

Homework Due Tue 8:50 am

Office Hours **today?**

I am free 11-noon, 2:30-3 **today,**

Erin 56 CBB): 9-12, 3-5 **today**

Monday: I am free most of the day
show up in class to let me know when
you will show up

TODAY

1. Comments on homework
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.**

Hints and corrections to Homework #1

Problem 24 (c): answer given on p. 37 in text

Problem 28

(a) **Correction:** $D_r H^0$ should be $\Delta_r H^0$ (a misprint I believe)

(b) **Clarification:** “Energy equivalent” = ΔH^0
(in this case, for 20 kg of sucrose for the reaction in (a))

(c) Hint: convert kJ from part (b) per 10,000 m² per hour to kW/m². (recall $1 \text{ W} = 1 \text{ Js}^{-1}$.)

From Handout 1a RETRACTION

**** 10 d. ~~you will need to remember what boiling means: liquid water evaporating into bubbles of water vapor because the vapor pressure of the water = the applied pressure on the surface of the liquid.~~

This statement is badly worded, and also not relevant to problem 10d

There is NO BOILING in problem 10(d).

Water will NOT boil at the boiling point. It must be a little above the boiling point for bubbles to grow. We will talk about this later in the semester.

The following statement is also not necessary for the problem:.

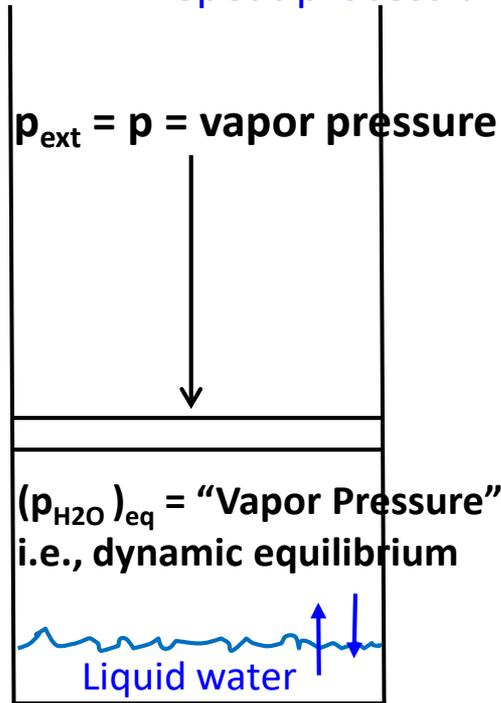
(water will boil at exactly 298 K if in a partial vacuum such that the air pressure = 2536 Pa (from Table 2.2) (=0.02536 bar =0.02569 atm.)

Problem 10 d (liquid water \rightarrow water vapor (no air present))

“A liquid at its **boiling point** is converted **reversibly** into its vapor, at constant T and 1 bar pressure”

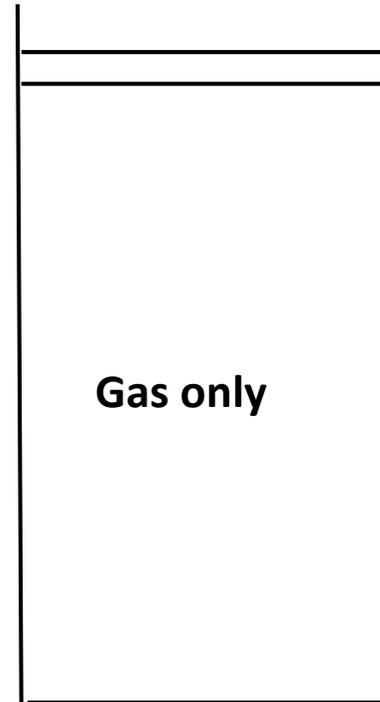
(boiling point = temperature at which the **vapor pressure** = p_{ext})

1. move piston up a **tiny amount** (so it will be “reversible”)
2. Gas expands and **$p_{\text{H}_2\text{O}} < \text{vapor pressure}$** (temporarily).
3. A **tiny amount** of liquid evaporates until **equilibrium** is reached again.
4. Repeat process until all liquid is gone.



Heat Bath T = boiling point

Reversibly
move piston up
very slowly \rightarrow



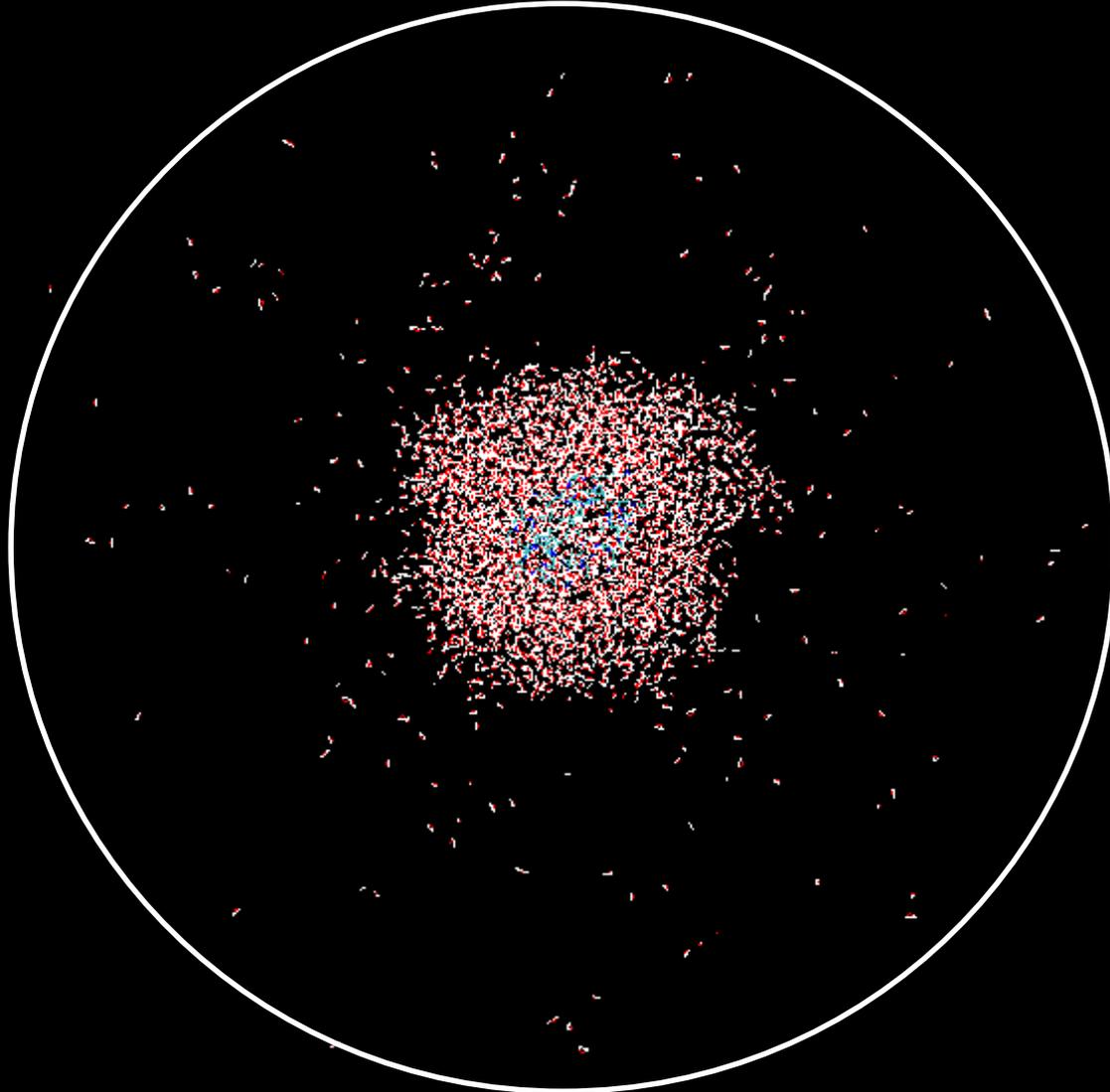
Heat Bath T = boiling point

What is vapor pressure?

Imagine a small water droplet with a few thousand water molecules. The oxygens are red and hydrogens are white. A small protein (blue) is in the center of the droplet. The drop is surrounded by a glass sphere.



After **dynamic equilibrium** established. The partial pressure of water now = **“the vapor pressure”**



“Vapor Pressure” is simply the Equilibrium Constant for the “reaction”

Liquid → Vapor

Vapor Pressure visualized:

Molecular Dynamics Simulation of evaporation from a small drop of water in the glass sphere.

[361 website Vapor Pressure Movie \(15th Grade Version\)](#)

- Simulation by Jose R. Tusell, CHARMM
- Graphics using VMD <http://www.ks.uiuc.edu/Research/vmd/>

Finding ΔU of a reaction

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

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

Ignore volume of solids and liquids

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

because T is constant

where Δn is the change of moles of *gases* only.

C_p vs. C_v heat capacities continued: How much more heat is required for constant pressure? (*ideal gases only*)

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)

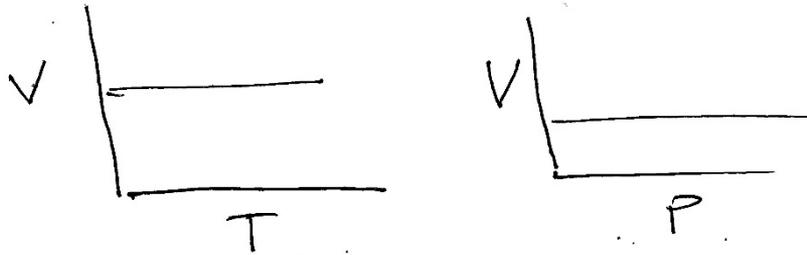
$$\begin{aligned} q_p = C_p \Delta T &= \Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta(nRT) \\ C_p \Delta T &= C_v \Delta T + nR \Delta T \end{aligned}$$

Therefore: $C_p = C_v + nR$ (for ideal gas)

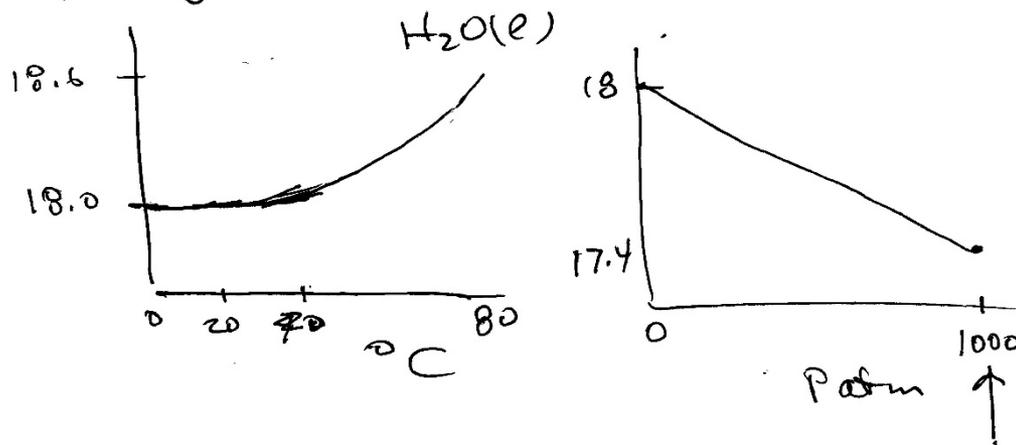
SOLIDS and LIQUIDS

Much less compressible than gases

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



But if magnify the scale.



At 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 ($\Delta_r H$)

(and Phase Changes treated the same way)

State 1 \rightarrow State 2
Reactants \rightarrow Products

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

(this is an abstract, useless statement)

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

$$\Delta_r H^0 = \sum \Delta_f H^0_{298} (\text{products}) - \sum \Delta_f H^0_{298} (\text{reactants})$$

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”

TABLE A.5 Inorganic Compounds* (cont.)

NOTE: S, Not Δ S

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

From a table of $\Delta_f H^\circ_{298}$ for a few dozen reactions we can know the $\Delta_r H^\circ$ for thousands of reactions that may have never been measured.

These numbers are for **1 mole** of the substance in the left column

* 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° , 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.)

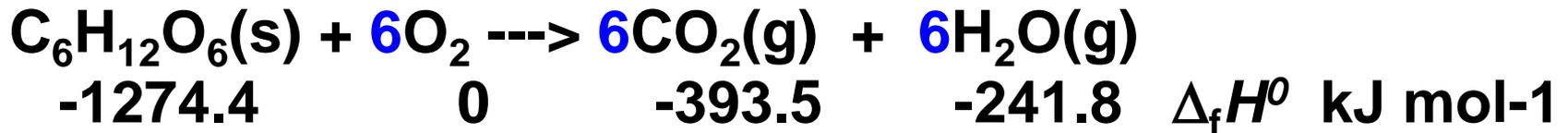
Consider a generic chemical reaction



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:



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

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

Generally, how one balances a chemical reaction is arbitrary, so ***must state how many moles of one of the reactants or products.***

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.)

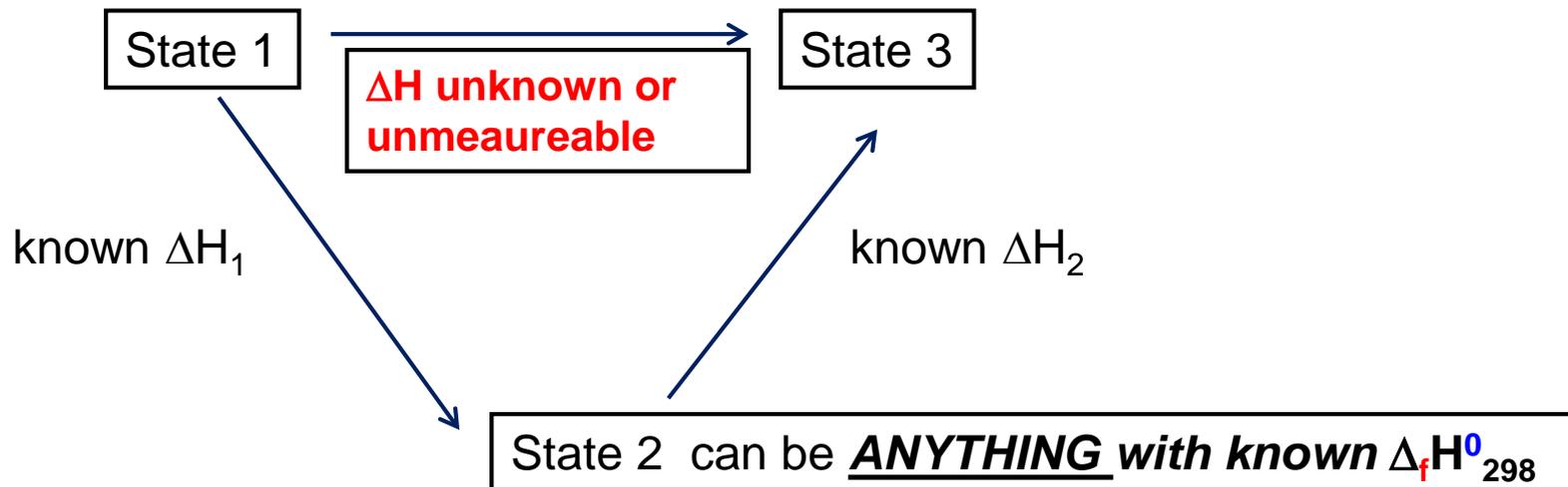
f means **formation** of **1 mole** from the **most stable** form of the **elements** at the given temperature (298 in this case)

Quiz: What chemical reaction has:

1. $\Delta H_{298} = \Delta_f H^0_{298}$ for $H_2O(g)$ $H_2(g) + 1/2 O_2(g) \rightarrow H_2O(g)$
2. $\Delta H_5 = \Delta_f H^0_5$ for $H_2O(g)$ $H_2(s) + 1/2 O_2(s) \rightarrow H_2O(g)$
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: Hesse's Law

Powerful Exploitation of State Function Concept in Thermodynamics



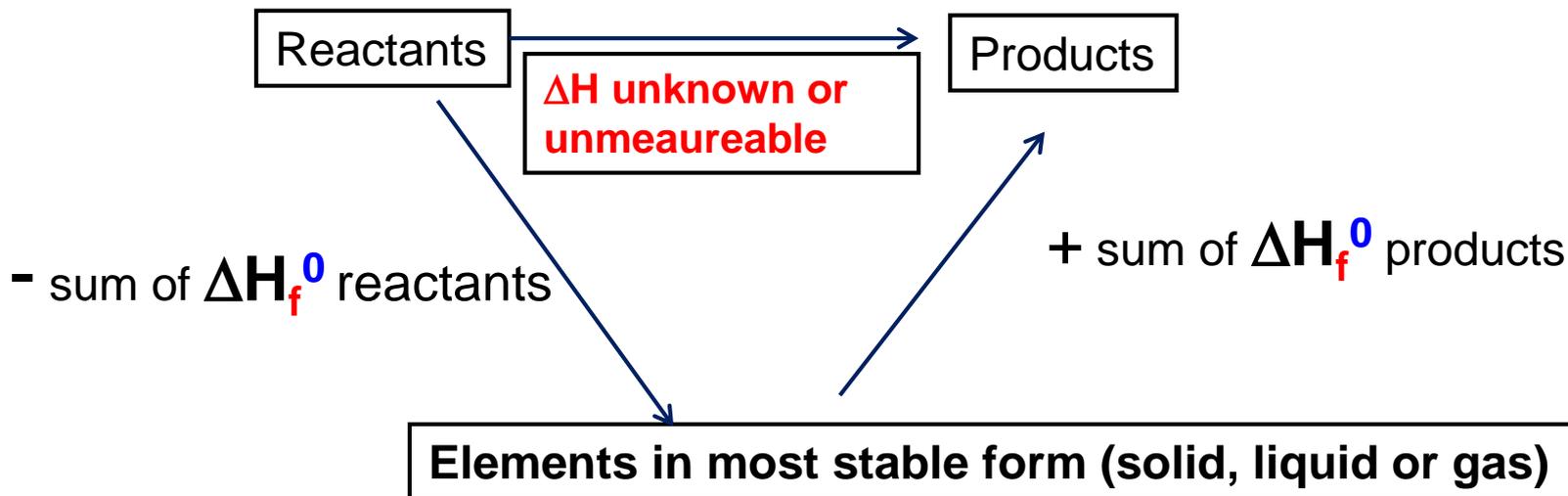
Path does not matter. H is a STATE FUNCTION

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

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

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

Problem 34b

Table 2.3 Average bond dissociation energies at 25°C

Bond	D (kJ mol ⁻¹)
<u>C—C</u>	<u>344</u> weaker
C=C	615
C≡C	812
C—H	415 weaker
C—N	292
<u>C—O</u>	<u>350</u> weaker
<u>C=O</u>	<u>725</u> - strong
C—S	259
N—H	391
O—O	<u>143</u> WEAK
<u>O—H</u>	<u>463</u> - strong
S—H	339
H ₂	436.0
** N ₂	<u>945.4</u> VERY STRONG
O ₂	498.3
C(graphite)	716.7

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

N=O

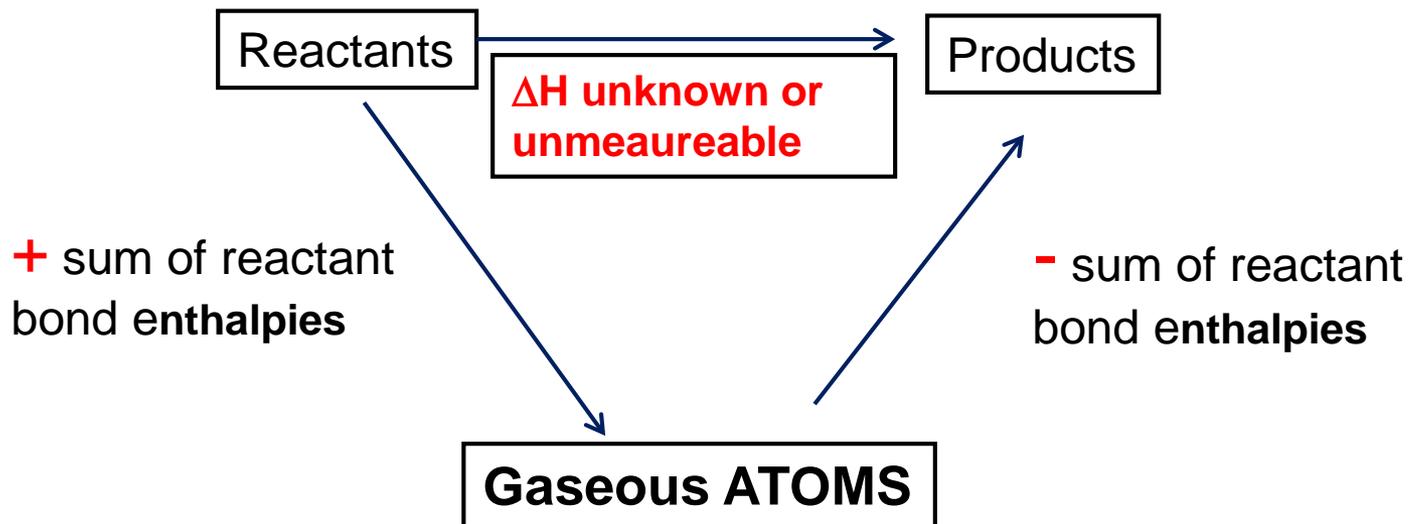
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Bond Energies (Enthalpies)

1. This is for **ESTIMATING** $\Delta_r H$
2. Is defined oppositely from from $\Delta_r H^0_f$
3. Provides **chemical intuition**

“Bond Enthalpies”

Another Exploitation of State Function Concept in Thermodynamics



Path does not matter. H is a STATE FUNCTION

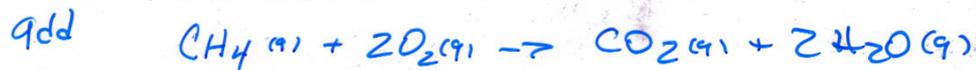
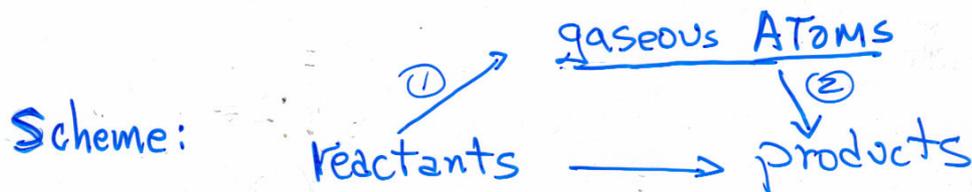
$$\Delta H^0_{\text{unknown}} = +\Delta H_{\text{BE}}^0 (\text{reactants}) - \Delta H_{\text{BE}}^0 (\text{products})$$

Why the sign change???

Bond Enthalpy is DEFINED *differently!*

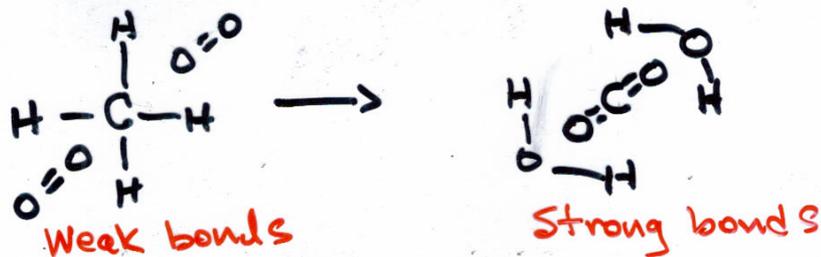
It is the Enthalpy of bond breaking (not making)

ESTIMATING ΔH FROM BOND ENERGIES



ΔH ① = Sum of Bond energies of Reacts.

② - Sum of " " " Products.



$$\begin{aligned} \Delta H &\cong 2 \text{BE}(\text{O}=\text{O}) + 4 \text{BE}(\text{C}-\text{H}) - 2 \text{BE}(\text{C}=\text{O}) - 4 \text{BE}_{(\text{O}-\text{H})} \\ &= 2(498) + 4(415) - 2(725) - 4(463) \\ &\cong -646 \text{ kJ/mol} \end{aligned}$$

20% error ☹️

Exact from $\Delta H_f^\circ = -802.3$

(The glass is 80% FULL) 😊