Energy, Heat and Chemical Change

Chemistry 35

Fall 2000

Thermochemistry

- A part of *Thermodynamics* dealing with **energy changes** associated with <u>physical and chemical reactions</u>

  <u>Why do we care</u>?

  -will a reaction proceed spontaneously?

  -if so, to what extent?

  <u>It **won't** tell us:</u>

  -how *fast* the reaction will occur

  -the *mechanism* by which the reaction will occur

What is Energy?

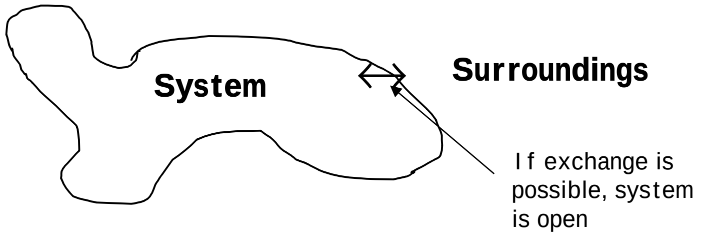
- Energy is the ***capacity to do work or to transfer heat***

-**Kinetic Energy**: energy associated with mass in motion (recall: $E_k = ½mv^2$)

-**Potential Energy:** energy associated with the *position* of an object relative to other objects (energy that is *stored* - can be converted to kinetic energy)

The System

- We must define what we are studying:



System: portion of the universe under study

Surroundings: everything else

Energy Transfer

- Energy can be transferred in two different ways:

1. By doing **Work** (applying a force over a distance)

   W = F x d

2. **Heat - q** (results in a change in temperature)

Note: ***W, q, and E all have the same units (Joule),*** but:

- W & q depend on *path* (path function)
- E is *independent of path* (state function)

First Law of Thermodynamics

- "The total energy of the universe is *constant*."
- "Energy is neither created or destroyed in a process, only converted to another form."

  -**Conservation of Energy**

- "*You can't win . . . you can only break even.*"

$$\boxed{\Delta E = q + w}$$

Change in energy of the system

Heat Flow:

+ is **into system**

- is out of system

Work: + is done **on system**

- is done **by system**

Example: Gas in a cylinder (fixed volume)

- Suppose we have a gas in a cylinder with a movable piston:

•<u>What if:</u>

•The piston is locked in a fixed position

-Volume is *constant*, so: **<u>w = 0</u>**

-> w = f x d OR <u>$w = P\Delta V = 0$</u>

<u>Thus</u>: $\Delta E = q_v$

•Now, if we add *heat* to the system:

q > 0, so <u>$\Delta E > 0$</u> (E incr.)

-temp incr -> $E_k = 3/2\ RT$ -> <u>$\Delta E_k = 3/2\ R\Delta T$</u>

Example: Gas in a cylinder (variable volume)

- Ok, now let's allow the piston to move, but let's ***disallow heat flow*** (q = 0) - <u>*adiabatic process*</u>

<u>So:</u> $\Delta E = w = -P\Delta V$

Movie!

- <u>Gas Compression</u>: $\Delta V < 0$ -> <u>*D**E is +***</u>
  -work is done *on* the system
  -temperature of the gas *increases*
- <u>Gas Expansion:</u> $\Delta V > 0$ -> <u>*D**E is -***</u>
  -work is done *by* the system
  -temperature of the gas *decreases*

Measuring ΔE

- We can measure ***q*** by the change in temperature:

  If **q > 0:** heat is *added* to the system
  -***endothermic*** (system absorbs heat)
  -temperature (*of the surroundings*) *<u>decreases</u>*

  If **q < 0:** heat is *given off* by the system
  -***exothermic*** (system loses heat)
  -temperature (*of the surroundings) <u>increases</u>*

Calorimetry: Measuring ΔE

- We can quantify heat flow (q) by measuring the change in temperature of a system: *Calorimetry*

  <u>Heat Capacity (C)</u>: amount of heat (q) required to raise the temperature of a substance by 1 K

  -if we calculate C for a *specific amount* of a particular substance, we call it the ***Molar Heat Capacity*** *(c_v at constant volume)* or the ***Specific Heat Capacity*** *(c_s, per gram of the substance)*

<u>Example:</u> for 100.0 g H_2O -> *specific heat = 4.184 J/g - K*

$$C = \text{mass x specific heat} = m \times c_s$$
$$= 100.0\text{ g} \times 4.184\text{ J/g - K}$$
$$= \underline{\mathbf{418.4\ J/K}}$$

Heat flow and temperature

- Now we can relate ***q*** and temperature:

$$\boxed{\mathbf{q = C\ (T_{final}\ -\ T_{initial})}}$$

Example: How much heat is required to raise the temperature of *232.0 g* H_2O from **25.0 ºC** to **78.0 ºC**?

$q = C\Delta T = (m \text{ x specific heat})(\Delta T)$

$= (232.0 \text{ g x } 4.184 \text{ J/g -K})(78.0 - 25.0)$

$= (970.688 \text{ J/K})(53.0 \text{ K})$

$= 51446.464 \text{ J} = \boldsymbol{5.14 \times 10^4 \text{ J}}$

$= \underline{\boldsymbol{51.4 \text{ kJ}}}$

Constant-Volume Calorimetry

- Use a "bomb" calorimeter:

-typically used with *combustion* reactions

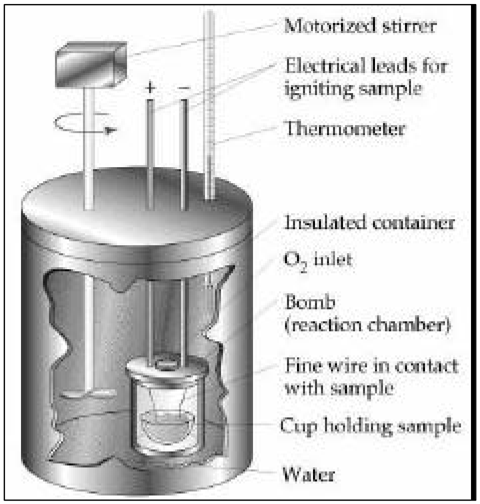
-heat (q) from rxn is transferred to the water and the calorimeter

-knowing the *heat capacity* of the calorimeter:

$q_{rxn} = -C_{cal} \times \Delta T$

So: $q_v = \Delta E$

(w=0 @ constant volume)



Enthalpy

- Chemistry is commonly performed at *constant pressure*, so:
  - -it is easy to measure *heat flow* (q_p)
  - -work ($P\Delta V$) is small (but finite) and hard to measure

Define a new term: **Enthalpy (H)**

$$\boxed{H = E + PV}$$

Relating Enthalpy and Heat

- Recall: $\Delta E = q + w$
- At constant pressure: $\Delta E = q_p - P\Delta V$
- Rearranging: $q_p = \Delta E + \Delta PV$

$$q_p = D(E + PV)$$

- Substituting: $\underline{q_p = DH}$

So, if we measure q_p, then we can obtain the enthalpy change (ΔH) directly

Constant-Pressure Calorimetry

- So-called “coffee-cup” calorimetry:

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

How are ΔE and ΔH related?

- From the definition of Enthalpy:

$$\Delta H = \Delta E + P\Delta V$$

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

So: $$\boxed{\Delta H = \Delta E + RT\Delta n}$$

q_p q_v **PV work**

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:***

$$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2 0\ (g) \qquad \Delta H = -483.6\ \text{kJ}$$

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 $\Delta H \ll 0$ 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): $\mathbf{Sn(s) + 2Cl_2(g) \rightarrow SnCl_4(l)}$	**-545.2 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:		<u>ΔH</u>
<u>Rxn(1):</u>	$4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(l)$	- 1531 kJ
<u>Rxn(2):</u>	$N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(l)$	- 367.4 kJ
<u>Rxn(3)</u><u>**:**</u>	$H_2(g) + ½O_2 \rightarrow H_2O(l)$	- 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 **÷ 2** = -1531 ÷ 2 = -765.5 kJ

ΔH_2 **x 3** = -367.4 x 3 = -1102.2 kJ

ΔH_3 **x (-3)** = - 285.9 x (-3) = 857.7 kJ

ΔH_{rxn} = -1010.0 kJ

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: ΔH^o_f (AgCl(s)) = -127.0 kJ/mol

Using Enthalpies of Formation

- Hess's Law and tablulated ΔH^o_f values are a powerful tool for predicting enthalpy changes for reactions:

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

Example: *The Thermite Reaction*

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

We know: $\Delta H^o_f\ (Fe_3O_4) = -1120.9$ kJ

$\Delta H^o_f\ (Al_2O_3) = -1669.8$ kJ

So:

$\Delta H^o = [4(-1669.8\ kJ/mol) + 9(0)] - [3(-1120.9\ kJ/mol) + 8(0)]$

$\Delta H^o = (-6679.2\ kJ) - (-3362.7) =$ ***-3316.5 kJ***

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!

We know: 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:

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

Putting it all together

- So, to get ΔH^o_f for $CO_2(g)$:

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

$CO_2(g) \rightarrow CO_2(s)$ $\Delta H = -50.02$ kJ/mol

Adding gives:

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

And, finally:

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

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

$\Delta H^o_{rxn} = 2(-601.70$ kJ/mol$) - (-443.53$ kJ/mol$) =$ ***-759.87 kJ***

Bond Enthalpies

- Armed with Hess's law and ΔH^o_f values, let's dissect the reaction process (i.e., the energetics of bond *making* and *breaking*):

<u>For CH_4 (methane):</u>

We know: $C(s) + 2\ H_2(g) \rightarrow CH_4(g)$ $\Delta H^o_f = -74.9$ kJ/mol

- <u>We *want* to know</u>: the ***bond enthalpy*** for the C-H bond

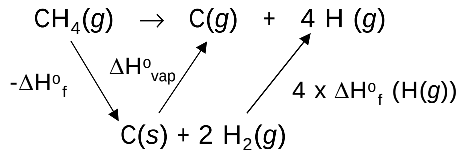
So, look at the reverse reaction:

$CH_4(g) \rightarrow C(g) + 4\ H\ (g)$ $\Delta H = 4 \times$ C-H bond enthalpy

Hess's Law to the rescue

- We want to do this:

<u>Enthalpy Cycle</u>



$CH_4(g) \rightarrow C(g) + 4\ H\ (g)$

$-\Delta H^o_f$

ΔH^o_{vap}

$4 \times \Delta H^o_f\ (H(g))$

$C(s) + 2\ H_2(g)$

$CH_4(g) \rightarrow C(s) + 2\ H_2(g)$ $-\Delta H^o_f = -(-74.9\text{ kJ})$

$C(s) \rightarrow C(g)$ $\Delta H^o_{vap} = 718.4\text{ kJ}$

$\underline{2\ H_2(g) \rightarrow 4\ H(g)}$ $4 \times \Delta H^o_f = \underline{4(217.9\text{ kJ})}$

$CH_4(g) \rightarrow C(g) + 4\ H\ (g)$ *1664.9 kJ*

So, **C-H bond enthalpy** = 1664.9 kJ/4 = ***<u>416.2 kJ</u>***

Bond Enthalpies:
What good are they?

- They indicate how *strong* a bond is:

N≡N	946 kJ/mol
H-H	436 kJ/mol

<u>In general</u>: ≡ > = > -

- If we assume that bond enthalpies for a particular bond are constant in all compounds, then we can use them to estimate ΔH_{rxn}:

$$\Delta H_{rxn} = \sum \text{Reactant Bond Enthalpies} - \sum \text{Product Bond Enthalpies}$$

(energy added to break bonds) (energy released by making bonds)

-This works well if there are no intermolecular forces (i.e., in the gas phase!)