

# TODAY

0. Why  $\Delta H = q$  (if  $p_{ext}=p=\text{constant}$  and no useful work)
1. Constant Pressure Heat Capacity (what we usually use)
2. “Heats” of Chemical Reactions:  $\Delta_r H$  (mechanics of obtaining from the table of *standard* “heats of formation”)
3. I can get  $\Delta_r H$  from table, BUT, how to get  $\Delta_r U$ ???
4. What exactly is  $\Delta_f H^0$ ?
5. **Hesse’s Law** (adding/subtracting chemical reactions): an example of exploiting the fact that  
changes in state functions are independent of path.

## Enthalpy: (defined because of the small work against atmosphere)

$$H = U + pV \quad \text{by definition (always true)}$$

$$dH = ?$$

$$= dU + d(pV) = dU + pdV + Vdp$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + p_2V_2 - p_1V_1$$

(not  $\Delta U + p\Delta V + V\Delta p$ )

$$pV = nRT \text{ (ideal gas)}$$

$\Delta(pV) = \Delta(nRT) = nR \Delta T$  also only depends on T

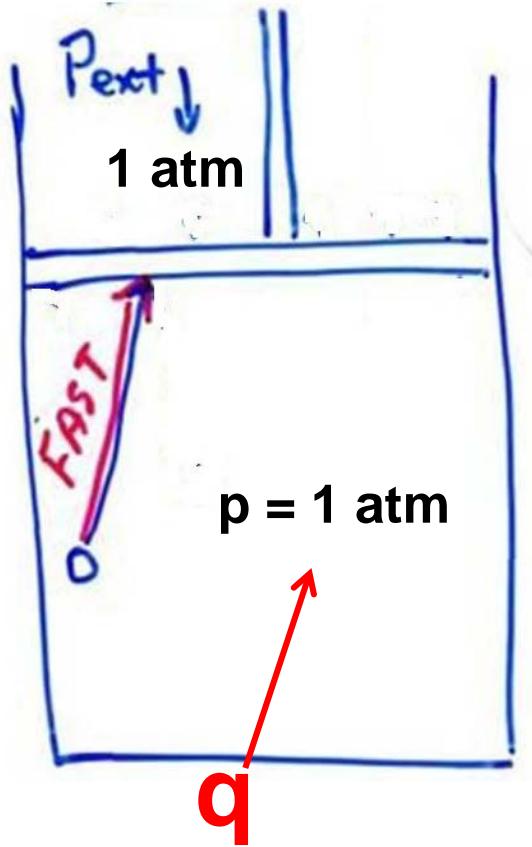
so both  $\Delta U$  and  $\Delta H = 0$  for ideal gas if isothermal process

$\Delta H = q$  (IF  $p_{ext} = p = \text{constant}$ , and only  $p_{atmosphere}V$  work done)

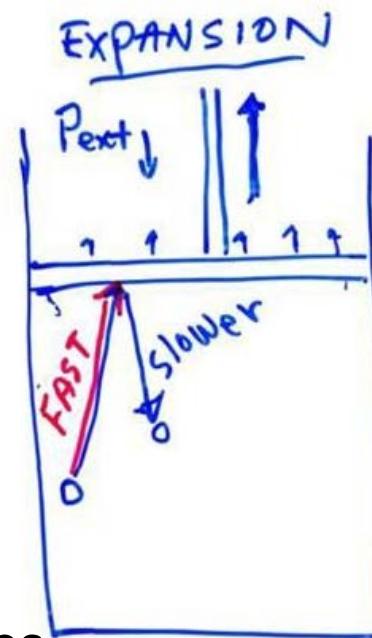
because  $\Delta U = q + w = q - p_{atmosphere}\Delta V + w_{\text{useful}}$  and  $\Delta pV = p_{atmosphere}\Delta V$

The annoying  $-p_{atmosphere}\Delta V$  term cancels!

# Heat Capacity of Gases at Constant Pressure: $C_p$



What happens if we **heat** the gas while keeping  $p = p_{ext} = \text{constant} = 1 \text{ bar}$ ?



But, expansion does some work, which has a cooling effect.  $\Delta T$  is smaller  $C = q/\Delta T$ , so **C is larger**.

More heat will be needed to raise the temperature than if volume is kept constant.

**$C_p > C_v$ , always**

Heating makes the molecules move faster, making the pressure increase, which causes **expansion**.

# How much more heat is required?

At **constant Volume**  $\Delta U = q$  (if no useful work done)

$$q_v = C_V \Delta T = \Delta U$$

At **constant Pressure**  $\Delta H = q$  (if no useful work done)

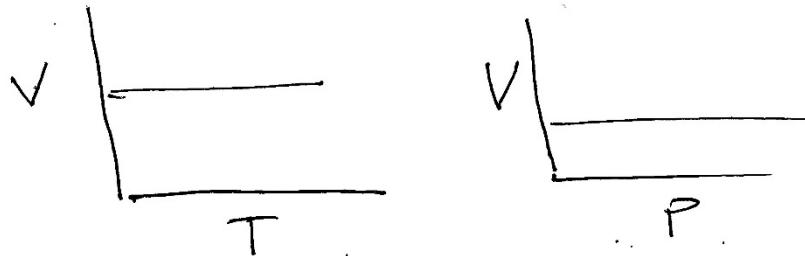
$$\begin{aligned} q_p &= C_P \Delta T = \Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta(nRT) \\ &\quad = C_V \Delta T + nR \Delta T \end{aligned}$$

$$C_P = C_V + nR$$

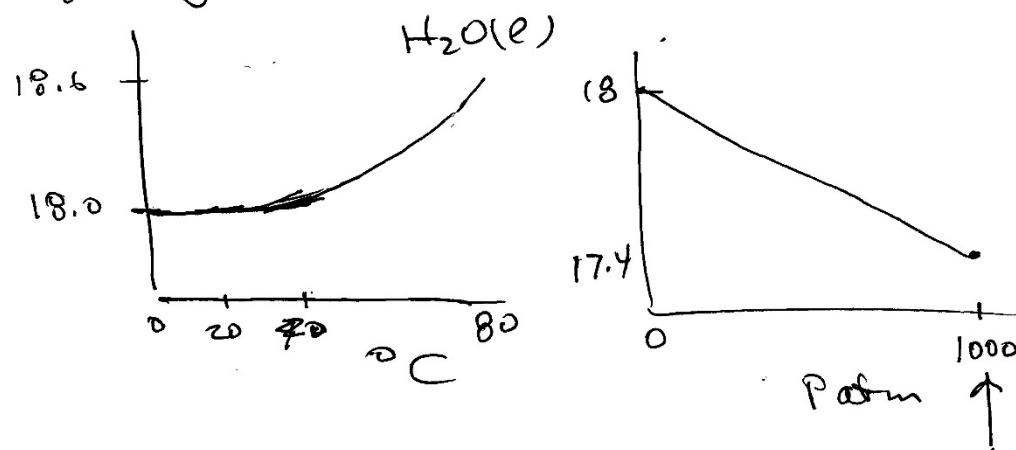
# SOLIDS and LIQUIDS

Much less compressible than gases

$$\therefore V(T, P) \approx \text{constant}$$



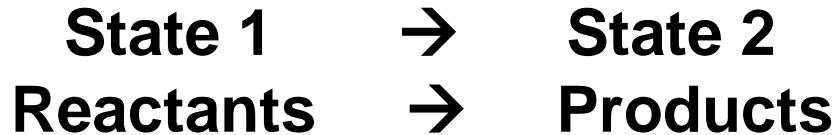
But if magnify the scale:



and ideal gas would be  $1000 \times$   
less  $V$  i.e.,  $V$  of a liquid

Very, very high pressure applied to a solid will often turn it into another crystal form that is more dense, e.g., graphite into diamond.

# Heats of CHEMICAL REACTIONS ( $\Delta_rH$ ) (and Phase Changes treated the same way)



$$\Delta_rH = \sum H_i(\text{products}) - \sum H_i(\text{reactants})$$

(this is an abstract useless statement)

In practice, we use a Table of **standard** heats of **formation**

$$\Delta_rH^0 = \sum \Delta_fH_{298}^0 \text{ (products)} - \sum \Delta_fH_{298}^0 \text{ (reactants)}$$

Tabulated at 1 bar and some T (usually 298 K)

(note that this is constant T and p) so,  $q = q_p = \Delta H$

In general: if weak bonds  $\rightarrow$  STRONG BONDS  
then the reaction is very **EXOTHERMIC** == “chemical energy”

## NOTE: S, Not $\Delta S$

TABLE A.5 Inorganic Compounds\* (cont.)

	$\Delta_f H^\circ$ (kJ mol <sup>-1</sup> )	$S^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta_f G^\circ$ (kJ mol <sup>-1</sup> )
HCO <sub>3</sub> <sup>-</sup> (aq)	-691.99	91.2	-586.77
CO <sub>3</sub> <sup>2-</sup> (aq)	-677.14	-56.9	-527.81
Fe(s)	0	27.28	0
Fe <sub>2</sub> O <sub>3</sub> (s)	-824.2	87.40	-742.2
H <sub>2</sub> (g)	0	130.79	0
H <sub>2</sub> O(g)	-241.82	188.93	-228.73
H <sub>2</sub> O(l)	-285.83	69.91	-237.13
H <sup>+</sup> (aq)	0	0	0
OH <sup>-</sup> (aq)	-229.99	-10.75	-157.244
H <sub>2</sub> O <sub>2</sub> (aq)	-191.17	143.9	-134.03
H <sub>2</sub> S(g)	-20.63	205.90	-33.56
H <sub>2</sub> SO <sub>4</sub> (g)	-735.13	298.8	-653.37
N <sub>2</sub> (g)	0	191.72	0
NH <sub>3</sub> (g)	-46.11	192.56	-16.78
NH <sub>3</sub> (aq)	-80.29	111.3	-26.50
NH <sub>4</sub> <sup>+</sup> (aq)	-132.51	113.4	-79.31
NO(g)	90.25	210.87	86.55
NO <sub>2</sub> (g)	33.18	240.17	51.47
NO <sub>3</sub> <sup>-</sup> (aq)	-205.0	146.40	-108.74
Na <sup>+</sup> (aq)	-240.12	59.0	-261.90
NaCl(s)	-411.15	72.13	-384.14
NaCl(aq)	-407.27	115.5	-393.13
NaOH(s)	-425.61	64.46	-379.49
O <sub>2</sub> (g)	0	205.25	0
O <sub>3</sub> (g)	142.7	239.04	163.4
S(rhombic)	0	31.80	0
SO <sub>2</sub> (g)	-296.83	248.33	-300.19
SO <sub>3</sub> (g)	-395.72	256.87	-371.22

\* Standard thermodynamic values at 25°C (298.15 K) and 1 bar pressure. Values for ions refer to an aqueous solution at unit activity on the molarity scale. Standard enthalpy of formation,  $\Delta_f H^\circ$ , third-law entropies,  $S^\circ$ , and standard Gibbs free energy of formation,  $\Delta_f G^\circ$ , are given.

† The standard state for all ions and for species labeled (aq) is that of a solute on the molarity scale.

(Data from *The NBS Tables of Thermodynamic Properties*, D. D. Wagman et al., eds., *J. Phys. Chem. Ref. Data*, 11, Suppl. 2 (1982), corrected to 1 bar pressure.)

From a table of  $\Delta_f H^\circ$ <sub>298</sub> for a few dozen reactions we can know the  $\Delta_f H^\circ$  for thousands of reactions that may have never been measured.

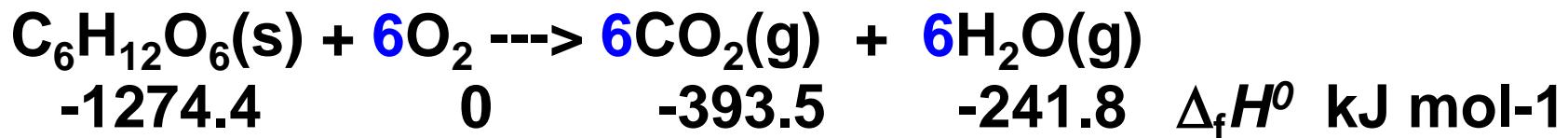
Consider a generic chemical reaction



where the  $a, b, c, d$  = the stoichiometric numbers  
and A,B,C,D are chemicals

$$\Delta_r H^0 = c \Delta_f H^0(C) + d \Delta_f H^0(D) - a \Delta_f H^0(A) - b \Delta_f H^0(B)$$

Example:



$$\begin{aligned} \Delta_r H^0 &= 6(-393.5) + 6(-241.8) - ((-1274.4) - 6(0)) \\ &= \mathbf{-2537.4 \text{ kJ/mol}} \text{ as } \underline{\text{written}} \end{aligned}$$

you MUST always associate the  $\Delta_r H^0$  with a **balanced** reaction

What EXACTLY is  $\Delta_f H^0_{298}$  ???

$\Delta_f H^0_{298}$  = **Standard Heat of Formation** (at 25° C)

The **superscript 0** means that all reactants and products are in their **standard state**, which means:

Gases: 1 bar and **ideal**

Liquids and solids: 1 bar applied and **pure**

Solutes: 1 molar (usually) and **ideal** (no solute-solute interaction)

*Note that temperature is NOT part of the definition. (There is a different table for every temperature.)*

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**f** means **formation** of **1 mole** from the **most stable** form of the **elements** at the given temperature (298 in this case)

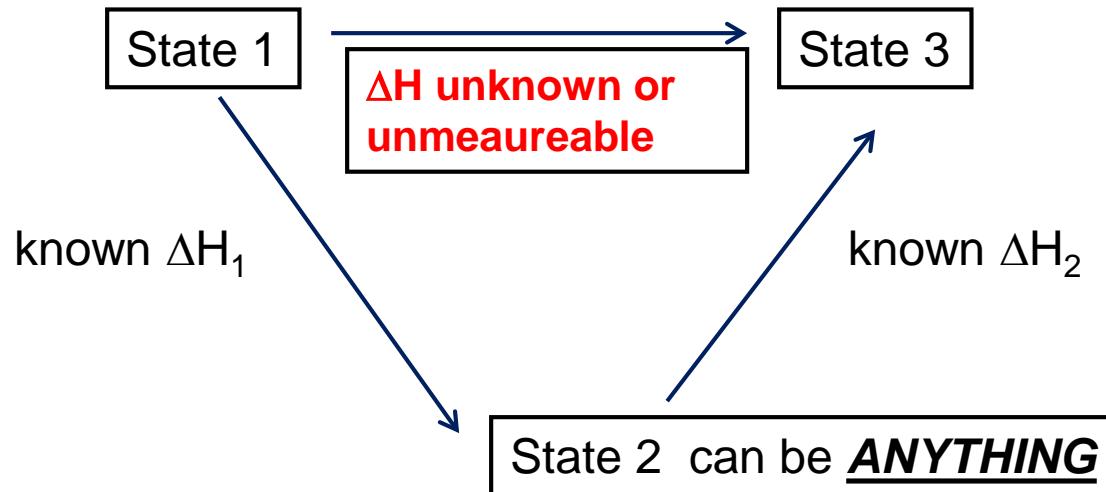
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**Quiz:** What chemical reaction has:

1.  $\Delta H_{298} = \Delta_f H^0_{298}$  for  $H_2O(g)$        $H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)$
2.  $\Delta H_5 = \Delta_f H^0_5$  for  $H_2O(g)$        $H_2(s) + 1/2O_2(s) \rightarrow H_2O(g)$
3. Why is  $\Delta_f H^0_{298} = 0$  for  $H_2(g)$ ,  $O_2(g)$ ,  $N_2(g)$  ... ?     $H_2(g) \rightarrow H_2(g)$

We will constantly be using:

## Powerful Exploitation of State Function Concept in Thermodynamics



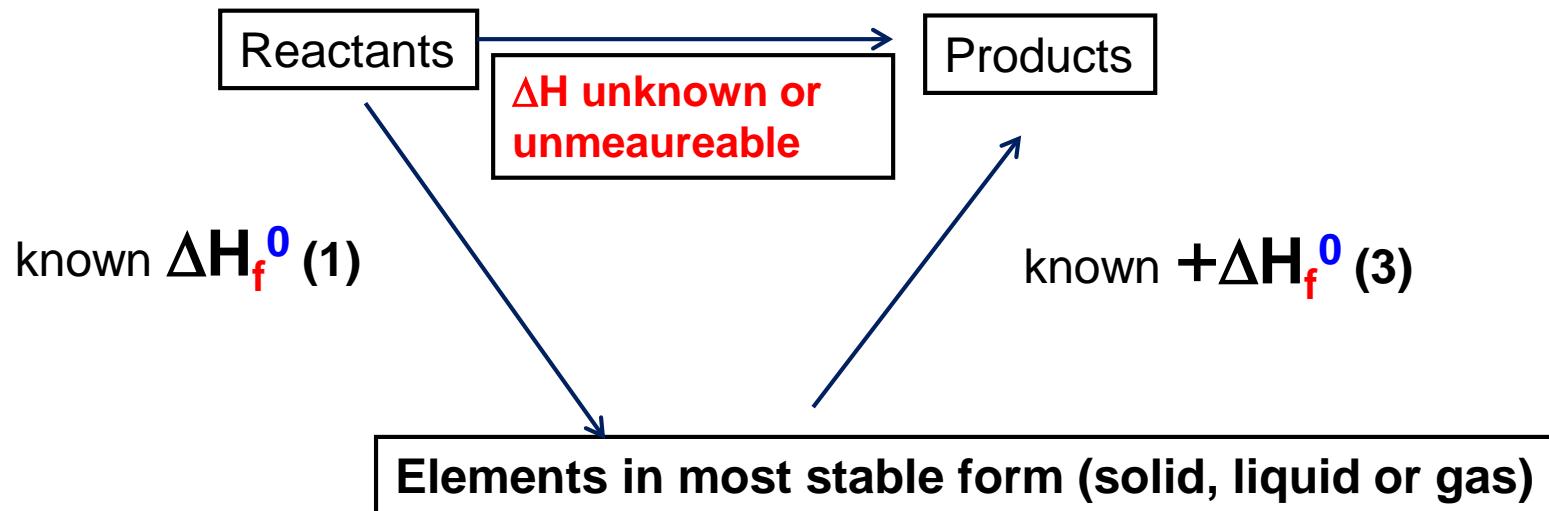
***Path does not matter.***  $H$  is a STATE FUNCTION

$$\Delta H_{\text{unknown}} = \Delta H_1 + \Delta H_2$$

When applied to chemical reactions this trick is known as **Hesses Law**

Hesse's Law is a:

## Powerful Exploitation of State Function Concept in Thermodynamics

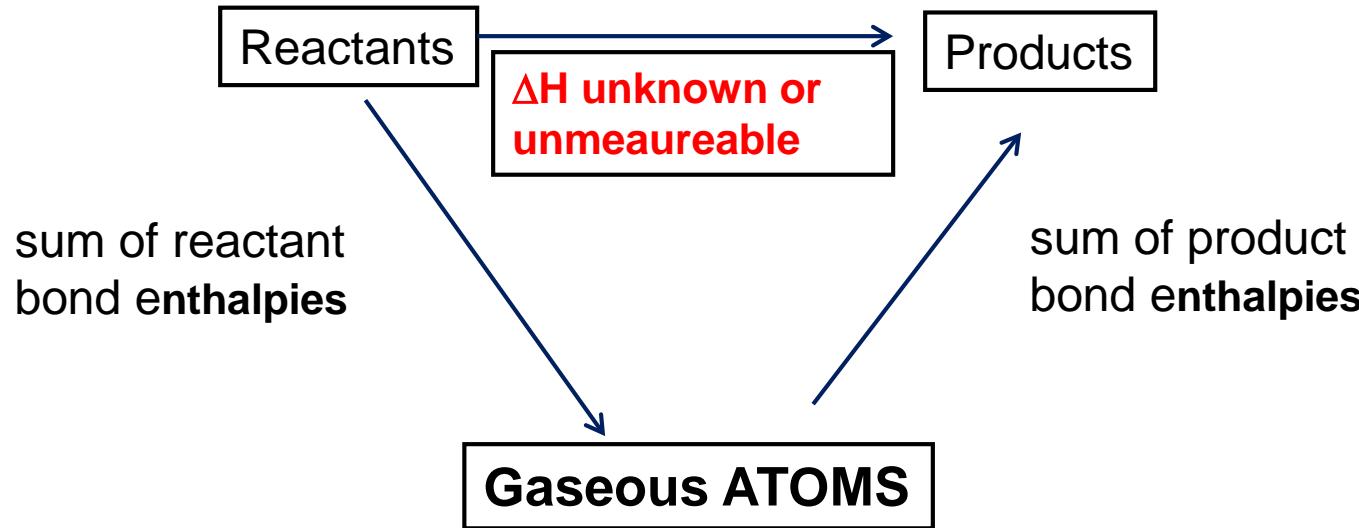


***Path does not matter: H is a STATE FUNCTION***

$$\Delta H^0_{\text{unknown}} = +\Delta H_f^0 \text{ (prod)} - \Delta H_f^0 \text{ (react)}$$

# “Bond Enthalpies”

## Another Exploitation of State Function Concept in Thermodynamics



***Path does not matter. H is a STATE FUNCTION***

$$\Delta H^0_{\text{unknown}} = +\Delta H_{\text{BE}}^0 \text{ (reactants)} - \Delta H_{\text{BE}}^0 \text{ (products)}$$

**Why the sign change???**

Bond Enthalpy is DEFINED as the:

Enthalpy of bond breaking (not making)

**Table 2.3** Average bond dissociation energies at 25°C

Bond	$D$ (kJ mol <sup>-1</sup> )
C—C	344
C=C	615
C≡C	812
C—H	415
C—N	292
C—O	350
C=O	725
C—S	259
N—H	391
O—O	143
O—H	463
S—H	339
H <sub>2</sub>	436.0
* N <sub>2</sub>	945.4
O <sub>2</sub>	498.3
C(graphite)	716.7

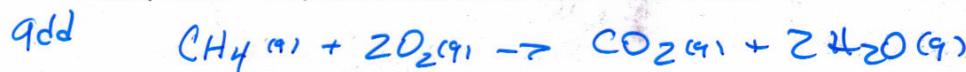
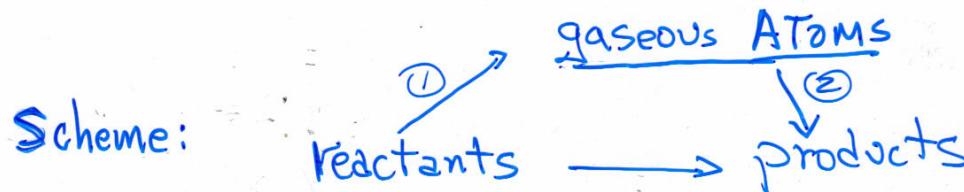
Source: After L. Pauling and P. Pauling,  
*Chemistry*, W. H. Freeman, San Francisco,  
1975.

No

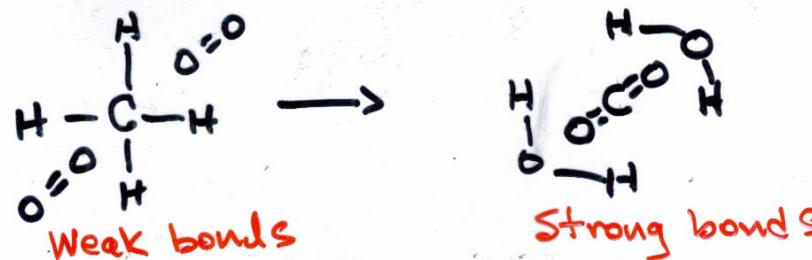
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## Bond Energies (Enthalpies)

# ESTIMATING $\Delta H$ from BOND ENERGIES



$\Delta H$  ① = Sum of Bond energies of Reacts.  
 ② = Sum of " " " " Products.



$$\begin{aligned} \Delta H &\approx 2 \text{ BE}(\text{O=O}) + 4 \text{ BE}(\text{C-H}) - 2 \text{ BE}(\text{C=O}) - 4 \text{ BE}_{(\text{O-H})} \\ &= 2(498) + 4(415) - 2(725) - 4(463) \end{aligned}$$

$$\approx -646 \text{ kJ/mol}$$

20% error ☹

Exact from  $\Delta H_f^\circ = -802.3$   
 (The glass is 80% FULL) ☺

# Finding $\Delta U$ of a reaction

$$\Delta H = \Delta U + \Delta(PV)$$

$$\Delta U = \Delta H - \Delta(PV)$$

**Ignore volume of solids and liquids**

Then  $\Delta U = \Delta H - \Delta(nRT) = \Delta H - \Delta n(RT)$

because T is constant

where  $\Delta n$  is the change  
of moles of **gases** only.