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

$\Delta G < 0 \rightarrow$ spontaneous

$\Delta H < 0 \rightarrow$ contributes to a spontaneous reaction

Enthalpically favorable

$\Delta S > 0 \rightarrow$ Entropically favorable

(helps make $\Delta G < 0$)

$-$	$-$	$+$	$\Delta H < 0 + \Delta S > 0 \rightarrow$ ALWAYS Spontaneous
$+$	$+$	$-$	$\Delta H > 0 + \Delta S < 0 \rightarrow$ NEVER Spontaneous
$+/-$	$-$	$-$	$\Delta H < 0 + \Delta S < 0 \rightarrow$ spontaneous at low Temp
$+/-$	$+$	$+$	$\Delta H > 0 + \Delta S > 0 \rightarrow$ Spontaneous @ high temps

OK... now we have seen two important equation that involve ΔG

$$\Delta G^\circ = -RT \ln K \quad \text{and} \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

combined $\longrightarrow$ $\quad -RT \ln K = \Delta H^\circ - T\Delta S^\circ$

rearranged $\longrightarrow$ $\quad \ln K = \dfrac{-\Delta H^\circ}{RT} + \dfrac{\Delta S^\circ}{R}$

We can use this expression to derive an equation that allows us to calculate how K responds to changing the Temperature

$$\ln K_1 = \dfrac{-\Delta H^\circ}{RT_1} + \dfrac{\Delta S^\circ}{R} \qquad\qquad \ln K_2 = \dfrac{-\Delta H^\circ}{RT_2} + \dfrac{\Delta S^\circ}{R}$$

$$\underbrace{\ln K_2 - \ln K_1}_{= \ln \frac{K_2}{K_1}} = \left[\dfrac{-\Delta H^\circ}{RT_2} + \dfrac{\Delta S^\circ}{R}\right] - \left[\dfrac{-\Delta H^\circ}{RT_1} + \dfrac{\Delta S^\circ}{R}\right]$$

Van't Hoff Equation

$$\ln \dfrac{K_2}{K_1} = \dfrac{\Delta H^\circ}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$$

$$\ln \dfrac{K_2}{K_1} = \dfrac{-\Delta H^\circ}{RT_2} + \dfrac{\Delta S^\circ}{R} + \dfrac{\Delta H^\circ}{RT_1} - \dfrac{\Delta S^\circ}{R} \qquad \text{these cancel}$$

$$\ln \dfrac{K_2}{K_1} = \dfrac{-\Delta H^\circ}{RT_2} + \dfrac{\Delta H^\circ}{RT_1} = \dfrac{\Delta H^\circ}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$$

Let's rationalize this conceptually: $\Delta H < 0$ → exothermic
                                          − heat is a product

exothermic: $A + B \rightleftharpoons C$ + heat (produced)

   @ low temp [heat] is small so reaction favors products (↑K)

   @ high temp [heat] is large. Reaction will favor more reactants (↓K)

   So, when $\Delta H < 0$ K increases as temperature decreases

   Endothermic: heat + $A + B \rightleftharpoons C$
              ↳ heat is a reactant (consumed)

   ↓T = ↓[heat]   so reactants are favored → small K
   ↑T = ↑[heat]   products are favored → high K

   when $\Delta H > 0$, K increases with Temperature

New terms:
      Exothermic → heat is produced $\Delta H < \emptyset$
      Endothermic → heat is a reactant $\Delta H > \emptyset$

Sample Problem:

   The equilibrium constant for the synthesis of methane has been determined at
   two temperatures. Determine $\Delta H°$ for this reaction.

773.15K 500 °C $K_P = 2.69 \times 10^3$ atm^{-1}
1173.15K 900°C $K_P = 51.43$ atm^{-1}

      Conceptually, what do we expect? $\Delta H > 0$ or $\Delta H < 0$
           low temp = larger K
           high temp = lower K

heat + react $\rightleftharpoons$ prod .... ↑T would ↑ K

K decreases with ↑T

heat must be a product → exothermic

$$\ln \frac{51.43}{2690} = \frac{\Delta H°}{8.314} \left(\frac{1}{773.15} - \frac{1}{1173.15} \right)$$

$$-3.957 = \frac{\Delta H°}{8.314} (0.000441)$$

Yep!

$$\Delta H° = -74,600 \frac{J}{mol}$$

$H_2O_{(\ell)} \rightleftharpoons H_2O_{(g)}$ $\Delta H = 44 \frac{kJ}{mol}$ $K = P_{H_2O}$

Determine vapor pressure @ 50°C

Note here that pressure (vapor pressure) $\underline{\underline{is}}$ K!

What you need to know: Boiling point is when vapor pressure is atmospheric pressure

$$K = 1 \text{ atm @ } 100°C \quad (373.15 K)$$

$K_1 = 1$ atm $T_1 = 373.15$ k
$K_2 = ?$ $T_2 = 323.15$ K

$$\ln \frac{K_2}{K_1} = \frac{+44000}{8.314} \left(\frac{1}{373.15} - \frac{1}{323.15} \right)$$

$$\ln \frac{K_2}{1} = 5292 \, K \left(-4.15 \times 10^{-4} \, K^{-1} \right)$$

$$\ln \frac{K_2}{1} = -2.19$$

$$\frac{K_2}{1} = 0.111$$

$$\boxed{K_2 = 0.111 \text{ atm}}$$

$$\boxed{K_2 = \text{vapor pressure} = 0.111 \text{ atm}}$$

Understanding the State Functions

Enthalpy (ΔH)

$\Delta H < 0 \rightarrow$ exothermic
$\rightarrow$ heat is released (it burns!)

$\Delta H > 0 \rightarrow$ endothermic
$\rightarrow$ heat is consumed (it's cold)

Two main contributers to reaction enthalpy:
- Bonds $\rightarrow$ breaking bonds = endothermic
  making bonds = exothermic
- phases $\rightarrow$ $s \rightarrow l \rightarrow g$ = endothermic
  $g \rightarrow l \rightarrow s$ = exothermic

It's hard to look at a reaction and figure out if it will be endo or exothermic
chemical

ENTROPY: Creating disorder is good! $\Delta S > 0$
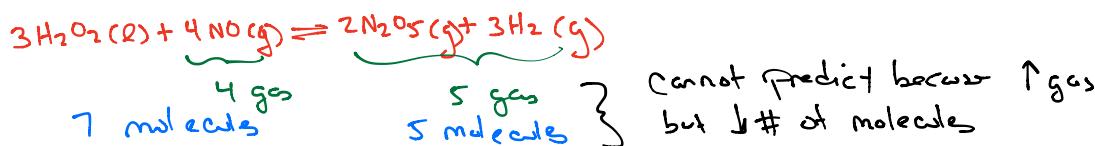
main contributers
phase: $s < l < g$
number of molecules: creating molecules = $\Delta S > 0$

Thinking about the phases of reactants/products allows
a reasonable guess at $\Delta S > 0$ or $\Delta S < 0$
- think Δn_{gas}

$2 P(s) + 3 Cl_2 (g) \rightleftharpoons 2 PCl_3 (g)$ $\Delta n_{gas} = 2-3 = -1$
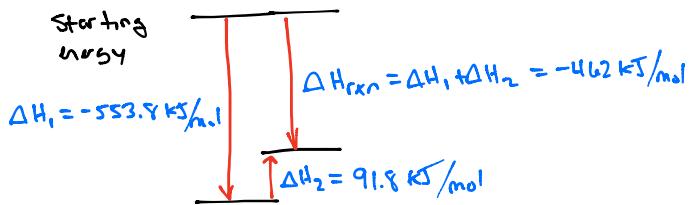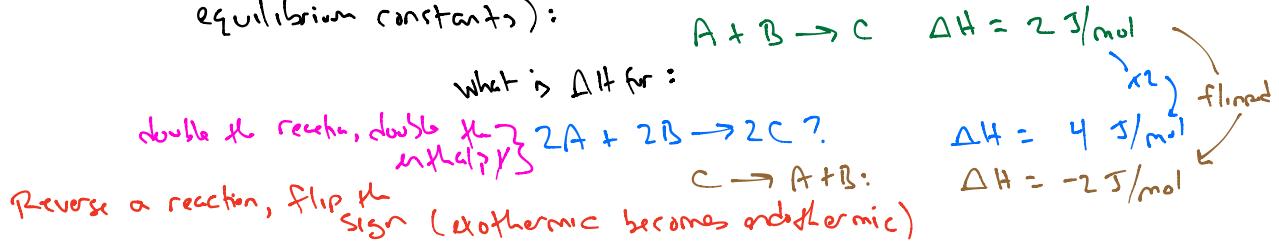
3 gas $\rightarrow$ 2 gas NOT favorable $\Delta S < 0$

$3 H_2 O_2 (l) + 4 NO (g) \rightleftharpoons 2 N_2 O_5 (g) + 3 H_2 (g)$
4 gas   5 gas   } Cannot predict because $\uparrow$ gas
7 molecules   5 molecules   but $\downarrow$ # of molecules
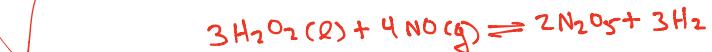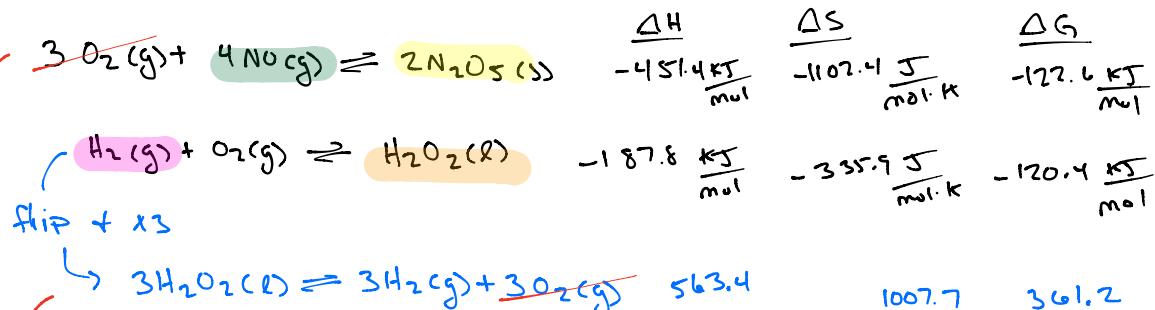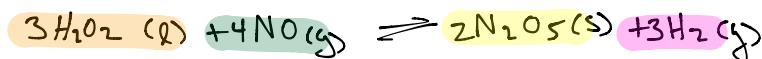
Path-independence is important for lots of reasons, but for our purposes, it allows us to apply Hess' Law: ΔH values (or any state function) are additive!

Starting energy

$\Delta H_1 = -553.8 \text{ kJ/mol}$

$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 = -462 \text{ kJ/mol}$

$\Delta H_2 = 91.8 \text{ kJ/mol}$

We can use Hess' Law in lots of ways. Here is one (similar to what we did with equilibrium constants):

$A + B \rightarrow C \qquad \Delta H = 2 \text{ J/mol}$

what is ΔH for:

double the reaction, double the enthalpy } $2A + 2B \rightarrow 2C$? $\qquad \times 2 \downarrow$ flipped $\qquad \Delta H = 4 \text{ J/mol}$

$C \rightarrow A + B: \qquad \Delta H = -2 \text{ J/mol}$

Reverse a reaction, flip the sign (exothermic becomes endothermic)

Given the following information, determine $\Delta G, \Delta H, + \Delta S$ for this reaction:

$$3 H_2O_2 \, (l) + 4 NO \, (g) \rightleftharpoons 2 N_2O_5 \, (s) + 3 H_2 \, (g)$$

	ΔH	ΔS	ΔG
$3 O_2 (g) + 4 NO (g) \rightleftharpoons 2 N_2O_5 (s)$	$-451.4 \frac{\text{kJ}}{\text{mol}}$	$-1102.4 \frac{\text{J}}{\text{mol} \cdot \text{K}}$	$-122.6 \frac{\text{kJ}}{\text{mol}}$
$H_2 (g) + O_2 (g) \rightleftharpoons H_2O_2 (l)$	$-187.8 \frac{\text{kJ}}{\text{mol}}$	$-335.9 \frac{\text{J}}{\text{mol} \cdot \text{K}}$	$-120.4 \frac{\text{kJ}}{\text{mol}}$

flip + $\times 3$

$\rightarrow 3 H_2O_2 (l) \rightleftharpoons 3 H_2 (g) + 3 O_2 (g) \qquad 563.4 \qquad\qquad 1007.7 \qquad 361.2$

combine (add up)

$3 H_2O_2 (l) + 4 NO (g) \rightleftharpoons 2 N_2O_5 + 3 H_2$

$\Delta H = 563.4 \frac{\text{kJ}}{\text{mol}} + -451.4 \frac{\text{kJ}}{\text{mol}}$

$\Delta S = 1007.7 \frac{\text{J}}{\text{mol} \cdot \text{K}} + -1102.4 \frac{\text{J}}{\text{mol} \cdot \text{K}} = -94.7 \frac{\text{J}}{\text{mol} \cdot \text{K}}$
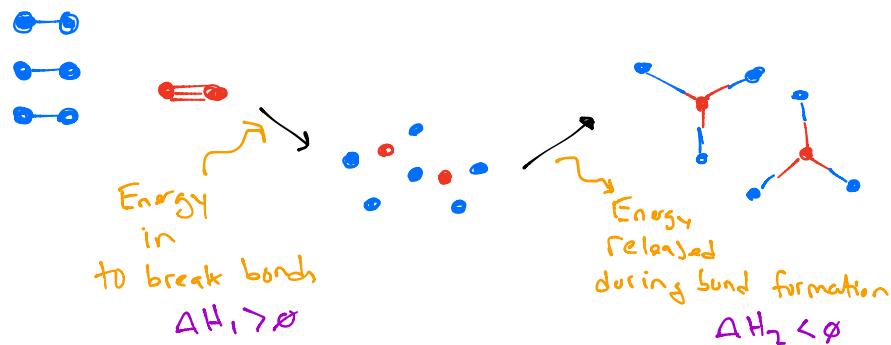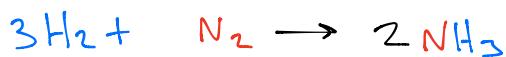
$\Delta G = 361.2 \text{ kJ/mol} + -122.6 \text{ kJ/mol} = 238.6 \text{ kJ/mol}$

Hess' Law has many applications that are <u>VERY</u> useful.
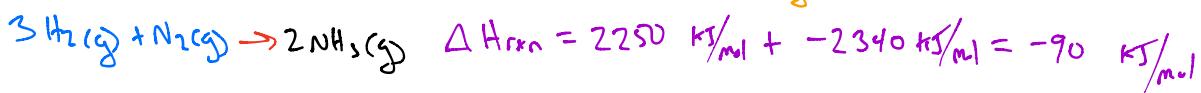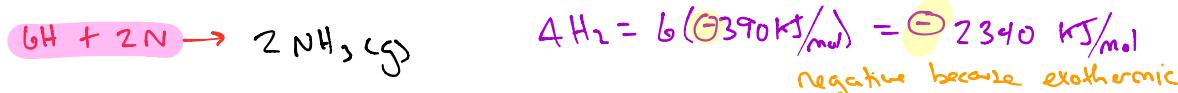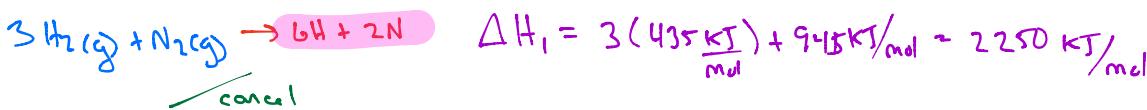
2 ways to calculate ΔH for a reaction — Both are applications of Hess' Law : - Bond Enthalpy
- Formation energies

· The enthalpy of a reaction can be described quite nicely by considering the strength of chemical bonds :

$$3H_2 + \quad N_2 \longrightarrow 2NH_3$$

Energy in to break bonds
$\Delta H_1 > \emptyset$

Energy released during bond formation
$\Delta H_2 < \emptyset$

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2$$

In this example: we broke 3 H-H bonds + 1 N≡N bond
$(\Delta H° = 435 \text{ kJ/mol})$ $(\Delta H° = 945 \text{ kJ/mol})$
- created 6 N-H bonds
$(\Delta H° = 390 \text{ kJ/mol})$ values available in tables!

$3H_{2(g)} + N_{2(g)} \rightarrow$ 6H + 2N $\Delta H_1 = 3(435 \frac{kJ}{mol}) + 945 kJ/mol = 2250 kJ/mol$

cancel

6H + 2N $\rightarrow 2NH_{3(g)}$ $\Delta H_2 = 6(\ominus 390 kJ/mol) = \ominus 2340 kJ/mol$
negative because exothermic

$3H_{2(g)} + N_{2(g)} \rightarrow 2NH_{3(g)}$ $\Delta H_{rxn} = 2250 kJ/mol + -2340 kJ/mol = -90 kJ/mol$

Weaknesses of this approach : ① Phase changes are not accounted for
② Assumption that all bonds are equal

Standard Formation Energies
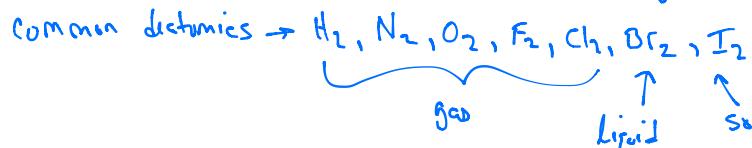
we can determine reaction ΔH, ΔS & ΔG in a variety of ways.

— Perhaps the most useful is Standard Formation Values.
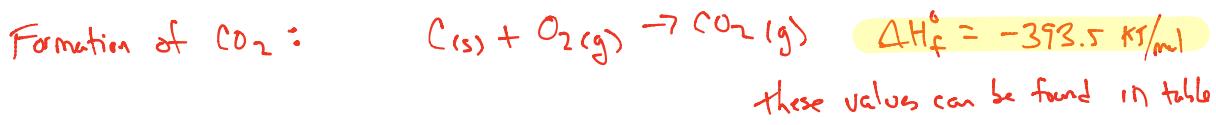
Let's use ΔH as an example:

-these values are the enthalpy changes associated with creating a compound from the individual elements (in their most stable form)

when you think of Oxygen, we think $O_2 \rightarrow O_2(g) =$ most common form

$$C \rightarrow C(s) \qquad F \rightarrow F_2(g) \qquad Fe = Fe(s), etc$$

Common diatomics $\rightarrow H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2$

gas   Liquid   Solid
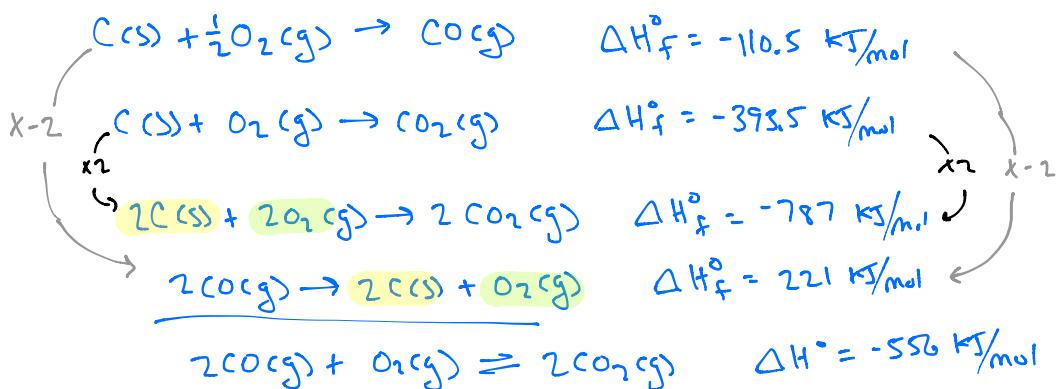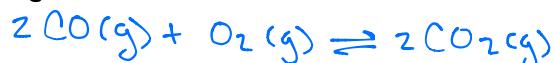
— most other things are elemental solids

Formation of CO_2: $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^{\circ}_f = -393.5 \ KJ/mol$

these values can be found in table

P. 488 (Table 14.3)

Formation of O_2: $O_2 \rightarrow O_2$ $\Delta H^{\circ}_f = \emptyset$

Elements in their most common form ALWAYS $\Delta H^{\circ}_f = \emptyset$

$\Delta G^{\circ}_f = \emptyset$

Using Hess' Law, determine ΔH for this reaction:

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$$

$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta H^{\circ}_f = -110.5 \ KJ/mol$$

$X-2$ $\qquad C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^{\circ}_f = -393.5 \ KJ/mol$

$X2$

$\qquad 2C(s) + 2O_2(g) \rightarrow 2CO_2(g) \qquad \Delta H^{\circ}_f = -787 \ KJ/mol$ $X2$ $X-2$

$\qquad 2CO(g) \rightarrow 2C(s) + O_2(g) \qquad \Delta H^{\circ}_f = 221 \ KJ/mol$

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) \qquad \Delta H^{\circ} = -556 \ KJ/mol$$
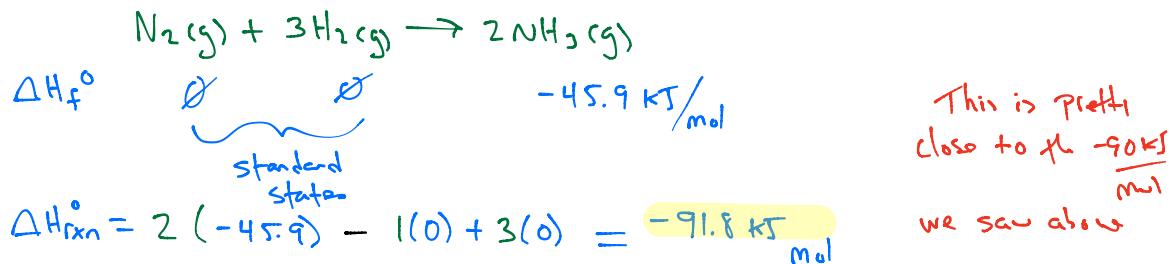
We can take a shortcut:
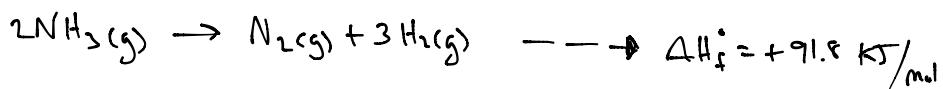
$$\Delta H^\circ_{rxn} = \sum \Delta H^\circ_f \text{ prod} - \sum \Delta H^\circ_f \text{ react}$$

$$\Delta H^\circ = 2\left(-393.5 \frac{kJ}{mol}\right) - \left(2\left(-110.5 \frac{kJ}{mol}\right)\right) = -566 \frac{kJ}{mol}$$

How about this one?

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

ΔH°_f $\cancel{0}$ $\cancel{0}$ $-45.9 \frac{kJ}{mol}$

⎵ standard states

This is pretty close to the $-90\frac{kJ}{mol}$ we saw above

$$\Delta H^\circ_{rxn} = 2(-45.9) - 1(0) + 3(0) = \boxed{-91.8 \frac{kJ}{mol}}$$

If we reverse this reaction:

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g) \quad ---\rightarrow \quad \Delta H^\circ_f = +91.8 \frac{kJ}{mol}$$

✱ If a reaction produces energy in the "forward" direction, exactly the same amount of energy gets consumed in the "reverse" direction

This approach (prod − react) is useful for <u>ALL</u> state functions (because of path independence)
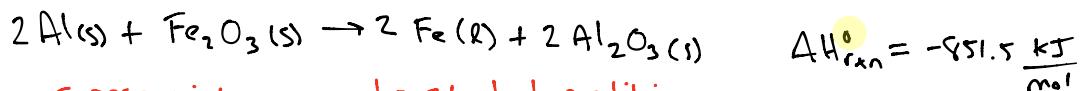
$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(kJ/mol)		PCl_5	PCl_3	Cl_2
(kJ/mol)	ΔH°_f	−374.9	−287.0	∅
(kJ/mol)	ΔG°_f	−305.0	−267.8	∅
(J/mol·k)	S°	364.6	311.8	223.1

$$\Delta H^\circ = (-287.0 + 0) - (-374.9) = 87.9 \ kJ/mol$$
$$\Delta G^\circ = (-267.8 + 0) - (-305.0) = 37.2 \ kJ/mol$$
$$\Delta S^\circ = (311.8 + 223.1) - (364.6) = 170.3 \ J/mol \cdot k$$

Thermochemical Reactions:

To write a thermochemical reaction, we need to add information about Enthalpy to the balanced reaction.

$$2\,Al_{(s)} + Fe_2O_{3\,(s)} \rightarrow 2\,Fe_{(\ell)} + 2\,Al_2O_{3\,(s)} \qquad \Delta H^0_{rxn} = -851.5 \frac{kJ}{mol}$$

ΔH^0_{rxn} ← superscript means under standard conditions → $P = 1$ bar for all gases
$\equiv$ Standard enthalpy change for a reaction $\qquad M = 1\,M$ for all solutes
$\qquad T = 25°C$

Note that the units are $\frac{kJ}{mol}$, so this is the heat change **if** exactly one mole equivalent reacts...

exothermic

For the reaction above, 851.5 kJ of energy will be release when 2 mol Al reacts with 1 mol of Fe_2O_3. 851.5 kJ will be released for every 2 mol of Fe produced.

$$\Delta H^0 = \frac{-851.5\,kJ}{2\,mol\,Al} = \frac{-851.5\,kJ}{1\,mol\,Fe_2O_3} = \frac{-851.5\,kJ}{2\,mol\,Fe}\cdots$$

Sample Problem:

If 30.0 g Fe_2O_3 is mixed with 15.0 g Al, determine the enthalpy change for this reaction. Assume 100% yield.

We need to know exactly how much product is formed (L.R. problem)

$$\frac{30.0\,g\,Fe_2O_3}{} \left|\frac{mol}{159.7\,g}\right|\frac{1\,mol\,Al_2O_3}{1\,mol\,Fe_2O_3} = 0.188\,mol\,Al_2O_3$$

$$\frac{15\,g\,Al}{} \left|\frac{mol}{26.98\,g}\right|\frac{1\,mol\,Al_2O_3}{2\,mol\,Al} = 0.278\,mol\,Al_2O_3$$

→ 0.188 mol Al_2O_3 produced → Now use ΔH^0 as a conversion factor

$$\frac{-851.5\,kJ}{1\,mol\,Al_2O_3}$$

$$\frac{0.188\,mol\,Al_2O_3}{} \left|\frac{-851.5\,kJ}{1\,mol\,Al_2O_3}\right. = -160.1\,kJ$$

✳ So in this reaction, 160.1 kJ of energy (heat) is transferred to the surroundings

– If you were to touch the reaction flask, you would be the surroundings and it would burn you!