

Chapter 19: Principles of Reactivity: Entropy & Free Energy

This chapter is a continuation of Chapter 6 (Chem 101 - see notes)
Both chapters form basis of Thermodynamics - the study of energy transfers and energy changes that accompany physical & chemical processes.

Review from Chem 101 (just what we need for Chapter 19)

Enthalpy - heat content of a substance at constant pressure

- designated by H

- $\Delta H = H_{\text{final}} - H_{\text{initial}}$

change in

- $\Delta H_{\text{rxn}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$

- sign convention

$\Delta H > 0$ reaction or process is endothermic (absorbs energy)

$\Delta H < 0$ reaction or process is exothermic (releases energy)

(1) process: $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$ boiling $\Delta H > 0$ process needs heat to go forward

(2) reaction: $2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g)$ $\Delta H < 0$ releases heat
combustion

Let's look closer:

(1) When 1 mol of H_2O boils, how exactly do we know how much heat is involved? We can use thermodynamic tables and Hess' Law of heat summation:

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

where n = stoichiometric coefficients

ΔH_f° = standard molar enthalpy of formation (kJ/mol)

In the Appendix, we find

$$\Delta H_{f,298}^\circ \text{H}_2\text{O}(g) = -241.83 \text{ kJ/mol}$$

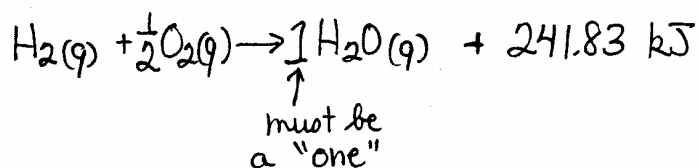
$$\Delta H_{f,298}^\circ \text{H}_2\text{O}(l) = -285.83 \text{ kJ/mol}$$

Note: $K = ^\circ\text{C} + 273.15$

$$\therefore 25^\circ\text{C} = 298.15 \text{ K}$$

What does $\Delta H_{f,298}^\circ \text{H}_2\text{O}(g) = -241.83 \text{ kJ/mol}$ mean?

Answer - When 1 mol of $\text{H}_2\text{O}(g)$ is formed from elements in their standard states, 241.83 kJ of heat is released at 25°C



Note: All elements in their standard states have $\Delta H_f^\circ = 0$.

<u>Element</u>	<u>standard state</u>
hydrogen	$\text{H}_2(g)$
oxygen	$\text{O}_2(g)$
mercury	$\text{Hg}(l)$
tin	$\text{Sn}(s)$
carbon	$\text{C}(\text{graphite}, s)$

So what is $\Delta H_{\text{rxn}}^\circ$ for $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$? Note: all data is for compds at 25°C

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= (1)(\Delta H_f^\circ \text{H}_2\text{O}(g)) - (1)(\Delta H_f^\circ \text{H}_2\text{O}(l)) \\ &= -241.83 \text{ kJ/mol} - (-285.83 \text{ kJ/mol}) \\ &= +44.00 \text{ kJ/mol}\end{aligned}$$

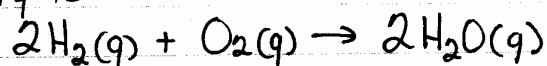
We can write: $\text{H}_2\text{O}(l) + 44.00 \text{ kJ} \rightarrow \text{H}_2\text{O}(g)$

How much heat is required to convert 100. mL of water (l) to gas at 25°C?

Plan: (1) Find moles of H_2O : $\text{mL} \xrightarrow{\text{Density}} \text{g} \xrightarrow{\text{FW}} \text{mol}$
 (2) Use $\Delta H_{\text{rxn}}^\circ$ to find heat.

$$\begin{aligned}?\text{ kJ} &= 100. \text{ mL H}_2\text{O} \times \frac{1 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \times \frac{+44.00 \text{ kJ}}{1 \text{ mol H}_2\text{O}} \\ &= 244 \text{ kJ}\end{aligned}$$

(2) How much heat is involved in combustion at 25°C?
according to:



Note: this is $2 \times \Delta H_{f,298}^\circ \text{H}_2\text{O}(\text{g})$ because

$$\begin{aligned} \therefore \Delta H_{\text{rxn}} &= (2 \times \Delta H_{f,298}^\circ \text{H}_2\text{O}(\text{g})) - (2 \times \Delta H_{f,298}^\circ \text{H}_2(\text{g}) + 1 \times \Delta H_{f,298}^\circ \text{O}_2(\text{g})) \\ &= (2 \times -241.83 \text{ kJ/mol}) - (2 \times 0 + 1 \times 0) \\ &= -483.66 \text{ kJ} \end{aligned}$$

We can write: $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + 483.66 \text{ kJ}$

How much heat is released if 7.00 g of hydrogen gas is burned at 25°C in presence of excess oxygen gas?

$$? \text{ heat released} = 7.00 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} \times \frac{483.66 \text{ kJ}}{2 \text{ mol H}_2} = 1680 \text{ kJ}_{\text{released}}$$

What is the sign of heat? It is $\oplus$ because we used the word released. If I had asked, "What is ΔH_{rxn} when 7.00 g H_2 is burned?", the answer would have been, $\Delta H_{\text{rxn}} = -1680 \text{ kJ}$.

State function: a quantity whose value is determined only by the state of a system. Changes in a state function depend only on initial + final state, + not on how the state was reached. (the path). In thermodynamics, such quantities are designated by a capital letter.

Pressure: P and ΔP

Temperature: T and ΔT

Volume: V and ΔV

Enthalpy: H and ΔH

(not q generic heat)
 w work

First Law of Thermodynamics: The total energy of the universe is constant where system under study + surroundings = universe

Now to Chapter 19

Spontaneous reaction or process: one that occurs in the forward direction without intervention.

Note: Will the reaction go forward until the limiting reactant is consumed?
Not necessarily! It will go to equilibrium where reactants convert to products just as fast as products turn into reactants: $\rightleftharpoons$

Examples:

product favored $\text{HCl} + \text{NaOH} \rightleftharpoons \text{NaCl} + \text{H}_2\text{O}$ essentially goes to completion
reactant favored $\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{CH}_3\text{COO}^-$ since CH_3COOH is weak acid

ΔH alone does not determine if a reaction is spontaneous.

Another key factor is a change in the freedom of motion of particles in a system and in the dispersal of their energy of motion.

What does this mean?

Every atom, molecule or ion has quantized (not continuous) electronic energy levels and kinetic energy levels - vibrational, rotational and translational. The number of these distinct microscopic states (microstate) is designated W .

Entropy (S), a thermodynamic state function, can be calculated

$$S = k \ln W \quad \text{where } k = \text{Boltzmann constant} \\ = 1.381 \times 10^{-23} \text{ J/K}$$

Note: we'll see k again for a mole of stuff

$$k = 1.381 \times 10^{-23} \text{ J/K} \times 6.02 \times 10^{23} = 8.314 \text{ J/mol}\cdot\text{K}$$

As W increases, entropy (S) increases. The more microstates there are for a system, the higher the dispersal of energy and matter, the greater is the entropy.

To simplify, the word "disorder" is used as synonym for entropy.

Examples:

lower entropy $\rightarrow$ higher entropy
fewer microstates $\rightarrow$ more microstates
more order $\rightarrow$ more disorder

- phase change: solid $\rightarrow$ liquid $\rightarrow$ gas
- dissolving salt: $\text{NaCl(s)} \xrightarrow{\text{H}_2\text{O}} \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- chemical change: $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
 $2\text{C(s)} + \text{O}_2(\text{g}) \rightarrow 2\text{CO(g)}$ [look at moles gas]
- molecular size/complexity $\text{CH}_4 < \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- temperature $\text{H}_2\text{O(l) at } 10^\circ\text{C} < \text{H}_2\text{O(l) at } 80^\circ\text{C}$
- volume $1\text{ mol N}_2(\text{g}) \text{ in } 1\text{ L} < 1\text{ mol N}_2(\text{g}) \text{ in } 2\text{ L}$
(this is why diffusion happens)

How do we know what the value of entropy is for a substance?

Look it up in a table!

S_{298}° is the absolute standard molar entropy. It is the measure of the "disorder" (no. of microstates) in 1 mole of compound at 25°C and 1 atm pressure.
Units: $\text{J/mol}\cdot\text{K}$. Examples

	S_{298}° ($\text{J/mol}\cdot\text{K}$)	
$\text{I}_2(\text{s})$	116.1	$>$ phase difference $>$ size difference
$\text{I}_2(\text{g})$	260.6	
$\text{Cl}_2(\text{g})$	223.1	

Note: all S_{298}° values are positive

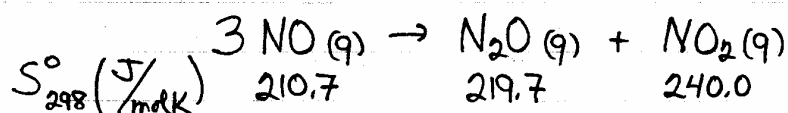
If we cool a perfect crystal of $\text{I}_2(\text{s})$ to absolute zero (in reality - impossible) there is less & less motion, more & more order, entropy approaches zero which leads us to

Third law of Thermodynamics: The entropy of a pure, perfect crystalline substance is zero at absolute 0 K.

How do we calculate ΔS_{298}° for a reaction or process?

Use Hess' Law - type calculation using tabulated data. since S is state function

Example: Calculate ΔS_{298}° for following reaction



$$\begin{aligned} \Delta S_{298}^\circ &= \sum n S_{\text{products}}^\circ - \sum n S_{\text{reactants}}^\circ \\ &= [(1)(219.7) + (1)(240.0)] - 3(210.7) \\ &= -172.4 \text{ J/K} \end{aligned}$$

Sign convention: if $\Delta S +$, entropy (disorder) increases
if $\Delta S -$, entropy (disorder) decreases

Does the sign of ΔS make sense here? The system starts with 3 moles gas $\rightarrow$ 2 moles gas and becomes more ordered/less disordered. So, yes - makes sense.

(What is ΔS_{298}° for $\text{N}_2\text{O (g)} + \text{NO}_2\text{ (g)} \rightarrow 3 \text{ NO (g)}$? ANS. $+172.4 \text{ J/K}$)

What part does entropy play in predicting spontaneity?

Second law of Thermodynamics: In any spontaneous reaction, the entropy/disorder of the universe increases.

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

$\uparrow$ calculated above $\uparrow$ calculated by $\frac{\Delta H_{\text{system}}}{T(\text{K})}$

Explanation of ΔS_{surr} : For an exothermic rxn ($\Delta H < 0$), heat is released to surroundings, the entropy of surroundings increases ($\Delta S > 0$). To remove the temperature effect, ΔH is divided by absolute T (K). To mesh the sign conventions, the negative sign is added.

Example: Determine if the reaction $3\text{NO}(g) \rightarrow \text{N}_2\text{O}(g) + \text{NO}_2(g)$ is spontaneous.

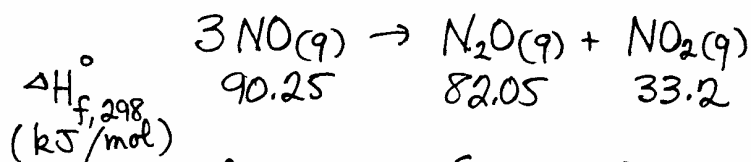
Plan: (1) calculate ΔS_{sys} (done)

(2) calculate ΔS_{surr} from ΔH_{syst} $\Delta S_{\text{surr}} = - \frac{\Delta H_{\text{syst}}}{T}$

(3) if $\Delta S_{\text{universe}} > 0$, reaction is spontaneous.

(1) $\Delta S_{\text{sys}} = -172.4 \text{ J/K}$

(2)



$$\Delta H_{\text{rxn}}^\circ = \Delta H_{\text{syst}} = [(1)(82.05) + (1)(33.2)] - (3)(90.25) = -155.5 \text{ kJ}$$

$$\Delta S_{\text{surr}} = - \frac{(-155.5 \text{ kJ})}{298.15 \text{ K}} = +0.5215 \text{ kJ/K}$$

← I'm using more significant figures since -155.5 has 4 sig. figs

(3) $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr.}}$

$$\begin{aligned} &= -172.4 \text{ J/K} + 0.5215 \text{ (kJ/K)} \\ &= -172.4 \text{ J/K} + 521.5 \text{ J/K} \\ &= +349.1 \text{ J/K} \end{aligned}$$

problem!!!

Yes, the reaction is spontaneous, since $\Delta S_{\text{univ.}} > 0$.

Rather than deal with the system and surroundings to predict spontaneity, we can work with a new thermodynamic quantity of the system: Gibbs Free Energy, G .

Gibbs Free Energy, G : thermodynamic state function of a system which indicates the amount of energy available for a system to do useful work.

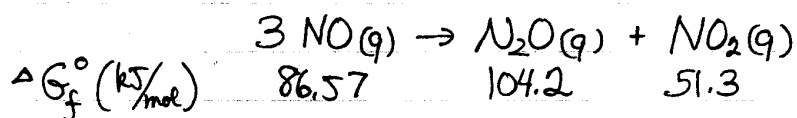
Gibbs Free Energy change, ΔG : maximum amount of useful work that can be done by a reaction at constant T and P. It is a state function.
Units: kJ/mol. Value can be calculated from tabulated $\Delta G_{f,298}^\circ$.

$\Delta G_{f,298}^\circ$ is the standard molar free energy of formation at 25°C. Values are in the Appendix. This is the free energy change when 1 mol of substance is formed from elements in their standard state.
Note: $\Delta G_f^\circ = 0$ for elements in their standard states.

- * $\Delta G_{rxn} = \Delta G_{sys}$ is indicator of spontaneity for reaction or physical change
- if $\Delta G < 0$ the rxn is spontaneous and will go forward (we don't know how fast)
 - if $\Delta G > 0$ the rxn is non spontaneous (reverse rxn IS spontaneous)
 - if $\Delta G = 0$ the rxn is at equilibrium reactants $\rightleftharpoons$ products

$$\Delta G_{rxn} = \sum n \Delta G_{f,products}^\circ - \sum n \Delta G_{f,reactants}^\circ$$

Example: Calculate ΔG_{rxn}° for $3NO(g) \rightarrow N_2O(g) + NO_2(g)$
Is the rxn spontaneous?



$$\Delta G_{rxn} = [(1)(104.2) + (1)(51.3)] - (3)(86.57) = -104.2 \text{ kJ}$$

Since $\Delta G < 0$, rxn is spontaneous.

Is there another way to calculate ΔG_{rxn} ? Yep! Gibbs-Helmholtz Egn.

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

Since we already know ΔH_{rxn} and ΔS_{rxn} for $3NO(g) \rightarrow N_2O(g) + NO_2(g)$,
Let's see if the ΔG_{rxn} calculated here agrees with the value just calculated!

$$\begin{aligned}
 \Delta G_{\text{rxn}} &= \Delta H - T \Delta S && \text{careful!!} \\
 &= -155.5 \text{ kJ} - (298.15 \text{ K})(-172.4 \text{ J/K}) \\
 &= -155.5 \text{ kJ} - (298.15 \text{ K})(-0.1724 \text{ kJ/K}) \\
 &= -155.5 \text{ kJ} + 51.4 \text{ kJ} \\
 &= -104.1 \text{ kJ}
 \end{aligned}$$

So, values of ΔG_{rxn} agree within rounding error.

Let's look closer at the formula: ΔG depends on temperature, ΔH , ΔS

$$\begin{array}{ccccccc}
 \Delta H & - & T \Delta S & = & \Delta G \\
 \uparrow & & \uparrow & & \uparrow \\
 \text{change in heat} & & \text{always } \oplus & & \text{change in} & & \text{Indicator of} \\
 \text{at constant P} & & \text{absolute T} & & \text{amount of} & & \text{spontaneity} \\
 & & & & \text{disorder} & &
 \end{array}$$

Case 1	$\Delta H < 0$ exothermic	$\Delta S > 0$ more disorder	ΔG must be < 0 rxn is spont. at all T
Case 2	$\Delta H < 0$ exothermic	$\Delta S < 0$ less disorder, more order	ΔG will be < 0 at lower T rxn is spont. at lower T
Case 3	$\Delta H > 0$ endothermic	$\Delta S > 0$ more disorder	ΔG will be < 0 at higher T rxn is spont at higher T
Case 4	$\Delta H > 0$ endothermic	$\Delta S < 0$ less disorder, more order	ΔG will <u>never</u> be < 0 rxn is non spontaneous at all T.

If we look at our reaction, $3\text{NO}(g) \rightarrow \text{N}_2\text{O}(g) + \text{NO}_2(g)$

$\Delta H < 0$ exothermic

$\Delta S < 0$ system is becoming less disordered, more ordered

$\therefore$ we have Case 2 and rxn is spont at lower T.

From our calculations, we know the rxn is spontaneous at 25°C .

All our calculations used data from the Appendix — set at 25°C
(298 K)

Example: Over what temperature range will the reaction be spontaneous? $3\text{NO}(g) \rightarrow \text{N}_2\text{O}(g) + \text{NO}_2(g)$

Plan: Find the temperature at which the rxn is at equilibrium
Use Case 1-4 to determine if rxn is spontaneous at Temp.
above or below equilibrium temp.

$$\begin{aligned}\text{At equilibrium, } \Delta G_{\text{rxn}} &= 0 = \Delta H - T_{\text{eq}} \Delta S \\ T_{\text{eq}} \Delta S &= \Delta H \\ T_{\text{eq}} &= \frac{\Delta H}{\Delta S} \\ &= \frac{-155.5 \text{ kJ}}{-0.1724 \text{ kJ}} \quad \leftarrow \text{be sure to change units!!} \\ &= 902.0 \text{ K}\end{aligned}$$

Since this is Case 2 ($\Delta H < 0$, $\Delta S < 0$), rxn is spontaneous at lower temperatures. Therefore, rxn is spontaneous at $T < 902.0 \text{ K}$.

We can use these same principles to estimate phase change temperatures. (boiling point, freezing/melting pt, sublimation pt) since at these temperatures, the system is at equilibrium

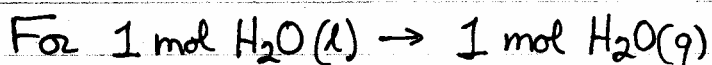
Example: Use thermodynamic data to estimate the normal boiling point (normal means at 1 atm). Assume ΔH , ΔS independent of T .

At the boiling pt, liquid + gas phases are at equilibrium: $\Delta G = 0$



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

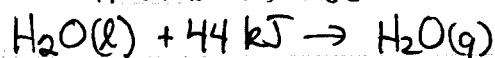
$$\text{So, } T_b = T_{\text{eq}} = \frac{\Delta H}{\Delta S}$$



$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= (1 \text{ mol})(\Delta H_{\text{f}}^{\circ} \text{H}_2\text{O}(\text{g})) - (1 \text{ mol})(\Delta H_{\text{f}}^{\circ} \text{H}_2\text{O}(\text{l})) \\ &= (1 \text{ mol})(-241.8 \text{ kJ/mol}) - (1 \text{ mol})(-285.8 \text{ kJ/mol}) \\ &= +44.0 \text{ kJ}\end{aligned}$$

↑ endothermic

Does this make sense?



$$\begin{aligned}\Delta S_{\text{rxn}}^{\circ} &= (1 \text{ mol})S_{\text{H}_2\text{O}(\text{g})}^{\circ} - (1 \text{ mol})S_{\text{H}_2\text{O}(\text{l})}^{\circ} \\ &= (1 \text{ mol})(188.7 \text{ J/mol}\cdot\text{K}) - (1 \text{ mol})(69.91 \text{ J/mol}\cdot\text{K}) \\ &= +118.8 \text{ J/K}\end{aligned}$$

↑ disorder increasing

Does this make sense?

$$T_b = \frac{\Delta H_{\text{rxn}}}{\Delta S_{\text{rxn}}} = \frac{44.0 \text{ kJ}}{0.1188 \text{ kJ/K}} = 370. \text{ K}$$

↑ change units

$$T_b(^{\circ}\text{C}) = 370. \text{ K} - 273 = 97^{\circ}\text{C} \quad \text{close to } 100^{\circ}\text{C}$$

The rest of the chapter will be covered in context - as we get to it in upcoming chapters.