1412 - E3
CH 16 - Thermodynamics
Notes
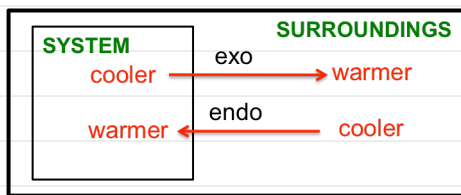
16

Chemical Thermodynamics — deals with HEAT–WORK–OTHER ΔE in relation to chemical and physical phenomena.

1st Law of Thermodynamics — Internal Energy

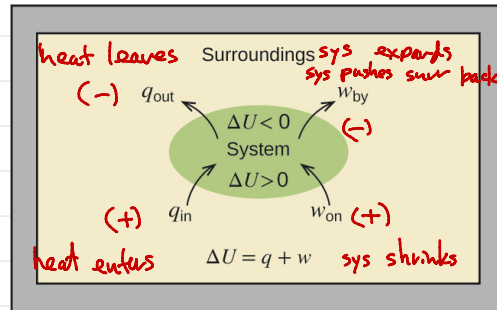$$\Delta U = Q + W$$

Universe = System + Surroundings

Phrases to remember

$$\begin{aligned} heat\ in &= heat\ out \\ heat\ lost &= heat\ gained \end{aligned}$$

• positive q is heat flow in; negative q is heat flow out
• positive w if work is done on the system; and negative w if work is done by the system.

heat leaves   Surroundings sys exparts
   sys pushes suur back

$(-)$ q_{out} w_{by}

$\Delta U < 0$ $(-)$
System
$\Delta U > 0$

$(+)$ q_{in} w_{on} $(+)$

heat enters $\Delta U = q + w$ sys shrinks

State Function – independent of path

Height = State Funct. ← Same Height
Path = not State Funct. ← Longer Path
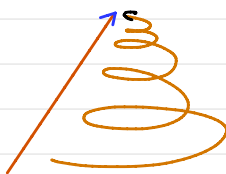
This is why Hess' Law ("Rack-n-Stack Equations") works

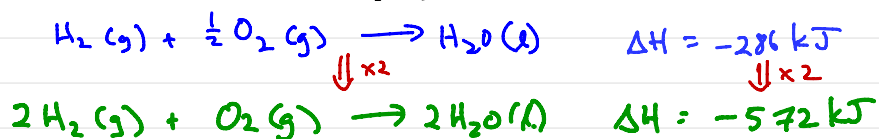## Enthalpy (heat at constant pressureP

$$\Delta H = q_p$$

Enthalpy = Heat @ P = k

- Three conventions

①・ΔH is associated with a particular chemical eq., with specified coefficients.
- ΔH is EXTENSIVE property, $= f(amt)$, and changing coefficient means changing ΔH value proportionately.
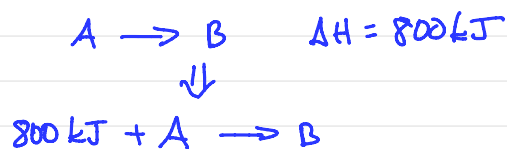
$$H_2 (g) + \tfrac{1}{2} O_2 (g) \longrightarrow H_2O (\ell) \qquad \Delta H = -286 \text{ kJ}$$
$$\Downarrow \times 2 \qquad\qquad\qquad\qquad \Downarrow \times 2$$
$$2 H_2 (g) + O_2 (g) \longrightarrow 2 H_2O (\ell) \qquad \Delta H = -572 \text{ kJ}$$

② Equations are also specific for phase (s, ℓ, g, aq).

- If $\Delta H = (-)$, then exo:
  write as PRODUCT

- If $\Delta H = (+)$, then ENDO
  write as REACTANT

$A \longrightarrow B \quad \Delta H = -800 \, kJ$
$\Downarrow$
$A \longrightarrow B + 800 \, kJ$

$A \longrightarrow B \quad \Delta H = 800 \, kJ$
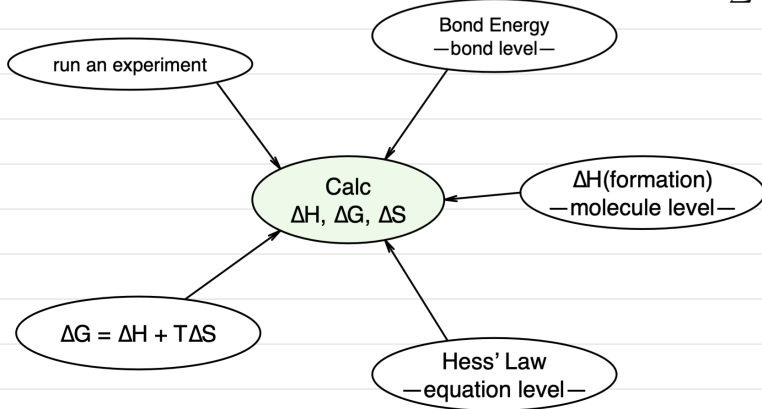$\Downarrow$
$800 \, kJ + A \longrightarrow B$
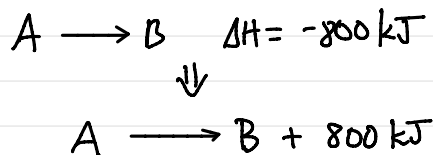
Two Types of ΔH "in-line" Problems

↳ ΔH for rxn given, calc ΔH for given quantity of material
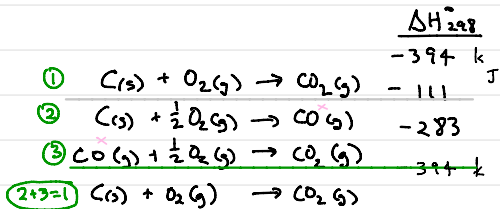↳ ΔH for quantity of material given, calc ΔH for rxn

★ BE !!! ...

$$\Delta H_{rxn} = \sum BE_{(broken)} - \sum BE_{(formed)}$$
$$= \sum BE_{(reactants)} - \sum BE_{(products)}$$

```
                    ( Bond Energy )
                    ( —bond level— )
( run an experiment )
                              ( Calc        )        ( ΔH(formation)      )
                              ( ΔH, ΔG, ΔS  ) ←───── ( —molecule level—   )
( ΔG = ΔH + TΔS )
                    ( Hess' Law        )
                    ( —equation level— )
```

$$\Delta H_{rxn} = \sum \Delta H_{f(reactants)}^{\,prod} - \sum \Delta H_{f(products)}^{\,react}$$

$\underline{\Delta H_{298}^{\circ}}$

		ΔH_{298}°
①	$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$	-394 kJ
②	$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$	-111
③	$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$	-283
②+③=①	$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$	-394 kJ

- standard state = reference point $\approx$ $0°C = fp(water)$
  - $\hookrightarrow$ (gas) $P = 1$ bar $= 0.987$ atm
  - $\hookrightarrow$ (aq) $M = 1 M$
  - $\hookrightarrow$ (s, l) pure
- "o" indicates std state:

STP

  - $\hookrightarrow$ $\Delta H°_{298}$ = occures under std state @ 298K
  - $\hookrightarrow$ ΔH = " NON-std-state conditions
- "mole reaction" (P 251/259)
  - $\hookrightarrow$ divided ΔH_{rxn} by amts (moles) of reactant s:
  - $\hookrightarrow$ yield INTENSIVE property frm 2 EXTENSIVE prop
    - ΔH and # moles
    - ... analogous to DENSITY (INTENSIVE)
      frm Mass (EXT) and Volume (EXT)

CHAPTER 16: THERMODYNAMICS

Spontaneity [16.1]

o <u>SPONTANEOUS</u> = occurs naturally (vs. NON spontaneous)

1st Factor: Total Energy is Decreased   (System becomes more stable)

o E.C. Diamond is <u>not</u> Forever ...
   Decomp of DIAMOND ⇄ GRAPHITE is FAVORABLE
   It happens, but very, very slowly, however
   <u>Bottom Line:</u> Thermodynamically FAVORABLE; but
   Kinetically, very slowly.

o recall: <u>allotropes</u>
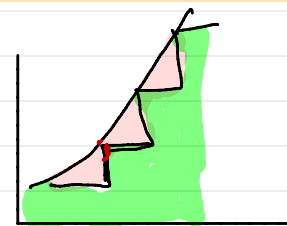   diff physical forms of the same material

C (diamond)

C (graphite)

ΔH

8

4
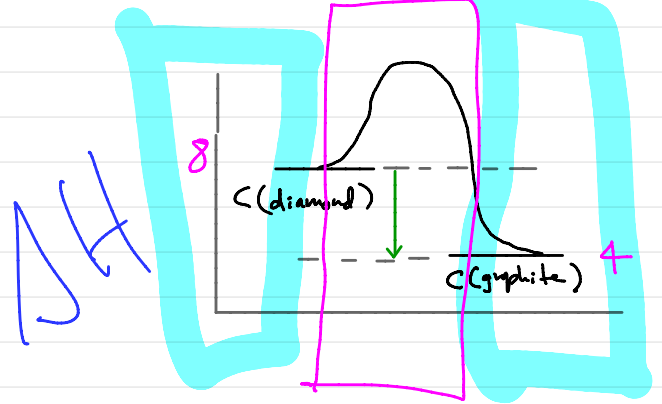
2nd Factor: Dispersal of Matter & Energy   (Energy becomes less usable)

o Both matter and energy naturally tend to Disperse.
   (Spread out ; Self-dilute ; Expand ;
      Take up more space ; become more uniform)

ΔS Wed/Oct 30

Entropy = a measure of DISORDER
… RANDOMNESS
… CHAOS
… FREEDOM

def:

$$\Delta S = \frac{q_{rev}}{T}$$

Enthalpy change for sys which never loses equilibrium

Temperature

relates heat flow for a process to Temp at which it occurs

$$S = k \ln W$$

microstate (W) = specific config of locations & energy of atoms/molecules

Boltzmann constant (1.38 E-23 J/K)

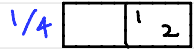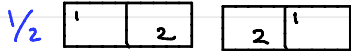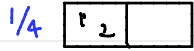$$\Delta S = S_f - S_i = k \ln \frac{W_f}{W_i}$$

$$\Delta S = \frac{q_{rev}}{T}$$

$$S = k\,lnW$$

$$S = k\,lnW = k\,ln\frac{W_f}{W_i}$$

$n^N \leftarrow$ (# items)
$\leftarrow$ # particles } each single combin'tion
$n \leftarrow$ # state } a MICRO state
(# rooms)

EG: Entropy change in allowing 2 particles in one box
to expand into two boxes.

1/4 | 1 2 | |
1/2 | 1 | 2 | | 2 | 1 |
1/4 | | 1 2 |

$n^N = 2^2 = 4$

$\Delta S = k \ln \frac{4}{1}$ 1.39

$= 1.38 E-23 \; J/k \; \ln 4$

$\Delta S = +1.91 \times 10^{-23} \; J/k$

	fav	un fav
ΔH_{rxn}	−	+
ΔS	+	−
ΔG	−	+

○ This is why perfume will spread from a small
vial to fill a room.
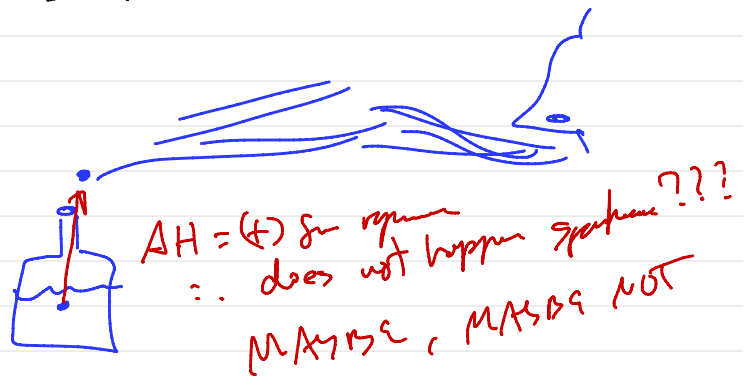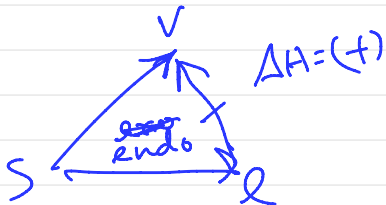
$\Delta H = (+)$

$\Delta H = (+)$ So rxn
∴ does not happen spontaneous ???

MAYBE, MAYBE NOT

ΔH=(+)
endo

Load

entropy → favorable
ΔH vap → endothermic

piz.

nuth

ΔH = (−)
ΔH vap = (+)
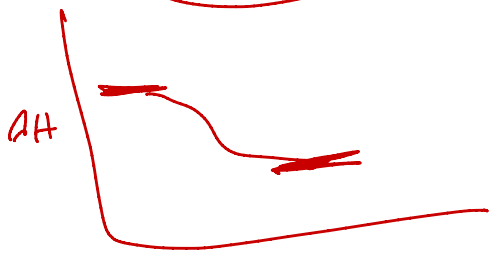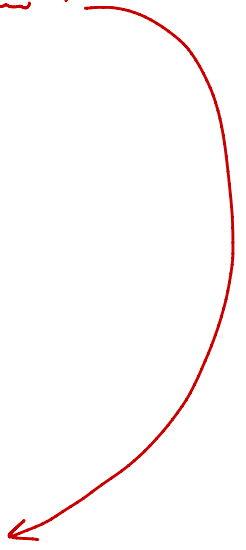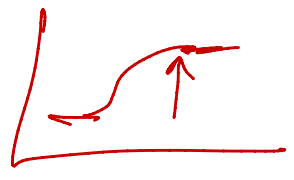
The Sign of ΔS

o $\Delta S > 0$, $\Delta S = (+)$ DISorder is increased:
        (spontaneous, natural, favorable)

o   Effect of TEMPERATURE:

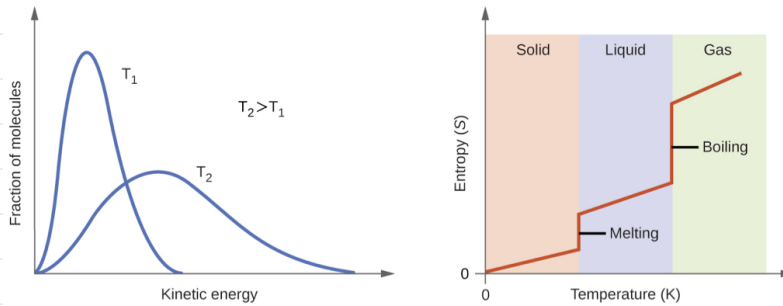Figure 16.11 Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

o Can often guess at Sign of ΔS by answering the questions:

¿ Did the System, or particles/energy that make up the system,
    ... become more: DISORDERED, SPREAD OUT, RANDOM
    ... achieve more   FREEDOM
    ... become less   RESTRICTD, CONFINED

(EX) Predict the sign of ΔS for a system   [16.3]

ⓐ 1 mol liq @ 25°C → 1 mol @ 50°C?
    incr randomness   ΔS = (+)

ⓑ $C_6H_6 (l) + 15/2\ O_2 (g) \longrightarrow 6\ CO_2 (g) + 3H_2 (l)$
    7.5 gas   6 gas
    fewer gas particles, less freedom ΔS = (−)

ⓒ $NaCl (s) \longrightarrow Na^+ (aq) + Cl^- (aq)$ Dissolve salt in water
    ions gain freedom to move about   ΔS = (+)

The Sign of "q"

$$\Delta S = \frac{q_{rev}}{T}$$

If it is understood/assumed to be a reversible system, then simply:

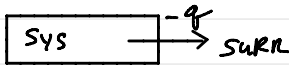$$\Delta S = \frac{q}{T}$$

$$\Delta S = \frac{q}{T}$$

q is negative (heat lost, heat out)

$$\Delta S_{sys} = \frac{-q}{T}$$

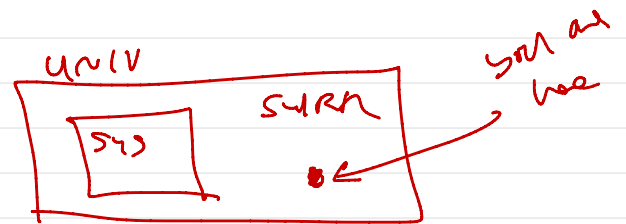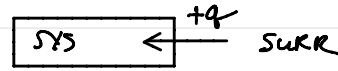If NEGATIVE, then heat flows from SYS into SURR

| SYS | $\xrightarrow{-q}$ SURR |

q is positive (heat gained, heat in)

$$\Delta S_{sys} = \frac{+q}{T}$$

If POSITIVE, then heat flows into SYS from SURR

| SYS | $\xleftarrow{+q}$ SURR |

UNIV

SURR

SYS

SYS and here

The 2nd Law of Thermodynamics (Entropy)

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr}$$

$\Delta S_{univ} > 0$ SPONTANEOUS

$\Delta S_{univ} < 0$ NON spontaneous
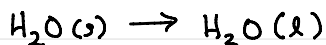
$\Delta S_{univ} = 0$ Reversible (@ Equil)

- If surroundings are vast (e.g. earth relative to camp fire),
  $\Delta H \rightleftharpoons$ to Surr is infinitesimally small, then $q_{surr} \simeq q_{rev}$, and...

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \frac{q_{surr}}{T} \simeq \Delta S_{univ}$$

$$H_2O\,(s) \longrightarrow H_2O\,(l)$$

knowing ......

- $\Delta S_{sys} = 22.1$ J/K $\longleftarrow$ see next page
- requires SURR transfer 6.00 kJ to SYS

ⓐ ¿ Is process spontaneous @ $-10.00°C$? (263.15 K)

ⓑ ¿   " $+10.00°C$? (283.15 K)

ⓐ AT $-10.00°C$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + q_{surr}/T$$

$$= 22.1\,\frac{J}{K} + \frac{-6.00 E3\,J}{263.15\,K} = \boxed{-0.7\,\frac{J}{K}}$$

$\Delta S < \emptyset$, ∴ NON-spontaneous @ $-10.00°C$

If SYS gains heat (q), then q is (+) for dS(sys); and q = (+) for dS(surr)

ⓑ AT $+10.00°C$
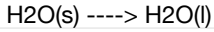
$$\Delta S_{univ} = \Delta S_{sys} + q_{surr}/T$$

$$= 22.1\,\frac{J}{K} + \frac{-6.00 E3\,J}{283.15\,K} = \boxed{+0.9\,\frac{J}{K}}$$

$\Delta S > \emptyset$, ∴ Spontaneous @ $+10.00°C$

H2O(s) ----> H2O(l)

Here is a change that we know is endothermic and occurs with an increase in entropy. At temperatures above 0oC (when the pressure is 1 atm), ice melts because the TS term is bigger than the H term. At lower temperatures, ice doesn't melt because the smaller value of T gives a smaller value for TS and the difference H-TS, is positive.

$$\text{ASIDE!} \quad \Delta S_{sys} = \frac{\Delta H_{fus}}{T} = \frac{6010 \text{ J}}{\text{mol}} \Big/ 273 \text{K}$$

$$= 22 \text{ J/K}$$

ΔS_{sys} for melting is the same at any temp... the amount of "ordering" is the same

TABLE 16.4   Results of the Calculation of ΔS_{univ} and $\Delta G°$ for the Process H$_2$O(s) → H$_2$O(l) at −10°C, 0°C, and 10°C*

T (°C)	T (K)	$\Delta H°$ (J/mol)	$\Delta S°$ (J/K · mol)	$\Delta S_{surr} = -\dfrac{\Delta H°}{T}$ (J/K · mol)	$\Delta S_{univ} = \Delta S° + \Delta S_{surr}$ (J/K · mol)	$T\Delta S°$ (J/mol)	$\Delta G° = \Delta H° - T\Delta S°$ (J/mol)
−10	263	6.03×10^3	22.1	−22.9	−0.8	5.81×10^3	$+2.2 \times 10^2$
0	273	6.03×10^3	22.1	−22.1	0	6.03×10^3	0
10	283	6.03×10^3	22.1	−21.3	+0.8	6.25×10^3	-2.2×10^2

This is what I thought to be the most logical explanation of the table myself at the beginning, since solid water does not exist at 10 degrees C (obviously). But my instructor told me that in the formula for ΔSsurroundings=-ΔH/T, T designates the temperature of the system. The aim of this table is to make a hypothetical assumption that solid water exists at all three temperatures, and measure the driving force behind its melting.

The 3rd Law of Thermodynamics (Perfect Crystal)

A perfect crystal at $0K$ constitutes a single microstate ($W=1$)

$\therefore S = k\,lnW = k\,ln1 = k \cdot 0 = 0$

, which means ...

"The entropy of a pure, perfect crystal at $0K$ is zero"

1ST $\Delta G = 0$
$univ$

2ND $\Delta S > 0$
$univ$

ΔS and Thermodynamic Quantities

All thermo equations which apply to ΔH apply analogously to ΔS, including HESS & FORMATION formulas:

0TH $S = 0$

e.g.

$$\Delta S = \Sigma\, nS^o_{298}(prod) - \Sigma\, nS^o_{298}(react)$$

ΔH

" BC "

ΔG

ΔE

$\Delta E \; {}^{2o}_{co}$

Mon, Nov 4

For SYSTEM   [here, "SYS" subscript omitted]

$$u \;=\; q + w$$
$$\Delta G \;=\; \Delta H - T\Delta S$$

$$y \;=\; -m \cdot x + b$$
$$\Delta G \;=\; -\Delta S \cdot T + \Delta H$$

ΔG = (–), Spontaneous

20

10
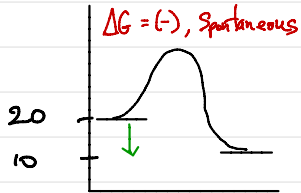
One Condition for Spontaneity: ΔG = (–)

Senario	ΔG	ΔH	ΔS	Result
1	−	−	+	spontaneous
2	+	+	−	non − spontaneous
3	+/−	+	+	depends
4	+/−	−	−	depends

−TΔS

(−)

+

ΔH > 0
ΔS < 0   Nonspontaneous

ΔH > 0
ΔS > 0

ΔH < 0
ΔS < 0   Spontaneous

ΔH < 0
ΔS > 0

Free energy

ΔG > 0

ΔG < 0

0

Increasing temperature (K)

$$U = q + w$$

$$\Delta G = \Delta H - T\Delta S$$

Senario	ΔG	ΔH	ΔS
1	$-$	$-$	$+$
2	$+$	$+$	$-$
3	$+/-$	$+$	$+$
4	$+/-$	$\ominus$	$\ominus$
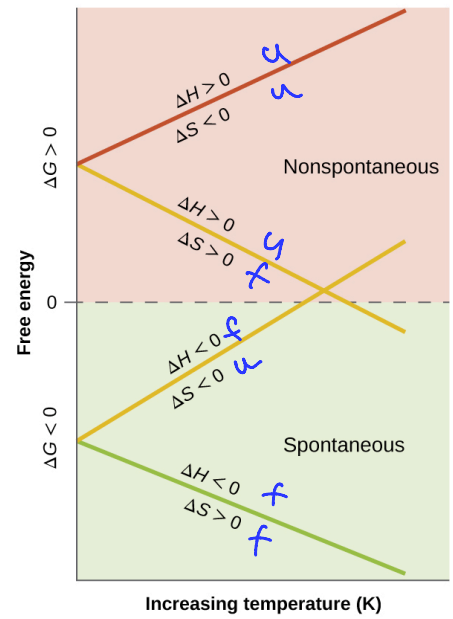
○ All formulas that apply to ΔH & ΔS apply to ΔG

○ These make up the key THERMODYNAMIC QUALITIES.

○ Tip: When SYS is at EQUIL → ΔG = 0

```
                              Bond Energy
                             —bond level—           bond

         run an experiment                                      P

  ΔG = ΔG° + RTlnQ  (not equal)    Calc         ΔH°(formation)        R
  ΔG° = –RTlnK (at equal)      ΔH, ΔG, ΔS      —molecule level—
                                                              molecular
         ΔG = ΔH + TΔS         Hess' Law
                             —equation level—

                                                  gas
```
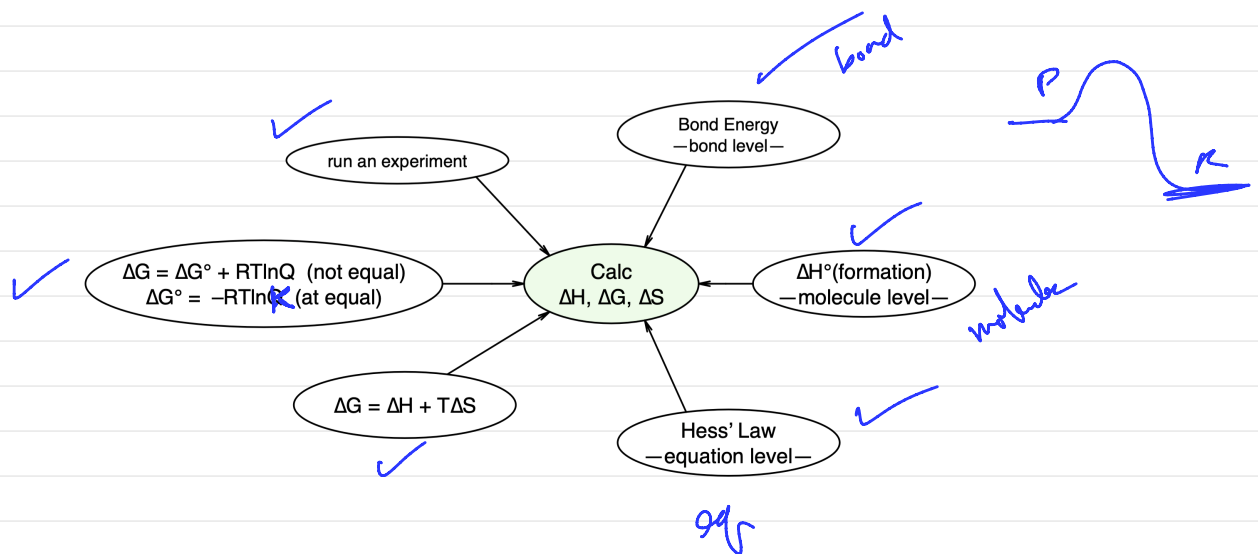
¿A gummy bear contains 2.67 g sucrose, C12H22O11 . When it reacts with 7.19 g potassium chlorate, KClO3 , 43.7 kJ of heat are produced. Determine the enthalpy change for the reaction, if sucrose is in excess...
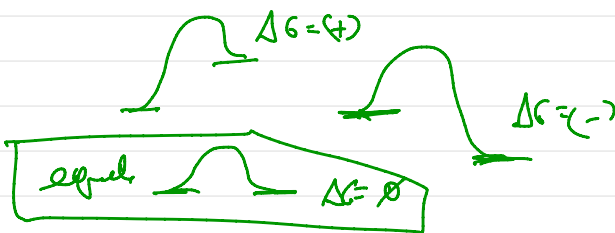
excess

2.67 g   7.19 g   TRICK: develop CF   43.7 kJ

$$C_{12}H_{22}O_{11} + 8 KClO_3 \longrightarrow 12 CO_2 + 11 H_2O + \boxed{5960} \, kJ \checkmark$$

$$\left(\frac{7.19 \, g_A}{43.7 \, kJ}\right) \left(\frac{43.7 \, kJ}{7.19 \, g_A}\right)$$

2x   CF's

$$\boxed{\square \, kJ} = \frac{43.7 \, kJ}{7.19 \, g \, KC} \bigg| \frac{122.52 \, KC}{1 \, mol \, KC} \bigg| \frac{8 \, mol \, KC}{} = 5{,}956 = \boxed{5960 \, kJ}$$

mol rxn

↑   ↑   ↑
CF   MM   given

¿Knowing the boiling point occurs when the solid and liquid phases are in equilibrium, estimate the boiling point of water based on tabulated thermodynamic data? (Data may reside in Appendix G)

$$H_2O(\ell) \rightleftharpoons H_2O(g)$$

$\Delta G = (+)$

$\Delta G = (-)$

elfuel $\quad \Delta G = \emptyset$
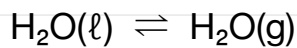
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

(equil) $\quad \emptyset = \Delta H^\circ - T\Delta S^\circ$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T = \frac{44.01 \times 10^3 \, J \, mol^{-1}}{118.8 \, K^{-1} \, J \, mol^{-1}}$$

$$\boxed{T = 370.5 \, K \ (97.3^\circ C)}$$

$\Delta H^\circ = PROD - REACT$

$= \Delta H_f^\circ [H_2O(g)] - \Delta H_f^\circ [H_2O(\ell)]$

$= [-241.82] - [-285.83] = 44.01 \, kJ/mol$

$= 44.01 \times 10^3 \, J/mol$

$\Delta S^\circ = \Delta S_f^\circ [H_2O(g)] - \Delta S_f^\circ [H_2O(\ell)]$

$= [188.8] - [70.0] = 118.8 \, J/K \cdot mol$

○ When $\Delta G = \emptyset$, forward & reverse driving forces are equal (EQUIL)

○ Review: Reaction Quotient, Q

$\qquad K > Q$, then right

$\qquad K < Q$, then left

$\qquad K = Q$, then at equilibrium

ΔG for NON-standard conditions

NON-standard $\boxed{\Delta G = \Delta G° + RT \ln Q}$

$$R = \frac{8.314 \; J}{mole \cdot K}$$

@ Equil $\bigg|$ Q=K, and $\Delta G = \emptyset$ $\quad \Delta G = \Delta G° + RT \ln K = 0$

at Equilibrium $\boxed{\Delta G° = -RT \ln K}$ note: $K = K_p$ for gases

$\qquad\qquad K = K_c$ for solutions

$\qquad 0 = \Delta G° + RT \ln K$ $\qquad K = K_{hom}$ for mixed

¿For the following reaction, K_p = 5.04E17 @ 25 °C   What is ΔG°?

STP

eg. constant

$$C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g)$$

$$\Delta G° = \boxed{}$$
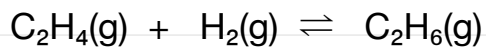
$$\Delta G = \Delta G° + RT \ln Q$$

$$\downarrow \text{at eq, } Q = K \text{ & } \Delta G = 0$$

← look for conditions in which this is true

$$0 = \Delta G° + RT \ln K$$

$$\boxed{\Delta G° = - RT \ln K}$$

$$= - \frac{8.314 \text{ J}}{\text{mol K}} \Big| 298 \text{K} \ln 5.04 \times 10^{17} = \frac{-1.01 \times 10^{5} \text{ J}}{\text{mol}}$$

$$= \boxed{-101 \text{ kJ/mol}}$$

run an experiment

Bond Energy
—bond level—

$\Delta G = \Delta G° + RT\ln Q$ (not equal)
$\Delta G° = -RT\ln Q$ (at equal)

Calc
ΔH, ΔG, ΔS

$\Delta H°$(formation)
—molecule level—

$\Delta G = \Delta H + T\Delta S$

Hess' Law
—equation level—