THERMODYNAMICS

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FIRST LAW OF THERMODYNAMICS

Thermodynamics is the study of heat and other forms of energy involved in chemical or physical processes.

First Law of Thermodynamics

Energy cannot be created nor destroyed, only converted from one to the other.

The first law of thermodynamics is essentially the law of conservation of energy applied to a thermodynamic system.

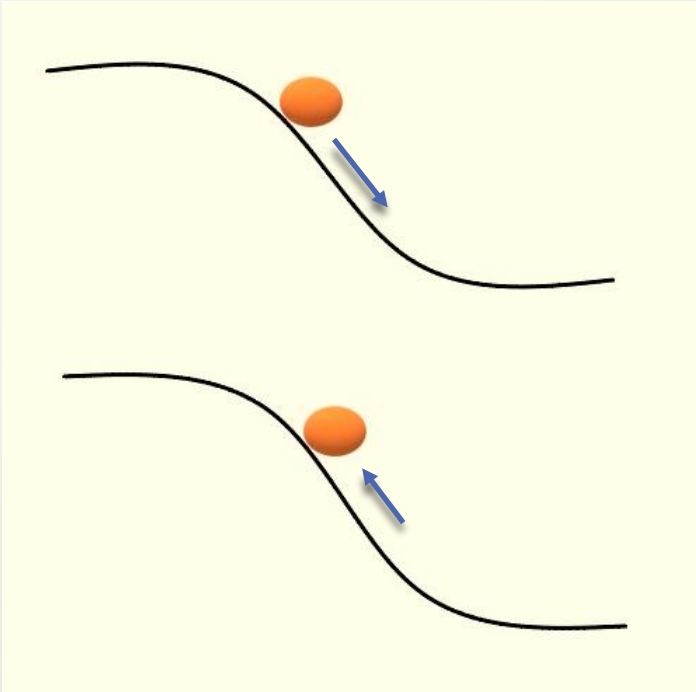
Review: When work is done on a system, heat is given out (exothermic) or heat is absorbed (endothermic).

In this chapter we will learn more on the second and third law of thermodynamics also.

SPONTANEOUS PROCESS

A **spontaneous process** is a physical or chemical change that occurs by itself. It does not require any outside force, and it continues until equilibrium is reached.

- If the direction of one process is spontaneous then the reverse process is non-spontaneous.



A ball rolling downhill is a spontaneous process

A ball rolling uphill is a nonspontaneous process

SPONTANEOUS PROCESS – ENERGY CHANGES

Generally, a process that results in lower energy state of products is spontaneous, energy is released (exothermic process). However, not all exothermic reactions are spontaneous.

$CH_{4(g)} + O_{2(g)} \longrightarrow H_2O_{(g)} + CO_{2(g)}$ ΔH = -890.4 kJ/mol

exothermic, spontaneous

$H_2O_{(s)} \longrightarrow H_2O_{(l)}$ ΔH = 6.01 kJ/mol

endothermic, but spontaneous

$H_2O_{(l)} \longrightarrow H_2O_{(s)}$ ΔH = -6.01 kJ/mol

exothermic but nonspontaneous

What these reactions tell us is there more to all exothermic processes being spontaneous. And that "more" is entropy.

ENTROPY, S

Entropy, *S,* is a thermodynamic quantity that is a measure of how dispersed the energy of a system is among the different possible ways that system can contain energy.

Simply said it is the measure of disorder/chaos in a system.

- High entropy = high chaos or high degree of disorder.
- Low entropy = less chaos or less disorder (higher order).

- To know if a reaction is spontaneous or not, we have to learn about "entropy".
- *For example*: A hot cup of coffee disperses its energy into the atmosphere surrounding it. The chaos/disorderliness is increased in the atmosphere – so entropy of the atmosphere is increased.

ENTROPY – AS A QUANTITY

Entropy is a state function, it depends on variables, such as temperature and pressure, that determine the state of the substance.

- Entropy is an extensive property. It depends on the amount of substance present.
- Entropy is measured in units of J/mol K.
- Entropy change is calculated as follows: $\Delta S = S_f - S_i$
- Standard entropy (ΔS^o) is the absolute entropy of a substance at 1 atm and 25 ^oC since most reactions are carried out at room temperature.
- Increase in entropy is shown as $+\Delta S$, while decrease is $-\Delta S$.
- One way to look at entropy is in a molecular way - the more molecules formed the higher the entropy. This works because more molecules have more energy to disperse.

PREDICTING ENTROPY

1) Entropy of states: Entropy is higher for gases than liquids than solids. When ice melts, the molecules become more disordered, again dispersing energy more widely and again when liquid turns to gas.

$H_2O_{(s)} \longrightarrow H_2O_{(l)} \longrightarrow H_2O_{(g)}$

6.01 J/mol K 69.9 J/mol K 188.7 J/mol K

2) Entropy of allotropes depends on degree of orderliness.

C (diamond) = 2.4 J/mol K C (graphite) = 5.69 J/mol K

3) In reactions it can vary from decomposition to synthesis reactions.

a) There is higher entropy in reactions when one molecule decomposes to give two, $N_2O_{4\,(g)} \longrightarrow 2NO_{2\,(g)}$

b) There is higher entropy when there is dissolving of solute in solvents, $NaCl_{(s)} \longrightarrow NaCl_{(aq)}$

c) Entropy is lowered in synthesis reaction, $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

4) Temperature: Entropy is higher at higher temperature than at lower temperature.

Keep in mind, as molecular disorder increases, as does entropy.

EXAMPLE 1: PREDICTING ENTROPY

Which of the following states and reactions will lead to or have higher (+) or lower (-) entropy.

Answer:

a) $CH_{4\,(g)} + H_2O_{\,(g)} \longrightarrow CO_{\,(g)} + 3H_{2\,(g)}$ $+\Delta S$

b) Hydrogen and oxygen combining to form to water $+\Delta S$

c) $NO_{2\,(g)}$ or $NO_{3\,(g)}$ NO_3 is higher $+\Delta S$

d) Solid sugar or sugar dissolved in water sugar in water $+\Delta S$

SECOND LAW OF THERMODYNAMICS

The total entropy of a system and its surroundings always increases for a spontaneous process.

Note: Entropy is a measure of energy dispersal, not a measure of energy itself.

For a spontaneous process at a constant temperature, there is more entropy in the universe. (System is where reaction takes place, surrounding is everywhere else, and universe is …the universe).

Spontaneous reaction: $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$

At equilibrium: $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$

ENTROPY AND ENTHALPY

Exothermic reactions give Energy to the surroundings: $\Delta S_{\text{surrounding}}$ increases.

Endothermic reactions take Energy to the surroundings: $\Delta S_{\text{surrounding}}$ decreases.

Which means $\Delta S_{\text{surrounding}} \propto -\Delta H_{\text{system}}$

+ entropy exothermic reaction

Change in entropy of the surrounding is inversely proportional to temperature and directly proportional to q, work. Work, q can be used at enthalpy for a reaction, which can then be used to calculate change in entropy.

$$\Delta S > \frac{q}{T} \qquad \Delta S_{\text{surrounding}} = \frac{-\Delta H_{\text{system}}}{T}$$

Using the equations so far if S is positive then reaction is spontaneous.

This equation can be rearranged to $T\Delta S_{\text{surrounding}} = -\Delta H$

THIRD LAW OF THERMODYNAMICS

A substance that is perfectly crystalline at zero Kelvin (0 K) has an entropy of zero.

The standard entropy of a substance—its absolute entropy, $S°$—is the entropy value for the standard state of the species. The standard state is indicated with the superscript degree sign.

For a pure substance, its standard state is 1 atm pressure. For a substance in solution, its standard state is a 1 *M* solution.

To compute $\Delta S°$ where n = moles

$$\Delta S^\circ_{\text{rxn}} = \Sigma n \Delta S^\circ_{\text{products}} - \Sigma n \Delta S^\circ_{\text{reactants}}$$

EXAMPLE 2: STANDARD ENTROPY

When wine is exposed to air in the presence of certain bacteria, the ethyl alcohol is oxidized to acetic acid, giving vinegar. Calculate the standard entropy change at 25 °C for the following similar reaction:

$$CH_3CH_2OH_{(l)} + O_{2\,(g)} \longrightarrow CH_3COOH_{(l)} + H_2O_{(l)}$$

The standard entropies, $S°$, of the substances in J/(K mol) at 25 °C are

$CH_3CH_2OH_{(l)}$,161; $O_{2(g)}$, 205;

$CH_3COOH_{(l)}$, 160; $H_2O_{(l)}$, 69.9.

Answer: $\Delta S°_{rxn} = \Sigma n \Delta S°_{products} - \Sigma n \Delta S°_{reactants}$

	$CH_3CH_2OH_{(l)}$	$O_{2\,(g)}$	$\longrightarrow$	$CH_3COOH_{(l)}$	$H_2O_{(l)}$
$S°$	161	205		160	69.9
n mol	1	1		1	1
$nS°$	161	205		160	69.9

366 229.9

$$\Delta S° = 229.9 - 366 = -136 \text{ J/K mol}$$

GIBBS FREE ENERGY

According to the 2nd law of thermodynamics a reaction is spontaneous when $\Delta S_{universe} > 0$. But we should be able to predict spontaneity by other means.

Starting from equation, $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} > 0$ and the equation relating entropy to enthalpy $T\Delta S_{surrounding} = -\Delta H$, physicist J. Willard Gibbs derived the equation:

$$G = H - TS$$

Where: G = Gibbs free energy; H = enthalpy; T = temperature; S = entropy.

Changes in these state functions (G, H and S) lead to:

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

(*Remember state functions mean only initial and final states matter, how to get from one to the other can be many different ways*).

FREE ENERGY AND SPONTANEITY

As a reaction proceeds, G changes:

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

The spontaneity of a reaction can now be determined by the sign of ΔG.

$\Delta G < 0$ kJ: negative; spontaneous

$\Delta G = 0$, reaction at equilibrium

$\Delta G > 0$ kJ: positive; nonspontaneous

PREDICTING SIGN FOR ΔG

This example is using the free energy equation:

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

Below is the table to show how a process can be indicated as spontaneous or nonspontaneous depending on entropy, enthalpy and temperature.

When ΔH is	And ΔS is	ΔG will be	Process will be	Example
-	+	-	Always spontaneous	$2H_2O_{2\,(aq)} \rightarrow 2H_2O_{(l)} + O_{2\,(g)}$
+	-	+	Always nonspontaneous	$3O_{2\,(s)} \rightarrow 2O_{3\,(g)}$
-	-	- When TΔS<ΔH + when TΔS>ΔH	Spontaneous at low T Nonspontaneous at high T	$H_2O_{(l)} \rightarrow H_2O_{(s)}$
+	+	- When TΔS>ΔH + when TΔS<ΔH	Spontaneous at high T Nonspontaneous at low T	$2HgO_{(s)} \rightarrow 2Hg_{(l)} + O_{2\,(g)}$

EXAMPLE 3: PREDICTING SPONTANEITY

1) Predict the conditions at which the reactions below will be spontaneous using Gibbs free equation.

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

ΔG should be negative for spontaneous reaction.

a) $N_{2\,(g)} + 2F_{2\,(g)} \longrightarrow N_2F_{4\,(g)}$ ΔH = -7.1 kJ

Answer: *H* is < 0; *S* is > 0; *G* will be negative at low *T*

b) $COCl_{2\,(g)} \longrightarrow CO_{\,(g)} + Cl_{2\,(g)}$ ΔH = +110.4 kJ

Answer: *H* is > 0; *S* is > 0; *G* will be negative at very high *T*

2) Predict if the reaction below will be spontaneous at 50 K and *S* is 22.5 kJ/molK?

$C_6H_{12}O_{6\,(s)} + 6O_{2\,(g)} \longrightarrow 6CO_{2\,(g)} + 6H_2O_{\,(g)}$ ΔH = -2540 kJ

Answer: ΔG = -2540 kJ - (50 K x 22.5 kJ/mol K) = -2540-1125 = -3665 kJ/mol. Yes, it is spontaneous at 50K

STANDARD FREE ENERGY

Standard Gibbs free energy change is the same equation except now all reactants and products are in their standard states for one mole of substance (pure at 1 atm and 25 ^{o}C).

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

Another way for calculating the standard free energy of formation is the same as that for standard enthalpy of formation, ΔH_f° or standard entropy, ΔS°. (n is the mols of each of the reactants and products). One can find the standard free energy values in thermodynamic data tables.

$$\Delta G^\circ_{rxn} = \Sigma n \Delta G^\circ_{products} - \Sigma n \Delta G^\circ_{reactants}$$

NOTE: ΔG tells us whether the reaction is spontaneous while ΔG° tells whether products are favored. This is especially useful in equilibrium reactions. $-\Delta G^\circ$ = large K products are favored

$+\Delta G^\circ$ = small K reactants are favored.

ΔG° value is important in industry which uses the standard Gibbs free energy equation to find the optimum temperature for a reaction.

EXAMPLE 5: STANDARD FREE ENERGY - 1

Using standard enthalpies of formation, ΔH_f° and the value of ΔS° from the previous problem (slide 12), calculate ΔG° for the oxidation of ethyl alcohol to acetic acid. $CH_3CH_2OH_{(l)} + O_{2(g)} \longrightarrow CH_3COOH_{(l)} + H_2O_{(l)}$

Answer:

	$CH_3CH_2OH_{(l)}$	$+ O_{2(g)}$	$\longrightarrow$	$CH_3COOH_{(l)}$	$+ H_2O_{(l)}$
ΔH_f° kJ/mol	$-277.6 \times (1)$	$0 \times (1)$		$-487.0 \times (1)$	$-285.8 \times (1)$
$n\Delta H_f^\circ$ kJ	-277.6	0		-487.0	-285.8
	-277.6 kJ			-772.8 kJ	

ΔH° = *product-reactants* = -772.8 kJ - (-277.6) kJ = -495.2 kJ

$\Delta S^\circ = -136$ J/K (from slide 12) = -0.136 kJ/K mol (change units to kJ)

$T = 298$ K

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

$\Delta G^\circ = -495.2$ kJ $- (298$ K $\times -0.136$ kJ/K mol)

$\Delta G^\circ = -495.2$ kJ + 40.5 kJ = **$\Delta G^\circ = -454.7$ kJ/mol** Reaction is spontaneous.

EXAMPLE 5: STANDARD FREE ENERGY-2

Calculate the free−energy change, $\Delta G°$, for the oxidation of ethyl alcohol to acetic acid using standard free energies of formation.

$$CH_3CH_2OH_{(l)} + O_{2\,(g)} \longrightarrow CH_3COOH_{(l)} + H_2O_{(l)}$$

Answer:

	$CH_3CH_2OH_{(l)} + O_{2\,(g)}$		$CH_3COOH_{(l)} +$	$H_2O_{(l)}$
$\Delta G_f°$, kJ/mol	$-174.8 \times (1)$	$0 \times (1)$	$-392.5 \times (1)$	$-237.2 \times (1)$
$n\Delta G_f°$, kJ	−174.8	0	−392.5	−237.2
(products – reactants)	−174.8 kJ		−629.7 kJ	= $\Delta G° = -454.9$ kJ

$$\Delta G°_{rxn} = \Sigma n\Delta G°_{products} - \Sigma n\Delta G°_{reactants}$$

NOTE: Slide 18 has the same problem but we came at the answer using Gibbs free energy, but the answer is the same.

KEY CONCEPTS

- Know all the 3 laws of thermodynamics
- Predict entropy using a chemical equation
- Calculation of standard entropies and free energy
- Predict spontaneity of a reaction using free energy