*

More on Enthalpy

- Enthalpy is an *extensive* property

  -the magnitude of ΔH depends on the ***quantity*** of reactant

- $\Delta H_{forward} = - \Delta H_{reverse}$

  - reverse reaction will have same ΔH, but with the *opposite* sign

- Reactions with $\underline{\Delta H \ll 0}$ often occur *spontaneously*

  -but not always; there are exceptions (wait until Thermodynamics to resolve this fully!)

Enthalpy of Reaction Calculation Example

- Calculate the ΔH for the reaction that occurs when *1.00 g H_2O_2* decomposes according to the following reaction:

$$H_2O_2\ (l) \rightarrow H_2O\ (l) + \tfrac{1}{2}\ O_2\ (g) \qquad \Delta H = -\ 98.2\ kJ$$

convert: *g $H_2O_2 \rightarrow$ kJ*

$$1.00\ g\ H_2O_2 \times \frac{1\ mol\ H_2O_2}{34.01\ g\ H_2O_2} \times \frac{-98.2\ kJ}{1\ mol\ H_2O_2} =$$

= ***2.89 kJ***

Hess’s Law

- ΔH is a *state function* so we can use *any* sequence of reactions (that sum to the desired reaction) to calculate a value of ΔH_{rxn}:

IF: Rxn(1) + Rxn(2) = Rxn(3)

Then: $\Delta H_1 + \Delta H_2 = \Delta H_3$

An example:	ΔH
Rxn(1): $Sn(s) + Cl_2(g) \rightarrow SnCl_2(s)$	-349.8 kJ
Rxn(2): $SnCl_2(s) + Cl_2(g) \rightarrow SnCl_4(l)$	-195.4 kJ
Rxn(3): $\mathbf{Sn(s) + 2Cl_2(g) \rightarrow SnCl_4(l)}$	**-595.2 kJ**

Hess’s Law: Example

- We can use Hess’s Law to calculate ΔH for reactions without ever actually having to perform the reaction:

Find DH for the following reaction:

$$2NH_3(g) + 3N_2O(g) \rightarrow 4N_2(g) + 3H_2O(l)$$

What we know:	ΔH
Rxn(1): $4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(l)$	- 1531 kJ
Rxn(2): $N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(l)$	- 367.4 kJ
Rxn(3): $H_2(g) + \frac{1}{2}O_2 \rightarrow H_2O(l)$	- 285.9 kJ

Hess's Law Example: Cont'd

- We need to react only *TWO mol NH_3*, so <u>divide rxn(1) by 2:</u>

  $\mathbf{2}NH_3(g) + \mathbf{3/2}\, O_2(g) \rightarrow N_2(g) + \mathbf{3}H_2O(l)$

- We need to react *THREE mol N_2O*, so <u>multiply rxn(2) by 3:</u>

  $\mathbf{3}N_2O(g) + \mathbf{3}H_2(g) \rightarrow \mathbf{3}N_2(g) + \mathbf{3}H_2O(l)$

- We need to get rid of the stuff not in the final rxn (H_2, O_2, and excess H_2O), so <u>reverse rxn(3) and multiply by 3:</u>

  $\mathbf{3}H_2O(l) \rightarrow \mathbf{3}H_2(g) + \mathbf{3/2}\, O_2(g)$

- Add 'em up!

$$\mathbf{2}NH_3(g) + \cancel{\mathbf{3/2}\, O_2(g)} + \mathbf{3}N_2O(g) + \cancel{\mathbf{3}H_2(g)} + \cancel{\mathbf{3}H_2O(l)} \rightarrow$$
$$N_2(g) + \mathbf{3}H_2O(l) + \mathbf{3}N_2(g) + \cancel{\mathbf{3}H_2O(l)} + \cancel{\mathbf{3}H_2(g)} + \cancel{\mathbf{3/2}\, O_2(g)}$$

Hess's Law Example: The Thrilling Conclusion!

- Whatever was done to the *reaction equations*, we need to do to the ΔH values:

ΔH_1 <u>**÷ 2**</u> = -1531 ÷ 2 = -765.5 kJ

ΔH_2 <u>**x 3**</u> = -367.4 x 3 = -1102.2 kJ

ΔH_3 <u>**x (-3)**</u> = - 285.9 x (-3) = <u>857.7 kJ</u>

<u>**ΔH_{rxn} = -1010.0 kJ**</u>

Enthalpies of Formation

- A *consistent* way to tabulate ΔH values:
  - -for a *defined* reaction type (formation from elements)
  - -for a *fixed* amount of compound (1 mol)
  - -under *standard* conditions (25 °C, 1 atm)

Called: ***The Standard Molar Enthalpy of Formation***

or

$$\Delta H^o{}_f$$

Example:

$Ag(s) + \frac{1}{2}Cl_2(g) \rightarrow AgCl(s)$ ΔH = -127.0 kJ

Then: $\Delta H^o{}_f$ (AgCl(s)) = -127.0 kJ/mol

Using Enthalpies of Formation

- Hess's Law and tablulated $\Delta H^o{}_f$ values are a powerful tool for predicting enthalpy changes for reactions:

$$\boxed{\Delta H^o = \Sigma\ \Delta H^o{}_f\ (\text{products}) - \Sigma\ \Delta H^o{}_f\ (\text{reactants})}$$

<u>Example:</u>   *The Thermite Reaction*

$8\ Al(s) + 3\ Fe_3O_4(s) \rightarrow 4\ Al_2O_3\ (s) + 9\ Fe(s)$

<u>We know:</u> $\Delta H^o{}_f$ (Fe_3O_4) = -1120.9 kJ

$\Delta H^o{}_f$ (Al_2O_3) = -1669.8 kJ

So:

ΔH° = [4(-1669.8 kJ/mol) + 9(0)] - [3(-1120.9 kJ/mol) + 8(0)]

ΔH° = (-6679.2 kJ) - (-3362.7) = ***<u>-3316.5 kJ</u>***

Demo Example: Burning Mg

- The overall reaction is:

$$2\ Mg(s) + CO_2(s) \rightarrow 2\ MgO(s) + C(s)$$

ΔH^o_f : ***0*** ***??*** ***-601.70*** kJ/mol ***0***

How do we find ΔH^o_f for *SOLID* CO_2?

Use Hess's Law!

<u>We know:</u> ΔH^o_f for $CO_2(g)$ = -393.51 kJ/mol

But how do we deal with *phase changes?*

Enthalpies of Phase Changes

- There are enthalpy changes associated with *physical processes*:

$CO_2(s) \rightarrow CO_2(l)$ $\Delta H_{fusion} = 6.01$ kJ/mol

$CO_2(l) \rightarrow CO_2(g)$ $\Delta H_{vap} = 44.01$ kJ/mol

So:

$CO_2(s) \rightarrow CO_2(g)$ $\Delta H_{sublimation} = \Delta H_{fusion} + \Delta H_{vap}$

$\Delta H_{sublimation} = 50.02$ kJ/mol

We want:

$CO_2(g) \rightarrow CO_2(l)$ $\Delta H = -\Delta H_{sub} = -50.02$ kJ/mol

Putting it all together

- So, to get ΔH^o_f for $CO_2(g)$:

$C(s) + O_2(g) \rightarrow CO_2(g)$ ΔH^o_f = -393.51 kJ/mol

$CO_2(g) \rightarrow CO_2(l)$ ΔH = -50.02 kJ/mol

Adding gives:

$C(s) + O_2(g) \rightarrow CO_2(s)$ ΔH^o_f = -443.53 kJ/mol

<u>And, finally:</u>

$2\ Mg(s) + CO_2(s) \rightarrow 2\ MgO(s) + C(s)$

ΔH^o_f : ***0 -443.53 kJ/mol -601.70 kJ/mol 0***

ΔH^o_{rxn} = 2(-601.70 kJ/mol) - (-443.53 kJ/mol) = ***<u>-759.87 kJ</u>***