

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).

WORK AND ENERGY

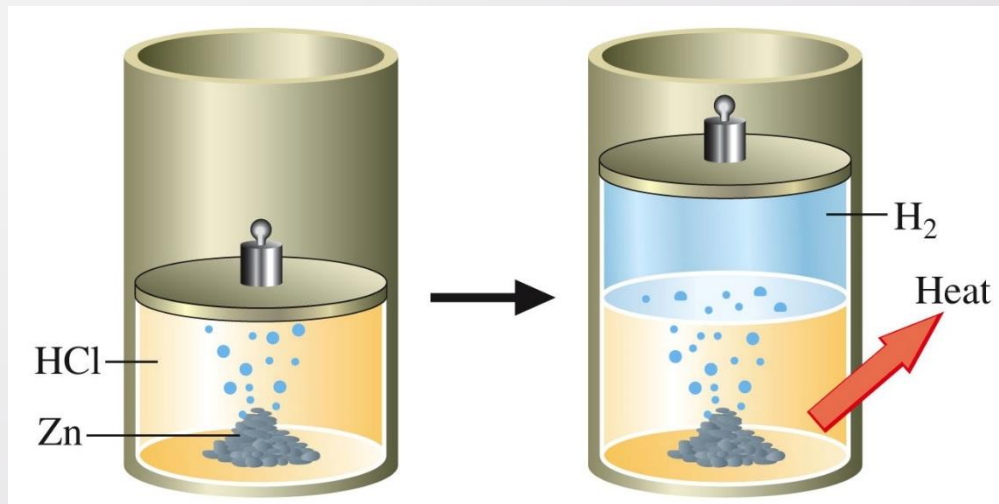
Exchanges of energy between the system and its surroundings are of two types: heat, q , and work, w .

$$\text{Work (} w \text{)} = -P\Delta V$$

When system expands, ΔV is positive so w is negative (*system does work on the surrounding*)

When system contracts, ΔV is negative so w is positive (*surroundings do work on the system*)

In the reaction below, ΔV is positive, so work is negative.



FIRST LAW OF THERMODYNAMICS - EQUATION

At constant pressure: $q_p = \Delta H$

The first law of thermodynamics can now be expressed as follows:

$$\Delta U = \Delta H - P\Delta V$$

U = internal energy

H = enthalpy

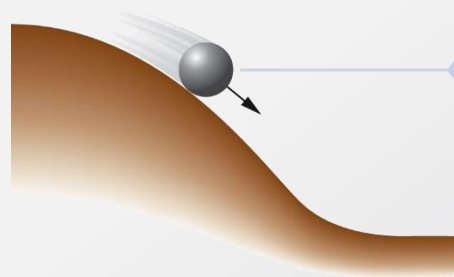
P = pressure

V = volume

To understand why reactions occur in a particular direction, we have to study spontaneous process.

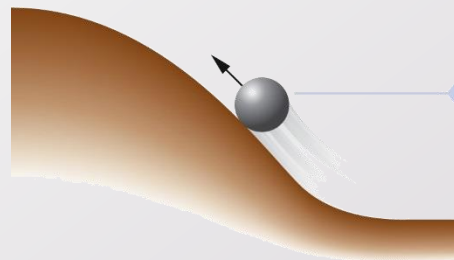
SPONTANEOUS PROCESS

- 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.



The rolling of a rock downhill is a spontaneous process. The rock eventually comes to equilibrium at the bottom of the hill.

Spontaneous process



The rolling of a rock uphill is a nonspontaneous process.

Nonspontaneous process

ENTROPY

- To figure out if a reaction is spontaneous or not, we have to learn about “entropy”.
- **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. (or basically how chaotic a system is –
 - High entropy = high chaos or high degree of disorder
 - Low entropy = less chaos or less disorder (higher order)
- For example: energy from a hot cup of coffee disperses 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/K.
- Entropy change is calculated as follows:

$$\Delta S = S_f - S_i$$

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, we can state the second law of thermodynamics in terms of only the system:

$$\Delta S = \text{entropy created} + \frac{q}{T}$$

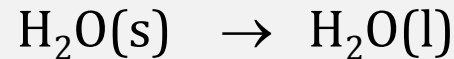
For a spontaneous process:

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

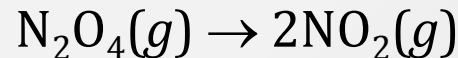
One way to look at entropy is in a molecular way - the more molecules formed the higher the entropy. This works because more molecules have more energy to disperse.

ENTROPY AND MOLECULES

- When ice melts, the molecules become more disordered, again dispersing energy more widely.



- When one molecule decomposes to give two, as in



more disorder is created because the two molecules produced can move independently of each other. Energy is more dispersed.

- In each of these cases, molecular disorder increases, as does entropy.
- Note: this molecular entropy disorder applies only to molecules – not to big objects like a desk.
- So: liquids > solids gases > liquids solutions > salt (s)
- Entropy at higher temp is > lower temp.

CRITERIA FOR A SPONTANEOUS REACTION

The criteria for a reaction to be spontaneous is that entropy of the system and its surroundings should increase.

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

$$\Delta S > \frac{\Delta H}{T}$$

$$T\Delta S > \Delta H$$

$$0 > \Delta H - T\Delta S \text{ or } \Delta H - T\Delta S < 0$$

THIRD LAW OF THERMODYNAMICS

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

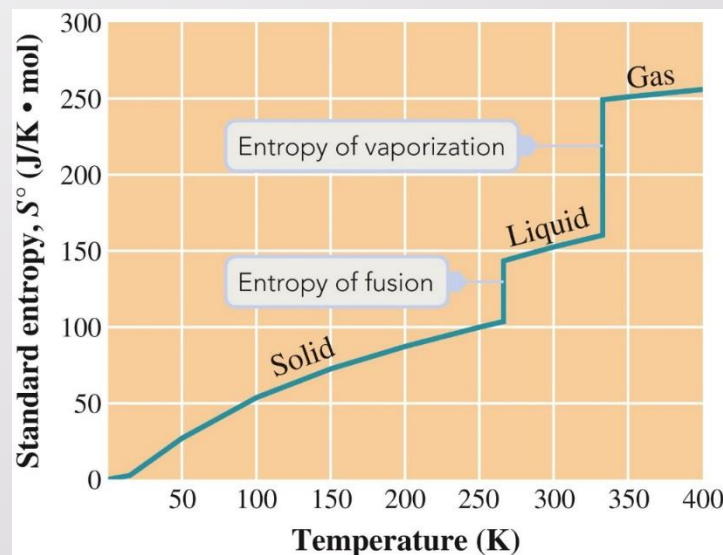
The standard entropy of a substance—its absolute entropy, S° —is the entropy value for the standard state of the species. The standard state is indicated with the superscript degree sign.

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

On the right is entropy of Bromine.

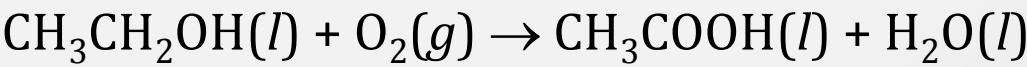
To compute ΔS° where $n =$ moles

$$\Delta S^\circ = \sum nS^\circ (\text{products}) - \sum nS^\circ (\text{reactants})$$



EXAMPLE: 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 entropy change at 25°C for the following similar reaction:



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

$\text{CH}_3\text{CH}_2\text{OH}(l)$, 161; $\text{O}_2(g)$, 205;
 $\text{CH}_3\text{COOH}(l)$, 160; $\text{H}_2\text{O}(l)$, 69.9.

Solution:

	$\text{CH}_3\text{CH}_2\text{OH}(l) + \text{O}_2(g) \rightarrow \text{CH}_3\text{COOH}(l) + \text{H}_2\text{O}(l)$			
S°	161	205	160	69.9
$n \text{ mol}$	1	1	1	1
nS°	161	205	160	69.9
	366		229.9	

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

FREE ENERGY AND SPONTANEITY

Physicist J. Willard Gibbs introduced the concept of **free energy, G** . Free energy is a thermodynamic quantity defined as follows:

$$G = H - TS$$

As a reaction proceeds, G changes:

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

Standard free energy change:

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

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

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

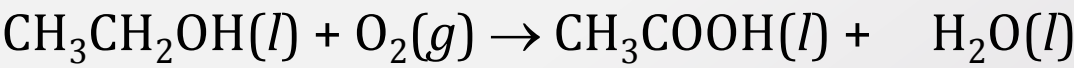
$\Delta G^\circ = 0$, reaction at equilibrium

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

EXAMPLE: FREE ENERGY - 1

Using standard enthalpies of formation, ΔH_f° and the value of ΔS° from the previous problem, calculate ΔG° for the oxidation of ethyl alcohol to acetic acid. $\text{CH}_3\text{CH}_2\text{OH}(l) + \text{O}_2(g) \rightarrow \text{CH}_3\text{COOH}(l) + \text{H}_2\text{O}(l)$

Solution:



$\Delta H_f^\circ \text{ kJ/mol}$	$-277.6 \times (1)$	$0 \times (1)$	$-487.0 \times (1)$	$-285.8 \times (1)$
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$n\Delta H_f^\circ \text{ kJ}$	<u>-277.6</u>	<u>0</u>	<u>-487.0</u>	<u>-285.8</u>
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$(\text{product}-\text{reactants})$	-277.6 kJ	$-772.8 \text{ kJ} = -495.2 \text{ kJ}$
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$\Delta H^\circ = -495.2 \text{ kJ}$

$\Delta S^\circ = -136 \text{ J/K (from previous example)} = -0.136 \text{ kJ/K (change units to kJ)}$

$T = 298 \text{ K}$

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

$\Delta G^\circ = -495.2 \text{ kJ} - (298 \text{ K})(-0.136 \text{ kJ/K})$

$\Delta G^\circ = -495.2 \text{ kJ} + 40.5 \text{ kJ} = \Delta G^\circ = -454.7 \text{ kJ}$ The reaction is spontaneous.

EXAMPLE: FREE ENERGY - 2

Calculate the standard free-energy change for the following reaction.



Solution

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= \sum n\Delta G^\circ_{\text{products}} - \sum m\Delta G^\circ_{\text{reactants}} \\ &= [2(-408.3 \text{ kJ/mol}) + 3(0)] - [2(-289.9 \text{ kJ/mol})] \\ &= -816.6 - (-579.8) = -236.8 \text{ kJ/mol (spont)}\end{aligned}$$

(This example shows a different way of working the problem)

PREDICTING SIGN FOR ΔG

This example is using the free energy equation:

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

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TABLE 18.3

Predicting the Sign of ΔG Using Equation 18.11 and the Signs of ΔH and ΔS

When ΔH Is	And ΔS Is	ΔG Will Be	And the Process Is	Example
Negative	Positive	Negative	Always spontaneous	$2\text{H}_2\text{O}_2(aq) \longrightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$
Positive	Negative	Positive	Always nonspontaneous	$3\text{O}_2(s) \longrightarrow 2\text{O}_3(g)$
Negative	Negative	Negative when $T\Delta S < \Delta H$ Positive when $T\Delta S > \Delta H$	Spontaneous at low T Nonspontaneous at high T	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(s)$ (freezing of water)
Positive	Positive	Negative when $T\Delta S > \Delta H$ Positive when $T\Delta S < \Delta H$	Spontaneous at high T Nonspontaneous at low T	$2\text{HgO}(s) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$

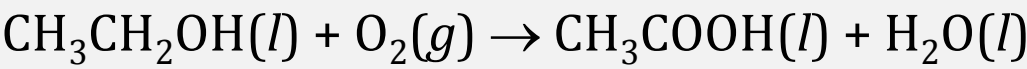
STANDARD FREE ENERGY

- The standard free energy of formation is the free-energy change that occurs when 1 mol of substance is formed from its elements in their standard states at 1 atm and at a specified temperature, usually 25°C.
- The corresponding reaction for the standard free energy of formation is the same as that for standard enthalpy of formation, ΔH_f° .
- To find the standard free energy change for a reaction where n = moles:

$$\Delta G^\circ = \sum n\Delta G^\circ (\text{products}) - \sum n\Delta G^\circ (\text{reactants})$$

EXAMPLE: STANDARD FREE ENERGY

Calculate the free-energy change, ΔG° , for the oxidation of ethyl alcohol to acetic acid using standard free energies of formation.



Solution:

	$\text{CH}_3\text{CH}_2\text{OH}(l)$	$+$	$\text{O}_2(g)$	$\rightarrow$	$\text{CH}_3\text{COOH}(l)$	$+$	$\text{H}_2\text{O}(l)$
$\Delta G_f^\circ, \text{kJ/mol}$	$-174.8 \times (1)$		$0 \times (1)$		$-392.5 \times (1)$		$-237.2 \times (1)$
$n\Delta G_f^\circ, \text{kJ}$	<u>-174.8</u>	<u>0</u>			<u>-392.5</u>		<u>-237.2</u>
(products – reactants)	-174.8 kJ				-629.7 kJ		$= \Delta G^\circ = -454.9 \text{ kJ}$

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