Chapter 15: Chemical Thermodynamics

thermo + dynamics
\[ \uparrow \]
energy \[ \uparrow \]
movement
(heat) \[ \text{or} \]
transfer

thermodynamics: study of energy transfer and energy changes that accompany physical and chemical processes.

We were introduced to these concepts in Ch. 13 in heat transfer calculations e.g. heat of fusion: amount of heat required to melt one gram of solid at its melting point. These processes were physical processes that involved heat.

All chemical reactions involve energy changes as well. These energy changes can be easily calculated from tables of thermodynamic data (Appendix K, p. A.31). We will learn to do this.

Information determined from the study of thermodynamics allows us to answer certain vital questions:

1. Will 2 (or more) substances react when mixed under specified conditions?
   - If they do react - the reaction is called **spontaneous**
   - If they do NOT react - the reaction is called **non-spontaneous**

In Ch. 4, we memorized some kinds of reactions that "go" due to removal of ions:
- Acid-base reactions \( \rightarrow \) salt + water
- Precipitation reactions \( \rightarrow \) solid

Now we will be able to calculate if a reaction will go or not.

2. If the substances react, will energy as heat be released (exoergic) or absorbed (endoergic)?
This energy change is called an enthalpy change, $\Delta H$ (kJ/mol) (more about this later). There is a sign convention:

<table>
<thead>
<tr>
<th>heat is released</th>
<th>exothermic</th>
<th>$\Delta H -$</th>
</tr>
</thead>
<tbody>
<tr>
<td>heat is absorbed</td>
<td>endothermic</td>
<td>$\Delta H +$</td>
</tr>
</tbody>
</table>

However, thermodynamics does NOT tell us
1. how fast a spontaneous reaction will occur (in seconds or millions of years)
2. the mechanism of a reaction i.e. the order in which bonds are broken and formed in a reaction to make the products.

These subjects will be covered in Ch 16: Chemical Kinetics.

Demonstration of spontaneous reaction (reactions that go!!)
"The Frozen Beaker" (figure top of p 547)

Reaction: $\text{Ba} (\text{OH})_2 \cdot 8\text{H}_2\text{O}(s) + 2 \text{NH}_4\text{SCN}(a) \xrightarrow{\text{heat}} \text{Ba} (\text{SCN})_2(aq) + 2 \text{NH}_3(l) + 10 \text{H}_2\text{O}(l)$

Questions before solids are combined - Review (I hope)
1. Is this a redox reaction? No - no element changes oxidation number.
2. Why does the reaction go? Formation of the weak electrolytes, $\text{NH}_3 + \text{H}_2\text{O}$, increase in the thermodynamic quantity: entropy.

Procedure: The reagents are mixed in a flask, resting on a wet board. The flask became so cold, it froze to the board.

Question: Did the reaction require heat or produce heat? required heat
The reaction is endothermic; $\Delta H_{\text{rxn}}$ is positive value
:: heat is a reactant

This is an example of an endothermic spontaneous reaction.
Concept: system + surroundings = universe

system: substances involved in chemical and physical changes of interest
:: all reagents (reactants & products)
   e.g. Ba(OH)₂·8H₂O, NH₄SCN, Ba(SCN)₂, etc
surroundings: everything in the system's environment
   e.g. flask, air, wet board, Houston, etc.
(we are generally only concerned with immediate surrounding)

In this case, the system took heat from the surroundings, including the
water on the board — so much heat that the temperature of the water
lowered to its freezing point and H₂O changed phase (froze).

But the energy of the universe remained the same. This is the ...

First Law of Thermodynamics: The total amount of energy in the universe
is constant (includes E = mc²)

Definitions and Terms:

thermodynamic state of a system: defined by a set of conditions that completely
specifies all properties of system. This set includes temperature, pressure,
composition and physical state (gas, liquid or solid) among others.

state function: the properties of a system eg P, T, V. The value of a
state function depends only on the state of system and not on how the
state is reached. It is designated by a capital letter. State functions have
two important properties: (1) assigning values to a few state functions
(usually 2 or 3) automatically fixes values of others. (2) When the state of
a system is changed, the change of a state function depends only on the
initial and final states of the system and NOT on how the change is made.

Examples of familiar state functions: T and ΔT (T_final - T_initial),
P and ΔP, V and ΔV
Example: For Interest

Consider a system where we have 1 mole of an ideal gas at \( T_1 \) and \( P_1 \).

1. We can calculate another state function, \( V_1 \), for the gas at this particular thermodynamic state using the ideal gas law:

\[
\frac{PV}{R} = \frac{RT}{P} \quad \text{for 1 mole of ideal gas}
\]

2. Let us change the state of this system from \( P_1 = 1 \text{ atm}, V_1 = 22.4 \text{ L} \) and \( T_1 = 273 \text{ K} \) (at STP) to a final state in which \( P_2 = 3 \text{ atm}, V_2 = 5.0 \text{ L} \) and \( T_2 = 183 \text{ K} \). Therefore:

- Pressure change, \( \Delta P = P_2 - P_1 = 2 \text{ atm} \)
- Volume change, \( \Delta V = V_2 - V_1 = -17.4 \text{ L} \)
- Temperature change, \( \Delta T = T_2 - T_1 = -90 \text{ K} \)

Therefore, the change in each of these state functions depends only on their values in the initial and final states of the system and not on how the change was accomplished.

For example, during the pressure change, the pressure could have risen to 100 atm, fallen to 0.1 atm and as long as the \( P_2 = 3 \text{ atm} \), \( \Delta P = P_2 - P_1 = 2 \text{ atm} \).

Quantities whose values are not independent of how a change occurs are not state functions.

For example, work \((= \text{force} \times \text{distance})\) is NOT a state function. Work depends on the particular path that is taken ie the distance travelled. Notice that work, abbreviated by \( w \), is in lower case letters — not capital letters. And so, heat, \( q \), is also not a state function since it is not capitalized. (Reasoning: First Law of Thermo. states: \( \Delta E \) = constant for reaction. Therefore because \( \Delta E = q + w \) and work is not a state function, \( q \) cannot be a state function.)
Work: Work done in Path 1 > work done in Path 2. W is not a state function.

Other examples of state functions (properties that are INDEPENDENT of pathway):
- **E**, internal energy: \( E = \sum \text{all internal energies of a specific amount of a substance (includes kinetic energy of molecules, bonding energy, etc.)} \) unit: \( \text{kJ/mol} \)
- **H**, enthalpy: total heat content of a specific amount of a substance.
  - \( ^\Delta H\text{ negative} \): heat is released "exothermic".
  - \( ^\Delta H\text{ positive} \): heat is absorbed "endothermic".
  unit: \( \text{kJ/mol} \)
- **S**, entropy: measure of the degree of randomness of a system.
  unit: \( \text{J/mol}\cdot\text{K} \)
- **G**, Gibbs free energy: indicates the amount of energy available for a system to do useful work. (Note: \( ^\Delta G\) for a process or reaction is the indicator for spontaneity.)
  - \( ^\Delta G\text{ negative} \Rightarrow \) spontaneous reaction.
  - \( ^\Delta G\text{ positive} \Rightarrow \) non-spontaneous reaction.

More state functions: \( ^\Delta E\), change in internal energy.

\( ^\Delta H\), change in enthalpy

\( ^\Delta S\), change in entropy

\( ^\Delta G\), change in Gibbs free energy

**Internal Energy, E**

E cannot be measured directly, but changes in E \( (^\Delta E) \) can be measured for a system.

The internal energy, E, of a system can be changed if:
1. heat, \( q \), is added to or removed from the system
2. the system does work, \( w \), or work is done on the system.
Let \( E_1 = \) initial energy of a system  
\( E_2 = \) final energy of a system  
\( q = \) heat added to the system  
\( W = \) work done on the system

**Sign Convention:**
- If \( q \) is \(+\), heat is added to system.
- If \( q \) is \(-\), heat is removed from system.
- If \( W \) is \(+\), work is done on the system by the surroundings.
- If \( W \) is \(-\), work is done by the system on the surroundings.

Therefore, we have:
\[
E_1 + (q) + (W) = E_2
\]
\[
E_2 - E_1 = (q) + (W)
\]
\[
\Delta E = q + W
\]

If \( \Delta E \) is \(+\), energy is absorbed by the system.
If \( \Delta E \) is \(-\), energy is released from the system.

**Example:** If 1200 J of heat are removed from a system in energy state, \( E_1 \), and the system does 800 J of work on the surroundings,

(a) What is the energy change for the system?

\[
\Delta E = E_2 - E_1 = q + W = (-1200 J) + (800 J) = -2000 J
\]

(b) What is the energy change for the surroundings?

\[
\Delta E = q + W = (+1200 J) + (+800 J) = +2000 J
\]

**Note:** \( E_1, E_2, \Delta E \) are state functions.
\( q, W \) are not state functions and depend on the path taken.
But \((q + W)\) is a state function since \( q + W = \Delta E \).
Let us discuss energy changes that occur during chemical reactions that may involve gases as products and/or reactants. Since most reactions in the laboratory occur in open beakers, the pressure of the system is constant (P = atmospheric pressure) and ΔP = 0. Also, temperature remains constant.

\[ ^\Delta E = \Delta H - P \Delta V \]

Also \( ^\Delta E = q - n g g o R T \) if \( T, P \) constant since \( \Delta n g g o R T = \Delta (pV) = p \Delta V + V \Delta p \)

Example: Calculate the work done on the following system at 127°C and 1 atm.

\[ 2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \]

Given: 4 mol \( H_2 \) \( \rightarrow \) 2 mol \( H_2O \)

In this reaction, the number of moles (hence V) of gaseous products < number of moles (hence V) of gaseous reactants.

As the reaction proceeds, the volume of the system decreases.

Why? The surroundings are doing work on the system.

So, work will be a positive quantity and the internal energy of the system will increase.

Calculation: Work, \( w \), done on the system = -PΔV

when 4 mol \( H_2 \) react with 2 mol \( O_2 \) to produce 4 mol of \( H_2O \).

\[ \Delta n g g o = 4 \text{ mol} - 6 \text{ mol} = -2 \text{ mol} \]

\[ \Delta n g g o R T = -2 \times R \times T \]

\[ \Delta n g g o R T = (4 \text{ mol} - 6 \text{ mol}) \times 8.314 \text{ molK}^{-1} \text{ atm}^{-1} \times (473 + 273) \]

\[ = +6651 \text{ J} \]

\[ = +6.651 \text{ kJ} \]
In some cases, there is **no** work done by a chemical reaction, e.g.

1. If there is no change in the number of moles of gas in the reaction at constant $T$ and $P$. Consider: $C_{\text{graphite}}(s) + O_2(g) \rightarrow CO_2(g)$

\[
\Delta n_{\text{gas}} = n_{\text{products}} - n_{\text{reactants}} = 1 - 1 = 0
\]

Since $\Delta n_{RT} = \Delta(PV) = PAV + \frac{VAP}{\Delta P = 0}$, work $= 0$.

2. If the reaction occurs in a closed constant volume container, such as a bomb calorimeter. Volume is forced to remain constant and $\Delta V = 0$. Therefore, work $= -PAV = 0$ (Note: there is potential energy stored $VAP$)

**Calorimeters**

Calorimeters are used to measure the amount of heat released or absorbed during a chemical reaction.

There are two types:

1. Bomb calorimeter, where the reaction occurs at constant volume
   $V$ is constant $\Rightarrow \Delta V = 0$

2. "Coffee cup" calorimeter, where the reaction occurs at constant pressure
   $P$ is constant $\Rightarrow \Delta P = 0$

(1) Bomb calorimeter: measure the heat evolved or absorbed for a reaction at constant volume. (in a closed container)

we recall: $\Delta E = q + w = q - PA \Delta V$

$= q - P(0)$ since $\Delta V = 0$

$= q$ since no work can be done.

$\Delta E = q_v \quad V \text{ means at constant volume}$

**: The heat measured by a bomb calorimeter is a direct measurement of $\Delta E$.**
A bomb calorimeter -
- a known mass of material is put into the sample cup with an excess of reactants. A known mass of water is put into the calorimeter and it is sealed.
- the reaction is initiated (with a spark if it is a combustion reaction), the stirrer is on, the thermometer is watched until the temperature stops rising or falling.

Example: A 1.00 g sample of n-pentane, C₅H₁₂ (72.1 g/mol), was mixed with excess O₂ in a bomb calorimeter. The bomb was immersed in 2000 g of H₂O (specific heat of H₂O = 4.18 J/g°C) at 23.14 °C. Combustion was initiated and T₂₀ rose to 27.93 °C. The heat capacity of the calorimeter is 1.843 kJ/C. Assuming complete combustion, determine ΔE for the combustion of 1 mole of pentane.

Note: you need to know that combustion reactions produce CO₂ and H₂O when starting with an organic compound containing C, H, and sometimes O and O₂ (g). You also must be able to balance the equation.

\[ C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l) \]

\[ \Delta E = q_v \]
heat lost (or produced) by the system = heat gained by the water + heat gained by calorimeter

heat gained by H₂O = specific heat of water × mass of water × ΔT
\[ = 4.18 \frac{J}{g\ ^\circ C} \times 2000 \ g \times (27.93 - 23.14) ^\circ C \]
\[ = 4.00 \times 10^4 \ J \]
\[ = 40.0 \ kJ \]

heat gained by calorimeter is calculated from the heat capacity of calorimeter - also called the "calorimeter constant."
heat gained by calorimeter = "calorimeter constant" (kJ/°C) x ΔT
heat capacity of calorimeter

= 1.843 kJ/°C x 4.79 °C
= 8.83 kJ

:. the amount of heat released by the combustion of 1.00 g pentane
   = heat gained by H₂O
   + heat gained by the calorimeter
   = 40.0 + 8.8 kJ
   = 48.8 kJ

/. ΔEₚᵣₒₐₜₙ = -48.8 kJ/100g pentane

Note: If we had burned 2.0 g pentane
ΔE = -2 x 48.8 kJ
   = -97.6 kJ

The amount of heat released by 1.00 mole of pentane

ΔEₚᵣₒₐₜₙ = -48.8 kJ/100g x \( \frac{72.1 g}{\text{mole}} \)
         = -3520 kJ/mole pentane consumed or \(-3520\) kJ/mole pentane

The amount of heat released by
ΔEₚᵣₒₐₜₙ = -3520 kJ/mole pentane x \( \frac{1 \text{ mole H}_2\text{O}}{6 \text{ mole pentane}} \)
         = -586 kJ/mole H₂O produced

However, a bomb calorimeter is not very convenient to use. It is much easier to measure the heat involved in reactions cut in the open where pressure is constant (= atmospheric pressure) using a….

(2) "Coffee cup" calorimeter: measures the heat evolved or absorbed during a reaction at constant pressure. This heat measured is ΔH, the enthalpy change.

ΔH = qₚ = heat measured at constant pressure
(for derivation, see next page)

if T of water decreases: if heat is absorbed, ΔH +
reaction is endothermic
if T of water increases: if heat is released, ΔH -
reaction is exothermic

Examples
15-1, 15-2
Lab #26, 14
There is a relationship between $\Delta H$ and $\Delta E$ for a reaction

$$H = E + PV$$

Total heat content

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

Internal energy

$$= \Delta E + \hat{P}AV + V \Delta P$$

External work

- Work done
- Stored energy due to build-up pressure
- $\Delta n g_a RT$
- at constant temperature

In bomb calorimeter, $\Delta V = 0$:

$$\Delta H = \Delta E + \hat{P}AV + V \Delta P$$

No work done

$$= 0$$

Where $\Delta E = q_v - \Delta f$

In coffee cup calorimeter, $\Delta P = 0$:

$$\Delta H = \Delta E + \hat{P}AV + 0$$

$$= q_o + W + \hat{P}AV = q_p$$

$$\Delta n g_a RT$$

Where $\Delta H = q_p$.

Therefore, we can always relate $\Delta H$ and $\Delta E$ using $\Delta H = \Delta E + \Delta n g_a RT$.

In the previous example, we calculated $\Delta E$ per mole of pentane combusted. Let us now calculate $\Delta H$ for the reaction of 1 mole of pentane.

$$C_5H_{12}(l) + 8 O_2(g) \rightarrow 5 CO_2(g) + 6 H_2O(l)$$

$$\Delta H = \Delta E + \Delta n g_a RT$$

$$= -3520 \text{ kJ/mol} + (5 - 8) 8.314 \frac{\text{J}}{\text{mol K}} (26 + 273 \text{ K})$$

$$= -3520 \text{ kJ/mole \_ mole} + (-7458 \text{ kJ/mol})$$

$$= -3520 \text{ kJ/mole \_ mole} - 7.5 \text{ kJ/mol} = -3530 \text{ kJ/mol pentane}$$

Note: different units!!
For most reactions \[ \Delta E \neq \Delta H \]
when \[ \Delta n_{gaseous} = 0 \]
\[ \Delta E = \Delta H \]

To conclude,
\[
\begin{align*}
\Delta H &= \Delta E + \Delta(PV) \\
\Delta H &= \Delta E + \Delta n_{gaseous}RT
\end{align*}
\]

- Using bomb calorimetry data, obtaining \( \Delta E \), it is possible to calculate \( \Delta H \) for the reaction using \( \Delta n_{gaseous}RT \)
- And using "coffee-cup" calorimetry data obtaining \( \Delta H \), one can calculate \( \Delta E \) for the reaction also using \( \Delta n_{gaseous}RT \).

**Standard State Conditions**

The thermodynamic standard state of a substance is its most stable state under standard pressure (1 atmosphere) and at some temperature usually 25°C (298.15 K).

*Note: Please do not confuse this temperature with standard temperature (STP) for gases = 0°C

Examples of elements in their standard states:

- Hydrogen: \( H_2(g) \)
- Helium: \( He(g) \)
- Chlorine: \( Cl_2(g) \)
- Bromine: \( Br_2(l) \)
- Iodine: \( I_2(s) \)
- Mercury: \( Hg(l) \)
- Sodium: \( Na(s) \)
- Carbon: \( C_{graphite}(s) \)
- Phosphorus: \( P_4(s) \) in white form
- Sulphur: \( S(s, rhombic) \)
Standard Molar Enthalpy of Formation, $\Delta H_f^o$

$\Delta H_f^o$: amount of heat absorbed in a reaction where 1 mole of a substance formation in a specific state is formed from elements in their standard states
(Appendix K, also Table 15-1, p 555)

convention: $\Delta H_f^o$ of an element in its standard state = 0.
$\Delta H_f^o$ for $\text{Cl}_2 (g) = 0$
$\Delta H_f^o$ for $\text{Ag} (s) = 0$

Example: $\Delta H_f^o$ for $\text{H}_2\text{O} (g) = -241.8 \ \text{kJ/mole}$
$\therefore$ there are 241.8 kJ of heat released in the reaction:
$\text{H}_2 (g) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{H}_2\text{O} (g)$

$\Delta H_f^o$ for $\text{H}_2\text{O} (l) = -285.8 \ \text{kJ/mole}$
$\therefore$ there are 285.8 kJ of heat released in the reaction:
$\text{H}_2 (g) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{H}_2\text{O} (l)$

Example: Calculate the enthalpy change for the reaction of one mole $\text{H}_2 (g)$ and one mole $\text{F}_2 (g)$ to form 2 moles HF(g) at 25°C and 1 atm.

$\text{F}_2 (g) + \text{H}_2 (g) \rightarrow 2 \text{HF} (g)$

we recognize that this is the reaction for formation of HF(g) from elements in their standard states and $\therefore \Delta H_{rxn}^o = 2 \times \Delta H_f^o$

since the reaction is forming 2 moles of HF, not 1 mole.

From the Appendix, $\Delta H_f^o$ for HF = $-271 \ \text{kJ/mol}$

$\therefore \Delta H_{rxn}^o = 2 \times \Delta H_f^o$
$= 2 \times (-271 \ \text{kJ/mol})$
$= -542 \ \text{kJ}$

and $\Delta H_{rxn}^o$ for $2 \text{HF} (g) \rightarrow \text{F}_2 (g) + \text{H}_2 (g)$ is $+542 \ \text{kJ}$
Dimensional Analysis:

\[ \Delta H_{\text{f}} = \Delta H^0 + n \Delta H_f \]

\[ \Delta H_{\text{f} \text{Al}_2\text{O}_3} = -1676 \frac{\text{kJ}}{\text{mol Al}_2\text{O}_3} \times \frac{\text{2 mol Al}_2\text{O}_3}{4 \text{ mol Al}} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times 15.0 \text{ g Al} = -466 \text{ kJ} \]

Example: Calculate the enthalpy change for the following reaction:

\[ 4 \text{ Al(s)} + 3 \text{ O}_2 (g) \rightarrow 2 \text{ Al}_2\text{O}_3 (s) \] at standard conditions using 15.0 g of Al(s) and excess O\(_2\) (g). \( \Delta H^0_{\text{f} \text{Al}_2\text{O}_3} = -1676 \frac{\text{kJ}}{\text{mol}} \)

Like the previous example, we are forming \( \text{Al}_2\text{O}_3 \) from elements in their standard state in this particular case.

Plan: g Al \rightarrow mol Al \rightarrow mol \text{Al}_2\text{O}_3

\[ \text{moles of } \text{Al}_2\text{O}_3 = \frac{1}{2} \times \text{mol Al} \]

\[ = \frac{1}{2} \times \frac{15.0 \text{ g Al}}{26.98 \text{ g/mole}} \]

\[ = 0.278 \text{ moles} \]

\[ \Delta H_{\text{rxn}} = 0.278 \text{ moles} \times (-1676 \frac{\text{kJ}}{\text{mol}}) = -466 \text{ kJ} \]

466 kJ of heat were released when 15.0 g of Al were oxidized to \( \text{Al}_2\text{O}_3 \) in the above exothermic reaction.

Hess' Law of Heat Summation

Since \( \Delta H \) is a state function, the enthalpy change for a reaction is the same whether it occurs by one step or a series of real or hypothetical steps. This allows us to determine the \( \Delta H_{\text{rxn}} \) for a system we cannot measure experimentally.

For example: we want to know the \( \Delta H_{\text{rxn}} \) for \( A \rightarrow D \)

We do know \( \Delta H_{\text{f}} \)'s for \( A \rightarrow B \) , \( B \rightarrow C \) and \( C \rightarrow D \)

we can now calculate \( \Delta H_{\text{rxn}} \) for \( A \rightarrow D \)

\[
\begin{align*}
\text{reaction} & \quad \Delta H_{\text{rxn}} \\
A & \rightarrow B \quad -10 \text{ kJ} \\
B & \rightarrow C \quad -20 \text{ kJ} \\
C & \rightarrow D \quad +5 \text{ kJ} \\
\hline
A & \rightarrow D \quad (-10)+(-20)+(5) \quad = -25 \text{ kJ} \\
\end{align*}
\]

If you add up the reactions and cancel out like terms, the desired reaction is the result. The \( \Delta H_{\text{rxn}} \) for this reaction is the sum of the \( \Delta H_{\text{f}} \)'s of the other reactions.
In using Hess' Law, we found reactions with known $\Delta H^\circ$s that when added together produced the desired reaction. So therefore we found another path from reactants to products. This is OK since $\Delta H$, a state function, is independent of pathway.

\[ \begin{align*}
B & \xrightarrow{\Delta H_{\text{rxn}} = -20 \text{ kJ}} C \\
A & \xrightarrow{\Delta H_{\text{rxn}} = -10 \text{ kJ}} D \\
A & \xrightarrow{\Delta H = ?} D
\end{align*} \]

This can get more complicated.

Example: Consider $\text{N}_2\text{O}(g) + \text{NO}_2(g) \rightarrow 3 \text{NO}(g)$. $\Delta H_{\text{rxn}}$ unknown

We wish to calculate $\Delta H_{\text{rxn}}$ and so we will use a set of reactions with known $\Delta H^\circ$s in order to derive it.

Given

1. $\text{Na}(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{N}_2\text{O}(g)$ \hspace{1cm} $\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_f = +82.05 \text{ kJ}$

2. $\frac{1}{2} \text{N}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{NO}(g)$ \hspace{1cm} $+90.25 \text{ kJ}$

3. $\frac{1}{2} \text{N}_2(g) + \text{O}_2(g) \rightarrow \text{NO}_2(g)$ \hspace{1cm} $+33.2 \text{ kJ}$

What we will do now is algebraically manipulate the equations and their corresponding $\Delta H^\circ$s and add them together so that the desired reaction (and its $\Delta H^\circ_{\text{rxn}}$) is obtained.
In this example, we used $\Delta H^\circ$ equations. We can do this with other equations also (see BOP examples).

$$
\begin{align*}
N_2O_4(g) & \rightarrow N_2(g) + \frac{1}{2} O_2(g) \\
3\left[\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g)\right] & \rightarrow NO(g) \\
+ NO_2(g) & \rightarrow \frac{1}{2} N_2(g) + O_2(g) \\
N_2O_4(g) + NO(g) & \rightarrow 3 NO(g)
\end{align*}
$$

$\Delta H_{\text{rxn}} = -82.05 \text{ kJ}$

$= 3 \times \Delta H_{\text{rxn}} = 270.75 \text{ kJ}$

$= -33.2 \text{ kJ}$

$\Delta H_{\text{rxn}} = +155.5 \text{ kJ}$

$= -\Delta H_{\text{rxn}1} + 3 \Delta H_{\text{rxn}2} - \Delta H_{\text{rxn}}$

We can restate Hess' Law in mathematical terms:

$$
\Delta H^\circ_{\text{rxn}} = \sum n \Delta H^\circ_{\text{products}} - \sum n \Delta H^\circ_{\text{reactants}}
$$

For the above example, $\Delta H^\circ_{\text{rxn}} = 3 \Delta H^\circ_{NO(g)} - (\Delta H^\circ_{NO_2(g)} + \Delta H^\circ_{N_2O_4(g)})$

$= 3 \Delta H^\circ_{NO(g)} - \Delta H^\circ_{NO_2(g)} - \Delta H^\circ_{N_2O_4(g)}$

Example: Calculate $\Delta H^\circ_{\text{rxn}}$ for the combustion of 16.8 g of propane (MW 44), from data in Appendix K.

$$
C_3H_8(g) + 5 O_2 (g) \rightarrow 4 H_2O (l) + 3 CO_2(g)
$$

$\Delta H^\circ_{298} = -103.8 \text{ kJ/mol}$

$\Delta H^\circ_{\text{rxn}} = 4 \left[\Delta H^\circ_{H_2O(l)} + 3 \left(\Delta H^\circ_{CO_2(g)}\right) - 1 \left(\Delta H^\circ_{C_3H_8(g)}\right) - 5 \left(\Delta H^\circ_{O_2(g)}\right)\right]$ 

$= 4 \left(-285.8\right) + 3 \left(-393.5\right) - 1 \left(-103.8\right) - 5 \left(0\right)$

$= -2219.9 \text{ kJ/mol of C}_3\text{H}_8$

$[\text{Note: } \Delta H^\circ_{\text{rxn}} = -2219.9 \text{ kJ/mol of C}_3\text{H}_8 \text{ or } 444.0 \text{ kJ/mol of O}_2, \text{ etc.}]$

but we do not have 1 mole of C$_3$H$_8$ – only 16.8 g = $\frac{16.8}{44.0} \text{ mol of O}_2$, etc.

$\therefore \Delta H^\circ_{\text{rxn}} = -2219.9 \text{ kJ/mol } \times 0.382 \text{ mol}$

$= -848 \text{ kJ}$
It is also possible to determine $\Delta H_f^\circ$ for a substance knowing $\Delta H_f^\circ$ reaction and the $\Delta H_f^\circ$'s for the other involved substances.

Example: Given the following information, calculate $\Delta H_f^\circ$ for gaseous $\text{H}_2\text{S}(g)$ in the reaction:

$$2\text{H}_2\text{S}(g) + \text{O}_2(g) \rightarrow 2\text{SO}_2(g) + 2\text{H}_2\text{O}(l)$$

$\Delta H_f^\circ (\text{kJ/mol})$ ? 0 -296.8 -285.8

and $\Delta H_{298 \text{K}}^\circ$ reaction = -1124 kJ

Hess' Law: $\Delta H_{\text{rxn}}^\circ = \sum n \Delta H_f^\circ$ products $- \sum n \Delta H_f^\circ$ reactants

$$-1124 \text{ kJ} = 2(-296.8) + 2(-285.8) - (2x + 0)$$

$$2x = -41.2$$

$$\Delta H_f^\circ \text{H}_2\text{S}(g) = x = -20.6 \text{ kJ/mole}$$

Applications of Hess' Law (Not to be tested)

(1) determination of the energy in a covalent bond (bond energy)
(2) determination of the energy in an ionic bond (crystal lattice energy) using the Born-Haber cycle (see book)

(1) We have been concerned with the heat involved in reactions. Where does this heat come from? The making and breaking of chemical bonds.

bond energy: the amount of energy required to break a covalent bond and separate the atoms in the gaseous phase.

Example: $\text{H}_2(g) \rightarrow 2\text{H}(g)$ $\Delta H_{\text{rxn}}^\circ = +435 \text{ kJ/mol H}_2$

:: the bond energy of the H-H bond is 435 kJ
Entropy, $S$

Entropy, $S$, is a thermodynamic measure of disorder.

Second Law of Thermodynamics: In any spontaneous reaction, the entropy (disorder) of the universe (not necessarily the system) increases.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

This is based on our experiences.

- E.g., when mirrors are dropped, they shatter.
- When my housework is left for a week, it gets messier and messier.
- When gas is put into an evacuated container, it will expand to fill the space.

$S^0_{298}$ is the absolute standard molar entropy. It is tabulated for many substances in Appendix K. Consider these examples:

$$S^0_{298} \ (\text{J/mol K})$$

$$
\begin{align*}
I_2(s) & : 116.1 \\
I_2(g) & : 260.6 \\
H_2O (l) & : 69.91 \\
H_2O (g) & : 188.7
\end{align*}
$$

we use these values to calculate $\Delta S_{\text{system}} = \Delta S_{\text{rxn 298}}$

as we can see, for a substance, the order of increasing disorder (entropy) is

- solid < liquid < gas
- most ordered < little molecular motion < most disordered

As a system becomes more ordered, its entropy is less. If we cool a perfect crystal of $I_2(s)$ to absolute zero (in reality an impossibility there is less and less motion, more and more order as the intermolecular forces come into play, and its entropy will approach 0. which leads us to ...

The Third Law of Thermodynamics: The entropy of a pure perfect crystalline substance is zero at absolute 0 K.
The principle driving force in many physical processes and chemical reactions is an entropy increase.

\[ S_{\text{after}} > S_{\text{before}} \]
\[ \therefore \Delta S_{\text{diffusion}} \text{ is a positive number} = S_{\text{after}} - S_{\text{before}} \]

If \( \Delta S \) + disorder increases
\( \Delta S \) - disorder decreases and order increases
(Note that the energy of the above system does not change.)

Example: Calculate \( \Delta S_{298}^o \) for the following reaction

\[ 3 \text{ NO}(g) \rightarrow \text{N}_2\text{O}(g) + \text{NO}_2(g) \]

\[ S_{298}^o \quad (\text{J mol}^{-1} \text{K}^{-1}) \]

\[ 219.7 \quad 219.7 \quad 240.0 \]

\[ \Delta S_{\text{rxn}} = \sum n S_{\text{product}}^o - \sum n S_{\text{reactants}}^o \]
\[ = (1)(+219.7) + (1)(+240.0) - 3(210.7) \]
\[ = -172.4 \quad \text{J/K} \]

\( \Delta S_{\text{rxn}} \) is negative, \( \therefore \) the system is more ordered. This makes sense since we have 3 moles gas \( \rightarrow \) 2 moles gas.

If we were determining \( \Delta S_{\text{rxn}}^o \) for \( \text{NO}_2(g) + \text{N}_2\text{O}(g) \rightarrow 3 \text{ NO}(g) \)
the answer would be ? \quad \text{ANS.} \quad +172.4 \quad \text{J/K} \]
Gibbs Free Energy, $\Delta G$: the thermodynamic state function of a system which indicates the amount of energy available for the system to do useful work.

Gibbs Free Energy change, $\Delta G$: maximum amount of useful work that can be done by a reaction at constant $T$ and constant $P$. It is a state function. Units: kJ/mole

$\Delta G_f^{\circ}$, the standard molar free energy of formation, are tabulated in Appendix K. Note that $\Delta G_f^{\circ} = 0$ for elements in their standard states.

* $\Delta G$ is the indicator of spontaneity of a reaction or physical change.
  if $\Delta G$ is $-$ the reaction will go (we don't know how fast)
  $\Delta G$ is $+$ the reaction will NOT go
  $\Delta G$ is 0 the system is at equilibrium i.e. reactants are changing into products just as fast as products are changing into reactants:
  reactants $\leftrightarrow$ products

$\Delta G_{rxn} = \sum n \Delta G_f^{\circ} \text{products} - \sum n \Delta G_f^{\circ} \text{reactants}$
  $\Delta G_f^{\circ} = 0$ for elements in standard state

Example: Calculate $\Delta G_f^{\circ}$ for the combustion of 1 mole of propane.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G_f^{\circ}$ (kJ/mol)</th>
<th>C$_3$H$_8$ (g)</th>
<th>5 O$_2$ (g)</th>
<th>3 CO$_2$(g)</th>
<th>4 H$_2$O (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-23.49</td>
<td>0</td>
<td>-394.4</td>
<td>-237.2</td>
</tr>
</tbody>
</table>

$\Delta G_{rxn} = 3 (\Delta G_f^{\circ} \text{CO}_2) + 4 (\Delta G_f^{\circ} \text{H}_2\text{O}) - 1 (\Delta G_f^{\circ} \text{C}_3\text{H}_8)$

$\Delta G_{rxn} = 3 (-394.4) + 4 (-237.2) - (-23.49) - 0$

$\Delta G_{rxn} = -2108.5 \text{ kJ}$

$\Delta G_{rxn} = -2108.5 \text{ kJ/mol propane} \alpha -2108.5 \text{ kJ/5 mole O}_2 \text{ etc.}$

Reaction is spontaneous at 25°C. The reverse reaction is non-spont.
There are two factors that affect $\Delta G$ and $\Delta S$ that affect the spontaneity of a reaction. These are shown in...

**Gibbs - Helmholtz Equation**

\[
\Delta G = \Delta H - T\Delta S \\
\text{at constant } T \\
\text{heat of cont. p} \\
\text{drive toward more disorder}
\]

This is very useful because $\Delta G$ and $\Delta H$ can be determined experimentally and this allows us to calculate $\Delta S$. Note: $\Delta H, \Delta S$ do not change much with $T$. $\Delta G$ does change with $T$.

**Example:** let us look at the combustion of propane:

\[
\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{ CO}_2(\text{g}) + 4\text{ H}_2\text{O}(\text{L})
\]

we have determined:

\[
\Delta G^\circ_{\text{rxn}} = -2108.5 \text{ kJ/mol propane} \\
\Delta H^\circ_{\text{rxn}} = -2219.9 \text{ kJ/mol propane}
\]

\[
\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}
\]

\[
\Delta S^\circ_{\text{rxn}} = \frac{\Delta H^\circ_{\text{rxn}} - \Delta G^\circ_{\text{rxn}}}{T}
\]

\[
= \frac{-2219.9 - (-2108.5)}{298.15 \text{ K}}
\]

\[
= -0.374 \text{ kJ/K} \text{ or } -374 \text{ J/K}
\]

entropy is decreasing; the system is becoming more ordered: 6 moles gas $\rightarrow$ 3 moles gas.

This is the same answer you would have obtained from tables of $S^\circ_{298}$:

\[
\Delta S^\circ_{\text{rxn}} = \Sigma n S^\circ_{298} \text{ products} - \Sigma n S^\circ_{298} \text{ reactants}
\]

$\Delta G^\circ_{\text{rxn}}$ is $-2108.5$. $\therefore$ the reaction is spontaneous at $25^\circ C$.

But we can ask over what temperature range is the reaction spontaneous. To do this we must use the Gibbs-Helmholtz equation.
\[ \Delta G = \Delta H - T \Delta S \]

Case 1. \( \Delta H \) is \(-\), \( \Delta S \) is \(+\), \( \Delta G \) must be \(-\) reaction is spontaneous at all \( T \)

Case 2. \( \Delta H \) is \(-\), \( \Delta S \) is \(-\), as \( T \) decreases, reaction becomes less spontaneous

Case 3. \( \Delta H \) is \(+\), \( \Delta S \) is \(+\), as \( T \) increases, reaction becomes more spontaneous

Case 4. \( \Delta H \) is \(+\), \( \Delta S \) is \(-\), \( \Delta G \) has to be \(+\) reaction is non spontaneous at all \( T \). \( T_{eq} = \frac{\Delta H}{\Delta S} = -\) impossible

Example: Consider the combustion of propane
\[ \Delta H_{rxn} = -2219.9 \text{ kJ/mol} \]
\[ \Delta S_{rxn} = -374 \text{ J/K} \]

At equilibrium: \( \Delta G = 0 = \Delta H - T \Delta S \)

\[ T_{eq} = \frac{\Delta H}{\Delta S} = \frac{-2219.9 \text{ kJ}}{-0.374 \text{ kJ/K}} = 5936 \text{ K} \]

This system is an example of case 2. \( \therefore \) reaction is spontaneous at \( T < 5936 \text{ K} \) (assuming \( \Delta H, \Delta S \) are independent of \( T \)).

We could have also said \( \Delta H - T \Delta S < 0 \) for spontaneity

Now substitute in the values:

\[ -2219.9 - T(-0.374 \text{ kJ}) < 0 \]
\[ -2219.9 + 0.374 (T) < 0 \]
\[ T < \frac{2219.9}{0.374} \]

When \( \times \) or \( \div \) by negative \( n \), the inequality flips.
We can use these same principles to estimate boiling points, and freezing points of substances since at the freezing or boiling temperature, the system is at equilibrium.

Example: Use thermodynamic data to estimate the normal boiling point of water (normal means the system is at 1 atm pressure)

Assumption: $\Delta H$, $\Delta S$ are independent of temperature.

At the boiling point, liquid and gas phases are in equilibrium: $\Delta G = 0$

$$H_2O (l) \rightleftharpoons H_2O (g)$$

$$\Delta G = 0 = \Delta H - T \Delta S$$

$$\therefore T_b = T_{eq} = \frac{\Delta H}{\Delta S}$$

For 1 mole of $H_2O (l) \rightarrow 1$ mole of $H_2O (g)$

$$\Delta H_{\text{m}}^0 = (1 \text{ mol}) \Delta H_f^0 \text{ H}_2\text{O} (g) - (1 \text{ mol}) \Delta H_f^0 \text{ H}_2\text{O} (l)$$
$$= (1 \text{ mol}) (-2418 \text{ kJ/mol}) - (1 \text{ mol}) (-285.8 \text{ kJ/mol})$$
$$= 44.0 \text{ kJ}$$

$$\Delta S_{\text{m}}^0 = (1 \text{ mol}) S^0_{\text{H}_2\text{O}(g)} - (1 \text{ mol}) S^0_{\text{H}_2\text{O}(l)}$$
$$= (1 \text{ mol}) (188.7 \text{ J/molK}) - (1 \text{ mol}) (69.91 \text{ J/molK})$$
$$= 118.8 \text{ J/K}$$

$$\therefore T_b = \frac{\Delta H_{\text{m}}}{\Delta S_{\text{m}}^0} = \frac{44.0 \text{ kJ}}{0.1188 \text{ kJ/K}} = 370 \text{ K or 97°C}$$

(very close to 100°C)