

Ch 17 Spontaneity of Reaction

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The goal of this chapter is to answer a basic question: Will a given reaction occur “by itself” at a particular temperature and pressure, without exertion of any outside force ?

↓

Is the reaction spontaneous ?

↓

To develop a general criterion for spontaneity, we will apply the principles of thermodynamics, the science that deals with heat and energy effects.

↓

Three different thermodynamic functions are of value in analyzing spontaneity.

1. ΔH , the change in enthalpy; **a negative value of ΔH** tends to make a reaction spontaneous.
2. ΔS , the change in entropy; **a positive value of ΔS** tends to make a reaction spontaneous.
3. ΔG , the change in free energy, **a reaction at constant temperature and pressure will be spontaneous if ΔG is negative**, no ifs, ands, or buts.

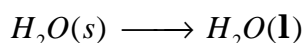
The free energy change, ΔG , can be also used to:

- g Determine the effect of temperature, pressure, and concentration on reaction spontaneity. (Ch. 17-5)
- g Calculate the equilibrium constant for a reaction. (Ch. 17-6)
- g Determine whether coupled reaction will be spontaneous. (Ch. 17-7)

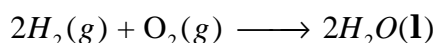
§ 17-1 Spontaneous Processes

Spontaneous process; for example:

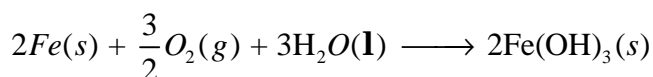
- g An ice cube melts when added to a glass of water at room temperature.



- g A mixture of hydrogen and oxygen burns if ignited by a spark.



g An iron (steel) tool exposed to moist air rusts.



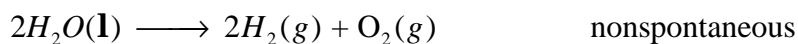
↓

These three reactions are spontaneous at 25 °C and 1 atm.

↓

The word “spontaneous” does not imply anything about how rapidly a reaction occurs. ⇒ reaction rate.

If a reaction is spontaneous under a given set of conditions, the reverse reaction must be nonspontaneous.



↓

However, it is often possible to bring about a nonspontaneous reaction by supplying energy in the form of work.

↓

Electrolysis can be used to decompose water to elements.

↓

To do this, electrical energy must be furnished, perhaps from a storage battery.

↓

A spontaneous process is one that moves the reaction toward equilibrium. A nonspontaneous process is moves the system away from equilibrium.

§ The energy factor ⇒ ΔH

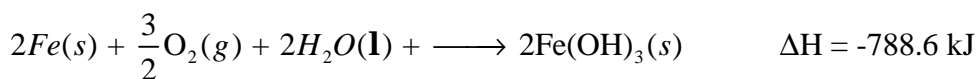
Many spontaneous process proceed with a decrease of energy.

↓

One might guess that spontaneous reactions would be exothermic ($\Delta H < 0$). ⇒ proposed by P.M. Berthelot.

↓

Nearly all exothermic chemical reactions are spontaneous at 25 °C and 1 atm. For example:



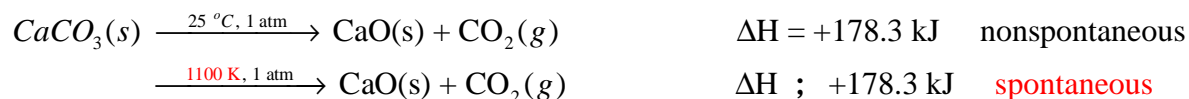
↓

On the other hand, the simple rule **fails** for many familiar phase changes.



The process is not an exothermic, but it takes place spontaneously at 1atm above 0 °C .

Endothermic reactions that are nonspontaneous at room temperature **often become spontaneous when the temperature is raised**. For example, the decomposition of the limestone.



↓

The endothermic reactions becomes spontaneous at high temperatures, despite that ΔH is positive.

ΔH is nearly independent of temperature (for this reaction).

§ The randomness factor $\Rightarrow \Delta S$

The direction of a spontaneous change is not always determined by the tendency for a system to go to a state of lower energy.

↓

Nature tends to move spontaneously **from a state of lower probability to one of higher probability**.

↓

Fig. 17-2 **the system has gone from a highly ordered state** (all the H_2 molecules on the left, all the N_2 molecules on the right) **to a more disordered, or random state** in which the molecules are distributed evenly between two bulbs.

↓

In general, nature tends to move spontaneously from more ordered to

more random states.

§ 17-2 Entropy, S

Entropy is often described as a measure of disorder or randomness.

↓

Boltzmann Relationships:

The absolute entropy S of the system is proportional to the natural logarithm of the possible combinations.

$$S = k \ln \Omega$$

Ω : the number of possible *combinations*.

k : proportional constant, "Boltzmann constant"

$$k = \frac{R}{N_a} ; 1.381 \times 10^{-23} \text{ J/K}$$

↓

An increase in the number of possible microstates (i.e., disorder) results in an increase of entropy.

↓

In general, the more random the state, the larger the number of its possible microstates, the more probable the state, thus the greater its entropy.

Entropy is a state property. That is, the entropy depends only on the state of a system, not on its history. The entropy change is determined by the entropies of the final and the initial states, not on the path followed from one state to another.

$$\Delta S = S_{final} - S_{initial}$$

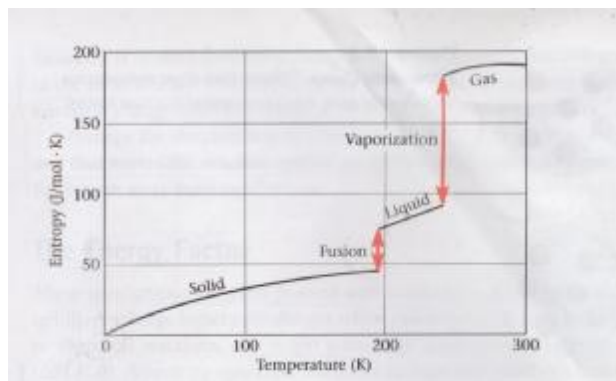


Fig. 17-4: Molar entropy of ammonia as a function of temperature.

Several factors influence the amount of entropy:

g A liquid has a higher entropy than the solid from which it is formed.

$$S(\mathbf{l}) > S(\mathbf{s})$$

$S(\mathbf{l})$: molecules can occupy many more positions as they move away from the lattice.

$S(\mathbf{s})$: molecules are confined to fixed position.

g A gas has a higher entropy than the liquid from which it is formed.

$$S(\mathbf{g}) > S(\mathbf{l})$$

g Increasing the temperature of a substance increase its entropy.

$$T \uparrow \Rightarrow S \uparrow$$

The third law of thermodynamics:

Absolute entropy approaches zero as the absolute temperature approaches zero.

g Melting and vaporization are accompanied by relatively large increase in entropy.

Ex. 17.1: Predict whether ΔS is positive or negative for each of the following processes:

a). taking dry ice from a freezer where its temperature is $-80\text{ }^{\circ}\text{C}$ and allowing it to warm to room temperature.

b). dissolving bromine in hexane.

c). condensing gaseous bromine to liquid bromine.

Ans:

a). $T \uparrow \Rightarrow S \uparrow \quad \therefore \Delta S \uparrow$

b). **Q** more random $S \uparrow \Rightarrow \Delta S > 0$

c). $S(\mathbf{g}) > S(\mathbf{l}) \quad \therefore \mathbf{g} \rightarrow \mathbf{l} \quad \Delta S \downarrow \Rightarrow \Delta S < 0$

§ Standard molar entropies, S°

The entropy of a substance, unlike its enthalpy, can be evaluated directly.



The only state property which has the absolute value.

g elements have nonzero standard entropies.

g standard molar entropies of pure substance (elements and compounds) are always positive quantities. ($S^\circ > 0$)

g aqueous ions may have negative values. Ex: $S^\circ_{F^-(aq)} = -13.8 \text{ J/mol} \cdot \text{K}$

Defined: $S^\circ_{H^+(aq)} = 0$

Among substances of similar structure and physical state, entropy usually increases with molar mass.

Ex:

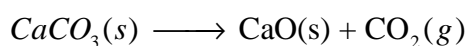
$CH_4(g)$	$S^\circ = 186.2 \text{ J/mol} \cdot \text{K}$
$C_2H_6(g)$	$S^\circ = 229.5 \text{ J/mol} \cdot \text{K}$
$C_3H_8(g)$	$S^\circ = 269.9 \text{ J/mol} \cdot \text{K}$

§ ΔS° for reactions

ΔS° , the standard entropy change, for reactions can be determined as:

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}} \quad (17-1)$$

Ex: Consider the reaction, calculate ΔS° :



$$\begin{aligned} \Delta S^\circ &= \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}} \\ &= [1 \cdot S^\circ_{CaO(s)} + 1 \cdot S^\circ_{CO_2(g)}] - (1 \cdot S^\circ_{CaCO_3(s)}) \\ &= [1 \cdot 39.8 + 1 \cdot 213.6] - (1 \cdot 92.9) \\ &= +160.5 \text{ J/K} \end{aligned}$$

$$\text{Q } \Delta n_g = 1 - 0 = 1 \quad \therefore \Delta S^\circ > 0$$

↓

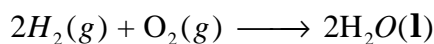
A reaction that results in an increase in the number of moles of gas is accompanied by an increase in entropy. Conversely, if the number of moles of gas decreases, ΔS° is a negative quantity.

↓

$$\Delta n_g \text{ "+"} \Rightarrow \Delta S^\circ > 0$$

$$\Delta n_g \text{ "-" } \Rightarrow \Delta S^\circ < 0$$

Ex.



$$\begin{aligned}\Delta S^\circ &= \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}} \\ &= (2 \cdot S^\circ_{H_2O(l)}) - [2 \cdot S^\circ_{H_2(g)} + 1 \cdot S^\circ_{O_2(g)}] \\ &= (2 \cdot 69.9) - [2 \cdot (130.6) + 1 \cdot (205.0)] \\ &= -326.4 \text{ J/K}\end{aligned}$$

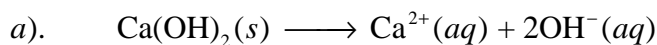
$$\Delta n_g = 0 - (2 + 1) = -3 \quad \text{"-"} \Rightarrow \Delta S^\circ < 0$$

Ex. 17.2: Calculate ΔS° for

a). dissolving one mole of calcium hydroxide in water.

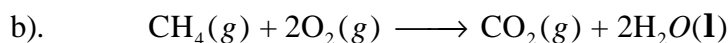
b). the combustion of one gram of methane to form carbon dioxide and liquid water.

Ans:



$$\Delta S^\circ : \quad +83.4 \quad \quad -53.1 \quad \quad -10.8 \text{ J/K}$$

$$\begin{aligned}\Delta S^\circ &= [1 \cdot S^\circ_{Ca^{2+}(aq)} + 2 \cdot S^\circ_{OH^-(aq)}] - (1 \cdot S^\circ_{Ca(OH)_2(aq)}) \\ &= [1 \cdot (-53.1) + 2 \cdot (-10.8)] - (1 \cdot 83.40) \\ &= -158.1 \text{ J/K} < 0 \quad \therefore \text{nonspontaneous}\end{aligned}$$



$$\Delta S^\circ : \quad +186.2 \quad +205.0 \quad \quad +213.6 \quad +69.9$$

$$\begin{aligned}\Delta S^\circ &= [1 \cdot S^\circ_{CO_2(g)} + 2 \cdot S^\circ_{H_2O(l)}] - [1 \cdot S^\circ_{CH_4(g)} + 2 \cdot S^\circ_{O_2(g)}] \\ &= [1 \cdot 213.6 + 2 \cdot 69.9] - [1 \cdot 186.2 + 2 \cdot 205.0] \\ &= -242.8 \text{ J/K} \quad \text{for the combustion of one mole of } CH_4(g)\end{aligned}$$

For the combustion of one gram of $CH_4(g)$ is:

$$\frac{1.00}{16.04} \cdot (-242.8) = -15.14 \text{ J/K}$$

§ The second law of thermodynamics:

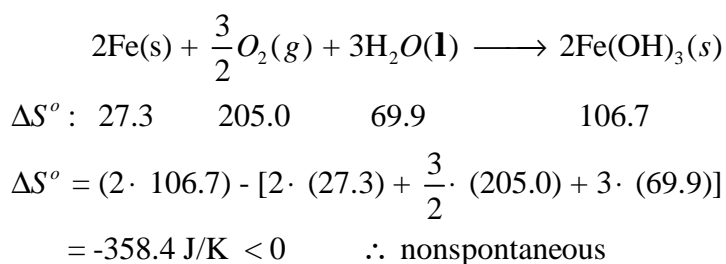
The relationship between entropy and spontaneity can be expressed through a basic principle of nature known as the second law of thermodynamics.



For an isolated system, if a spontaneous change occurs, it occurs with a concurrent increase in the entropy of the system.

$$\Delta S_{\text{universe}} = (\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}) > 0 \quad \text{spontaneous system}$$

For many spontaneous processes, the entropy change for the system is negative quantity. Consider, for example, the rusting of iron, a spontaneous process:



↓

All the law requires is that the entropy change of the surroundings be greater than 358.4 J/K, so that $\Delta S_{\text{universe}} > 0$.

↓

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

$$= (-358.4) + \Delta S_{\text{surroundings}} > 0$$

$$\Rightarrow \Delta S_{\text{surroundings}} > 358.4 \text{ J/K}$$

↓

The calculate the entropy change for the surroundings is not easy.

↓

We deals only with the thermodynamic properties of chemical systems.

§ 17-3 Free Energy, G

To put the enthalpy and the entropy together in such a way as to arrive at a single function whose sign will determine whether a reaction is spontaneous.

↓

J. W. Gibbs introduced a new quantity.

↓

Gibbs free energy, G. $G = H - TS$

↓

For a reaction taking place at constant pressure and temperature, ΔG represents that portion of the total energy change that is available (i.e., “free”) to do useful work. For example, ΔG for a reaction is -270 kJ, it is possible to obtain 270 kJ of useful work from the reaction. Conversely, if ΔG is +270 kJ, at least that much energy in the form of work must be supplied to

make the reaction take place.



G is a state property.



ΔG for a reaction depends only on the nature of products and reactants and the conditions (temperature, pressure, and concentration).

- g If ΔG is negative, the reaction is spontaneous.
- g If ΔG is positive, the reaction will not take place spontaneously. Instead, the reverse reaction will be spontaneous.
- g If ΔG is 0, the system is at equilibrium; there is no tendency for reaction to occur in either direction.

ΔG is a measure of the “driving force of a reaction”. Reactions, at constant pressure and temperature, go in such a direction as to decrease the free energy of the system.

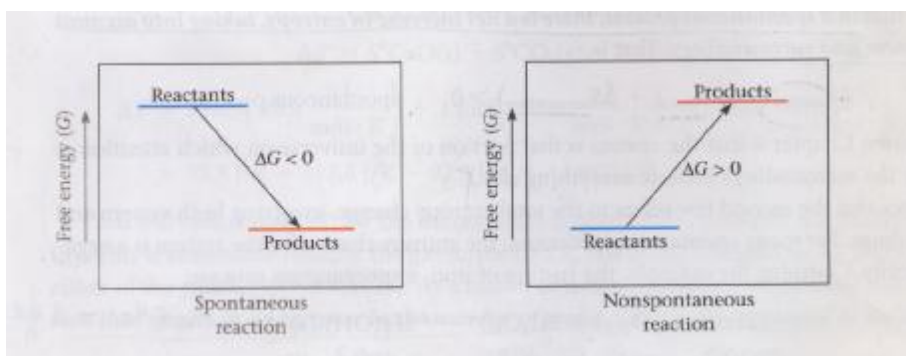


Fig. 17.5. Sign of free energy and spontaneity.

- g If the products at the specific conditions of temperature, pressure, and concentration have a lower free energy than the reactants ($G_{\text{products}} < G_{\text{reactants}} \Rightarrow \Delta G < 0$), the forward reaction will occur.
- g If the reverse is true ($G_{\text{reactants}} < G_{\text{products}} \Rightarrow \Delta G > 0$), the reverse reaction is spontaneous.
- g If $G_{\text{products}} = G_{\text{reactants}} (\Rightarrow \Delta G = 0)$ there is no driving force to make the reaction go in either direction.

§ Relation among ΔG , ΔH , and ΔS

Gibbs-Helmholtz equation: $\Delta G = \Delta H - T\Delta S$ at constant temperature.

Two factors tend to make ΔG negative and hence lead to a spontaneous reaction:

1. A negative value of ΔH :

Exothermic reaction ($\Delta H < 0$) tend to be spontaneous. On the molecule level, this means that there will be a tendency to form “strong” bonds at the expense of “weak” ones.

2. A positive value of ΔS :

$\Delta S > 0 \Rightarrow -T\Delta S < 0$. Hence there will be a tendency for a reaction to be spontaneous if the products are less ordered than the reactants.

§ 17-4 Standard Free Energy Change, ΔG°

Standard conditions: $T = 25^\circ\text{C}$

Gas: partial pressure = 1 atm.

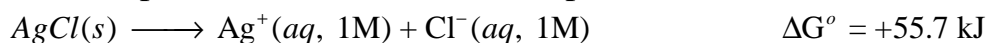
Molar concentration of ions or molecules in solution = 1 M.

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

1. If ΔG° is negative, the reaction is spontaneous at standard conditions.



2. If ΔG° is positive, the reaction is nonspontaneous at standard conditions.



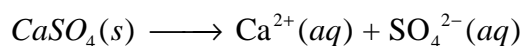
The reverse reaction is spontaneous.

3. If ΔG° is 0, the system is at equilibrium at standard conditions.



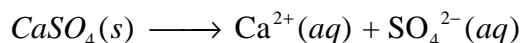
§ Calculation of ΔG° at 25°C ; free energy of formation

Ex. 17.3: Calcium sulfate, CaSO_4 , is used as a drying agent and sold under trade name Drierite. For the reaction:



Calculate a). ΔH° b). ΔS° c). ΔG° at 25 °C.

Ans:



$$\Delta H_f^\circ: \quad -1434.1 \qquad -542.8 \qquad -909.3 \text{ kJ}$$

$$S^\circ: \quad -106.7 \qquad -53.1 \qquad +20.1$$

$$\begin{aligned} \text{a). } \Delta H^\circ &= \sum \Delta H_{f, \text{products}}^\circ - \sum \Delta H_{f, \text{reactants}}^\circ \\ &= [1 \cdot \Delta H_{f, \text{Ca}^{2+}(aq)}^\circ + 1 \cdot \Delta H_{f, \text{SO}_4^{2-}(aq)}^\circ] - (1 \cdot \Delta H_{f, \text{CaSO}_4(s)}^\circ) \\ &= [1 \cdot (-542.8) + 1 \cdot (-909.3)] - [1 \cdot (-1434.1)] \\ &= -18.0 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \text{b). } \Delta S^\circ &= \sum S_{\text{products}}^\circ - \sum S_{\text{reactants}}^\circ \\ &= [1 \cdot (-53.1) + 1 \cdot (+20.1)] - [1 \cdot (-106.7)] \\ &= -139.7 \text{ J/K} = \mathbf{-0.1397 \text{ kJ/K}} \end{aligned}$$

$$\begin{aligned} \text{c). } \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= (-18.0) - 298 \cdot (-0.1397) \\ &= +23.6 \text{ kJ} \end{aligned}$$

§ Standard free energy of formation, ΔG_f°

ΔG_f° is analogous to the enthalpy of formation, ΔH_f° .

It is defined as the free energy per mole when a compound is formed from the elements in their stable states at 1 atm.

For most compounds, ΔG_f° is a negative quantity, which means that the compound can be formed spontaneously from the elements. This is true for water:



A few compounds, including acetylene, have positive free energies of formation ($\Delta G_{f, \text{C}_2\text{H}_2(l)}^\circ = +209.2 \text{ kJ/mol}$). These compounds cannot be made from the elements at ordinary temperatures and pressures; **they are potentially unstable with respect to the elements**. In the case of acetylene, the reaction:



occurs with explosive violent unless special precaution are taken.

$$\Delta G_{\text{reaction}}^{\circ} = \sum \Delta G_{f,\text{products}}^{\circ} - \sum \Delta G_{f,\text{reactants}}^{\circ} \quad (17-3)$$

$\Delta G_{\text{reaction}}^{\circ}$ is valid only at the temperature at which ΔG_f° data are tabulated, in this case 25 °C. ΔG° varies considerably with temperature, so this approach is not even approximately valid at other temperature.

Ex. 17.4: Using ΔG_f° values from Appendix 1, calculate the standard free energy change at 25°C for the reaction referred to in Example 17.3.

Ans:

$$\begin{aligned} \text{CaSO}_4(s) &\longrightarrow \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq) \\ \Delta G_f^{\circ}: & -1321.8 \qquad -553.6 \qquad -744.5 \text{ kJ} \\ \Delta G^{\circ} &= \sum \Delta G_{f,\text{products}}^{\circ} - \sum \Delta G_{f,\text{reactants}}^{\circ} \\ &= [1 \cdot \Delta G_{f,\text{Ca}^{2+}(aq)}^{\circ} + 1 \cdot \Delta G_{f,\text{SO}_4^{2-}(aq)}^{\circ}] - (1 \cdot \Delta G_{f,\text{CaSO}_4(s)}^{\circ}) \\ &= [1 \cdot (-553.6) + 1 \cdot (-774.5)] - [1 \cdot (-1321.8)] \\ &= +23.7 \text{ kJ} \approx \text{Ex. 17.3: } +23.6 \text{ kJ} \end{aligned}$$

§ Calculation of ΔG° at other temperature, ΔG_T

To a good degree of approximation, the temperature variation of ΔH° and ΔS° can be neglected. $\therefore \Delta H$ and ΔS always change in the same direction as the temperature changes.

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

At temperatures other than 25°C, you need only change the value of T.

Ex. 17.5: Iron, a large component of steel, is obtained by reducing iron (III) oxide (present in hematite ore) with hydrogen in a blast furnace. Steam is a byproduct of the reaction. Calculate ΔG° at 230°C for the reduction of one mole of Fe_2O_3 .

Ans:

$$\begin{aligned} \text{Fe}_2\text{O}_3(s) + 3\text{H}_2(g) &\longrightarrow 2\text{Fe}(s) + 3\text{H}_2\text{O}(g) \\ \Delta H_f^{\circ}: & -824.2 \quad 0 \quad 0 \quad -241.8 \text{ kJ} \\ S^{\circ}: & 87.4 \quad 130.6 \quad 27.3 \quad 188.7 \text{ J/K} \end{aligned}$$

$$\begin{aligned}\Delta H^\circ &= \sum \Delta H_{f, products}^\circ - \sum \Delta H_{f, reactants}^\circ \\ &= (3 \cdot \Delta H_{f, H_2O(1)}^\circ) - (1 \cdot \Delta H_{f, Fe_2O_3(s)}^\circ) \\ &= [3 \cdot (-241.8)] - [1 \cdot (-824.2)] \\ &= +98.8 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \sum S_{products}^\circ - \sum S_{reactants}^\circ \\ &= [2 \cdot (27.3) + 3 \cdot (188.7)] - [1 \cdot (87.4) + 3 \cdot (130.6)] \\ &= +141.5 \text{ J/K} = \mathbf{+0.1415 \text{ kJ/K}}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= (+98.8) - 503 \cdot (+0.1415) \\ &= +27.6 \text{ kJ}\end{aligned}$$

ΔG° , unlike ΔH° and ΔS° , is strongly dependent on temperature. This comes about, of course, because of the T is in the Gibbs-Helmholtz equation:

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

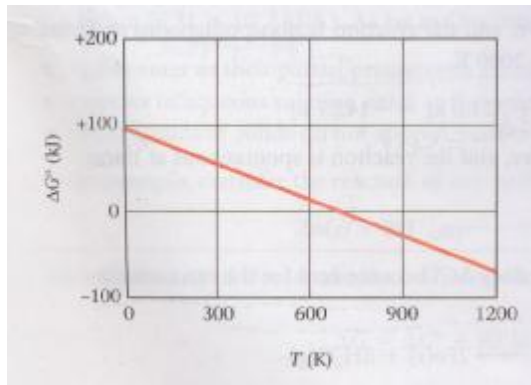


Fig. 17.6: Variation of ΔG° with T.

A plot of ΔG° versus T, should be linear, with a slope of $-\Delta S^\circ$ and a y-intercept (at 0 K) of ΔH° .

§ 17-5 Effect of Temperature, Pressure and Concentration on Reaction Spontaneity

A change in reaction conditions can, and often does, change the direction in which a reaction occurs spontaneously.

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

is readily applied to deduce the effect of temperature on reaction spontaneity.

§ Temperature

Table 17-2: Effect of temperature on reaction spontaneity.

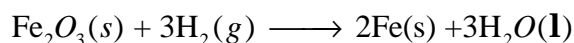
Case	ΔH°	ΔS°	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$	Remarks
I	-	+	always -	Spontaneous at all T; reverse reaction always nonspontaneous.
II	+	-	always +	Nonspontaneous at all T.
III	+	+	+ at low T - at high T	Nonspontaneous at low T, becomes spontaneous at high T.
IV	-	-	- at low T + at high T	Spontaneous at low T, becomes nonspontaneous as T is raised.

If ΔH° and ΔS° have opposite signs (case I and II), it is impossible to reverse the direction for spontaneity by a change in temperature alone.

Case III and IV, ΔH° and ΔS° have the same sign, at low temperatures, ΔH° predominates, and the exothermic reaction, which may be either the forward or the reverse reaction, occurs. As the temperature raises, the quantity $T\Delta S^\circ$ increase in magnitude and eventually exceeds ΔH° . At high temperatures, the reaction that leads to an increase in entropy occurs.

In most case, 25°C is a “low” temperature, at least at a pressure of 1 atm. This explains why exothermic reactions are usually spontaneous at room temperature and atmospheric pressure.

Ex. 17.6: At what temperature does ΔG° becomes zero for the reaction consider in Ex.17.5.



Ans:

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

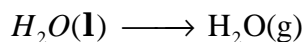
$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{98.8 \text{ kJ}}{0.1415 \text{ kJ/K}} = 698 \text{ K}$$

if $T > 698 \text{ K} \Rightarrow \Delta G^\circ < 0 \Rightarrow$ spontaneous reaction

We can say that the equation $T = \frac{\Delta H^\circ}{\Delta S^\circ}$ allows us to calculate the temperature at which a chemical or physical change is at equilibrium at 1 atm

atmosphere.

For example:



$\Delta H^\circ = +40.7 \text{ kJ}$; $\Delta S^\circ = +0.109 \text{ kJ/K}$. The temperature at which ΔG° is zero is:

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{40.7 \text{ kJ}}{0.109 \text{ kJ/K}} = 3733 \text{ K} = 100^\circ \text{C}$$

This is, of course, the normal boiling point of water (the temperature at which liquid water is at equilibrium with vapor at 1 atm).

§ Pressure and Concentration

It is possible to write a general relation for the free energy change, ΔG , valid under any conditions.

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (17-4)$$

Q: reaction quotient ----- Ch. 12

R: $8.31 \times 10^{-3} \text{ kJ/K}$

Q has the same mathematical form as the equilibrium constant, K; the difference is that the terms that appear in Q are arbitrary, initial pressures or concentrations rather than equilibrium values.

g Gas enter as their partial pressures (atm) in atmosphere.

g Species in aqueous solution enter as their molar concentrations.

g **Pure liquids or solids do not appear; neither does solvent in a dilute solution.**

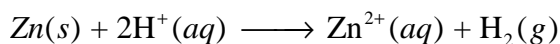
**平衡常數:

*(g): 以分壓(atm)計算

*(s)及(l)不列入計算, solvent for a solution 也不列入計算

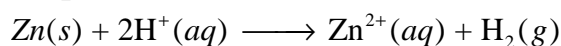
*(aq):以 M 計算

Ex: Consider the reaction of zinc with strong acid:



$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q \\ &= \Delta G^\circ + RT \ln \frac{[\text{Zn}^{2+}] \cdot P_{\text{H}_2}}{[\text{H}^+]^2}\end{aligned}$$

Ex. 17.7: When zinc is dissolved in a strong acid, zinc ions and hydrogen gas are produced.



At 25 °C, calculate.

- ΔG°
- ΔG when $P_{\text{H}_2} = 750$ mmHg, $\text{Zn}^{2+} = 0.10$ M, $[\text{H}^+] = 1.0 \times 10^{-4}$ M.
- The pH when $\Delta G = -100.0$ kJ, $P_{\text{H}_2} = 0.933$ atm, $[\text{Zn}^{2+}] = 0.220$ M and the mass of Zn is 155g.

Ans:

$$\begin{aligned}a). \Delta G^\circ &= [1 \cdot \Delta G_{f, \text{Zn}^{2+}(aq)}^\circ + 1 \cdot \Delta G_{f, \text{H}_2(g)}^\circ] - [1 \cdot \Delta G_{f, \text{Zn}(s)}^\circ + 1 \cdot \Delta G_{f, \text{H}^+(aq)}^\circ] \\ &= \Delta G_{f, \text{Zn}^{2+}(aq)}^\circ \\ &= -147.1 \text{ kJ}\end{aligned}$$

$$\begin{aligned}b). \Delta G &= \Delta G^\circ + RT \ln \frac{[\text{Zn}^{2+}] \cdot P_{\text{H}_2}}{[\text{H}^+]^2} \\ &= -147.1 + 8.31 \times 10^{-3} \cdot 298 \cdot \ln \frac{(0.10) \cdot (750/760)}{(1.0 \times 10^{-4})^2} \\ &= -147.1 + 39.9 = -107.2 \text{ kJ}\end{aligned}$$

$$c). \text{pH} = -\log[\text{H}^+]$$

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln \frac{[\text{Zn}^{2+}] \cdot P_{\text{H}_2}}{[\text{H}^+]^2} \\ -100.0 &= -147.1 + 8.31 \times 10^{-3} \cdot 298 \cdot \ln \frac{(0.22) \cdot (0.933)}{[\text{H}^+]^2}\end{aligned}$$

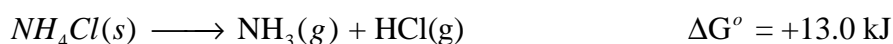
$$\ln \frac{0.205}{[\text{H}^+]^2} = 19.0$$

$$[\text{H}^+] = 3.39 \times 10^{-5}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(3.39 \times 10^{-5}) = 4.47$$

Changes in pressure and/or concentration can have considerable effect on ΔG .

Ex: The following reaction at 300 °C .



ΔG° “+” implies that ammonium chloride will not decompose at 300 °C to give NH_3 and HCl , both at 1 atm pressure. However, notice what

happens if $P_{\text{NH}_3} = P_{\text{HCl}} = 0.10 \text{ atm}$.

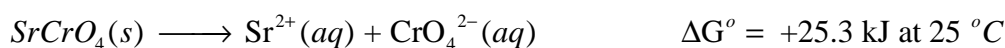
Ans:

$$Q = P_{\text{NH}_3} \cdot P_{\text{HCl}} = (0.10) \cdot (0.10) = 0.0100$$

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ &= (+13.0) + 8.31 \times 10^{-3} \cdot 573 \cdot \ln(0.0100) \\ &= (+13.0) + (-21.9) \\ &= -8.9 \text{ kJ} \end{aligned}$$

This means that NH_3 and HCl can be formed, each at 0.10 atm pressure, by heating NH_4Cl to 300 °C .

Ex: A change in concentration:



$$[\text{Sr}^{2+}] = 1.00 \text{ M}, [\text{CrO}_4^{2-}] = 1.00 \text{ M at } 25^\circ \text{C} \Rightarrow \Delta G^\circ = +25.3 \text{ kJ} \Rightarrow \text{nonspontaneous}$$

$$\text{if } [\text{Sr}^{2+}] = 0.0010 \text{ M}, [\text{CrO}_4^{2-}] = 0.0010 \text{ M}$$

$$\begin{aligned} \Rightarrow \Delta G &= \Delta G^\circ + RT \ln Q \\ &= (+23.3) + 8.31 \times 10^{-3} \cdot 298 \cdot \ln(0.00100)^2 \\ &= (+23.3) + (-34.2) \\ &= -8.9 \text{ kJ} \Rightarrow \text{spontaneous reaction} \end{aligned}$$

$$\text{if } [\text{Sr}^{2+}] = 0.0060 \text{ M}, [\text{CrO}_4^{2-}] = 0.0060 \text{ M}$$

$$\begin{aligned} \Rightarrow \Delta G &= \Delta G^\circ + RT \ln Q \\ &= (+25.3) + 8.31 \times 10^{-3} \cdot 298 \cdot \ln(0.0060)^2 \\ &= (+25.3) + (-25.3) \\ &= 0 \text{ kJ} \Rightarrow \text{at equilibrium} \end{aligned}$$

§ 17-6 The Free Energy Change and The Equilibrium Constant

Reaction spontaneity related to:

1. $\Delta G^\circ < 0 \Rightarrow$ spontaneous.
2. K (equilibrium constant), $K > 1 \Rightarrow$ spontaneous.

↓

ΔG° and K are related.

↓

$$\Delta G = \Delta G^\circ + RT \ln Q$$

When equilibrium is established $Q = K$ and $\Delta G = 0$.

$$\Rightarrow 0 = \Delta G^\circ + RT \ln K$$

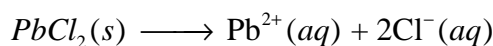
$$\therefore \Delta G^\circ = -RT \ln K \quad (17-5)$$

The expression for K, gases enter as their partial pressures in atmospheres and ions or molecules in solution as their molarities (M).

Ex. 17-8: Using ΔG_f° tables in Appendix 1, calculate the solubility product

constant K_{sp} for $PbCl_2$ at $25^\circ C$.

Ans:



$$\Delta G^\circ = [1 \cdot \Delta G_{f, Pb^{2+}(aq)}^\circ + 2 \cdot \Delta G_{f, Cl^-(aq)}^\circ] - (1 \cdot \Delta G_{f, PbCl_2(s)}^\circ)$$

$$= [1 \cdot (-24.4) + 2 \cdot (-131.2)] - [1 \cdot (-314.1)]$$

$$= +27.3 \text{ kJ}$$

$$\Delta G^\circ = -RT \ln K$$

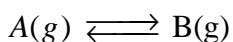
$$27.3 = -8.31 \times 10^{-3} \cdot 298 \cdot \ln \frac{[Pb^{2+}] \cdot [Cl^-]^2}{1}$$

$$27.3 = -8.31 \times 10^{-3} \cdot 298 \cdot \ln K_{sp}$$

$$\ln K_{sp} = \frac{27.3}{-2.42} = -11.0$$

$$K_{sp} = e^{-11.0} = 1.67 \times 10^{-5}$$

The relationship $\Delta G^\circ = -RT \ln K$ allows us to relate the standard free energy change to the extent of reaction. Consider:



$$\Delta G^\circ = 20 \text{ kJ}$$

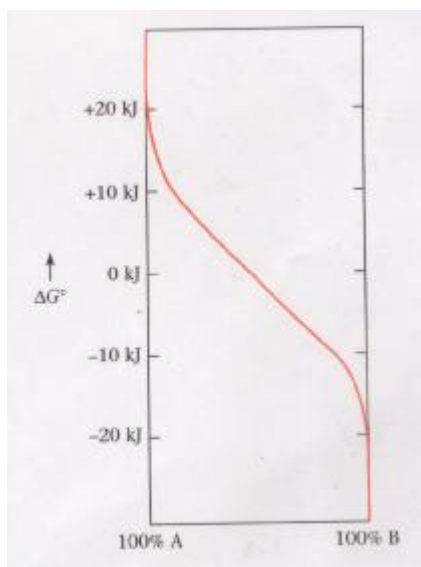


Fig. 17.8: Dependence of extent of reaction on the value of ΔG° for the general system $A(g) \rightleftharpoons B(g)$.

if $\Delta G^\circ \approx 20 \text{ kJ}$, the reaction does not occur \Rightarrow 100% A

if $\Delta G^\circ \leq -20 \text{ kJ}$, the equilibrium constant is so large that virtually all of A converted to B \Rightarrow 100% B.

if $-20 \text{ kJ} < \Delta G^\circ < 20 \text{ kJ}$ will the equilibrium mixture contain appreciable amount of both A and B.

if $\Delta G^\circ = 0$, $K = 1 \Rightarrow$ equal amount A and B.

§ 17-7 Additivity of Free Energy Change; Coupled Reaction

Free energy changes for reactions, like enthalpy or entropy, are additive. That is:

If

$$\text{Reaction 3} = \text{Reaction 1} + \text{Reaction 2}$$

Then

$$\Delta G_3 = \Delta G_1 + \Delta G_2$$

