

## 4.3: Day 29- Gibbs Free Energy, Chemical Equilibrium

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### Day 29: Gibbs Free Energy, Chemical Equilibrium

#### D29.1 Temperature Dependence of Gibbs Free Energy

Whether a reaction is product-favored, that is, whether the reactants are converted to products under standard-state conditions, is reflected in the arithmetic sign of its  $\Delta_r G^\circ$ . This equation

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

shows that the sign of  $\Delta_r G^\circ$  depends on the signs of  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$ , and, in some cases, the absolute temperature (which can only have positive values). Four possibilities exist:

- Both  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  are positive**—an endothermic process with an increase in system entropy.  $\Delta_r G^\circ$  is negative if  $T\Delta_r S^\circ > \Delta_r H^\circ$ , and positive if  $T\Delta_r S^\circ < \Delta_r H^\circ$ . Such a process is *product-favored at high temperatures and reactant-favored at low temperatures*.
- Both  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  are negative**—an exothermic process with a decrease in system entropy.  $\Delta_r G^\circ$  is negative if  $|T\Delta_r S^\circ| < |\Delta_r H^\circ|$  and positive if  $|T\Delta_r S^\circ| > |\Delta_r H^\circ|$ . Such a process is *product-favored at low temperatures and reactant-favored at high temperatures*. (Remember that  $|T\Delta_r S^\circ|$  represents the magnitude of  $T\Delta_r S^\circ$ , ignoring mathematical sign.)
- $\Delta_r H^\circ$  is positive and  $\Delta_r S^\circ$  is negative**—an endothermic process that with a decrease in system entropy.  $\Delta_r G^\circ$  is positive regardless of the temperature. Such a process is *reactant-favored at all temperatures*.
- $\Delta_r H^\circ$  is negative and  $\Delta_r S^\circ$  is positive**—an exothermic process with an increase in system entropy.  $\Delta_r G^\circ$  is negative regardless of the temperature. Such a process is *product-favored at all temperatures*.

These four scenarios are summarized in Figure 1.

	$\Delta_r H^\circ > 0$ (endothermic)	$\Delta_r H^\circ < 0$ (exothermic)
$\Delta_r S^\circ > 0$ (system entropy increase)	$\Delta_r G^\circ > 0$ at low temperatures $\Delta_r G^\circ < 0$ at high temperatures Product-favored at high temperatures	$\Delta_r G^\circ < 0$ at low temperatures $\Delta_r G^\circ < 0$ at high temperatures Product-favored at all temperatures
$\Delta_r S^\circ < 0$ (system entropy decrease)	$\Delta_r G^\circ > 0$ at low temperatures $\Delta_r G^\circ > 0$ at high temperatures Reactant-favored at all temperatures	$\Delta_r G^\circ < 0$ at low temperatures $\Delta_r G^\circ > 0$ at high temperatures Product-favored at low temperatures

**Figure 1.** There are four possible combinations of signs of  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$ . For two combinations, whether a process is reactant-favored or product-favored depends on temperature.

#### Activity 1: Temperature and Product-favored or Reactant-favored Reactions

Figure 2 illustrates the four scenarios graphically, where  $\Delta_r G^\circ$  is plotted versus temperature:

$\Delta_r G^\circ$	=	$-\Delta_r S^\circ(T)$	+	$\Delta_r H^\circ$
y	=	m(x)	+	b

**Figure 2.** These plots show the variation in  $\Delta_r G^\circ$  with temperature for the four possible combinations of arithmetic sign for  $\Delta_r G^\circ$ . Click on each “+” for more information.

For most reactions, neither  $\Delta_r H^\circ$  nor  $\Delta_r S^\circ$  change significantly as temperature changes. Thus, in Figure 2, the lines representing  $\Delta_r G^\circ$  are linear because the slope of each line ( $-\Delta_r S^\circ$ ) is the same at all temperatures. The orange and green plots (representing examples of scenario 1 and 2, respectively) cross from product-favored to reactant-favored (as reflected by the sign of  $\Delta_r G^\circ$ ) at a temperature that is characteristic of the specific process. This temperature is represented by the x-intercept, the value of  $T$  for which  $\Delta_r G^\circ$  is zero:

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

$$T_{\Delta_r G^\circ=0} = \frac{\Delta_r H^\circ}{\Delta_r S^\circ}$$

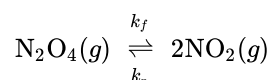
Hence, saying a process is product-favored at “high” or “low” temperatures is simply indicating whether the temperature is above or below  $T_{\Delta_r G^\circ=0}$ . These relative terms are reaction-specific, that is, what is a “high” temperature for one reaction may very well be a “low” temperature for another reaction.

## D29.2 Chemical Equilibrium

A chemical reaction is usually written with a single arrow, which suggests it proceeds in one direction, the direction of the arrow. But all chemical reactions are reversible, and both the forward and reverse reaction occur simultaneously. When reactions involve gases or solutions, where concentrations change as the reaction proceeds, the reaction eventually reaches a *dynamic* chemical equilibrium.

In a **chemical equilibrium**, *the forward and reverse reactions occur at the same rates, and the concentrations of products and reactants remain constant over time*. This implies that, if a reaction occurs in a closed system so that the products cannot escape, the reaction often does not yield 100% products. Instead, some reactants remain after the concentrations stop changing. At this point, when there is no further change in concentrations of reactants and products, we say the reaction is at equilibrium.

For example, when we place a sample of dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ , a colorless gas) in a glass vessel, the color becomes darker as  $\text{N}_2\text{O}_4$  is converted to nitrogen dioxide ( $\text{NO}_2$ , a red-brown gas) by the reaction:



### Activity 2: Reaction Energy Diagram

At the beginning of this reaction, there is pure  $\text{N}_2\text{O}_4$ . As soon as the forward reaction produces some  $\text{NO}_2$ , at rate  $= k_f[\text{N}_2\text{O}_4]_t$ , the reverse reaction begins to occur at rate  $= k_r[\text{NO}_2]_t^2$ , and  $\text{NO}_2$  starts to react to form  $\text{N}_2\text{O}_4$ . (The subscripts,  $t$ , indicate a time before equilibrium is reached.) As the reaction proceeds, the rate of the forward reaction decreases as  $[\text{N}_2\text{O}_4]_t$  decreases and the rate of the reverse reaction increases as  $[\text{NO}_2]_t$  increases. When the system reaches equilibrium, both  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  are present.

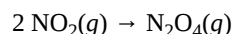
**Figure 3.** A container of  $\text{N}_2\text{O}_4(g)$  reacts toward equilibrium at  $75^\circ\text{C}$ . Colorless  $\text{N}_2\text{O}_4$  converts to brown  $\text{NO}_2$ . As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of  $\text{NO}_2$ . Once equilibrium has been reached, there is no further darkening of color.

At equilibrium,  $[\text{N}_2\text{O}_4]$  and  $[\text{NO}_2]$  no longer change over time because the rate of  $\text{NO}_2$  formation is exactly equal to the rate of  $\text{NO}_2$  consumption, and the rate of  $\text{N}_2\text{O}_4$  formation is exactly equal to the rate of  $\text{N}_2\text{O}_4$  consumption. *Chemical equilibrium is a dynamic process*: the numbers of reactant and product molecules remain constant, but the forward and reverse reactions do not stop.

We use the  $\rightleftharpoons$  arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. When we wish to speak about one particular aspect of a reversible reaction, we use a single arrow. For example, when the reaction in Figure 3 is at equilibrium, the rate of the forward reaction:



is equal to the rate of the reverse reaction:



An equilibrium can be established for a physical change as well as for a chemical reaction. For example:

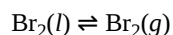


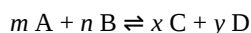
Figure 4 shows a sample of liquid  $\text{Br}_2$  at equilibrium with  $\text{Br}_2$  vapor in a closed container. When we pour liquid  $\text{Br}_2$  into an empty bottle in which there is no bromine vapor, some liquid evaporates: the amount of liquid decreases and the amount of vapor increases. If we seal the container so no vapor escapes, the amount of liquid and vapor will eventually stop changing; at that point an equilibrium between the liquid and the vapor has been established. If the container were not sealed, the bromine vapor would escape and no equilibrium would be reached.



**Figure 4.** Sample of bromine in a sealed glass tube. Liquid bromine is in the bottom of the tube with gaseous bromine above it.

### D29.3 Concentration Equilibrium Constants

A concentration **equilibrium constant** ( $K_c$ ) is a ratio of equilibrium concentrations of products and reactants that is constant for a given reaction at a given temperature. For example, consider this generic reversible reaction:

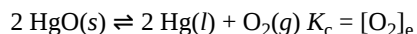


For this reaction, the concentration equilibrium constant,  $K_c$ , is:

$$K_c = \frac{[C]_e^x [D]_e^y}{[A]_e^m [B]_e^n}$$

This mathematical expression is called the equilibrium constant expression. The “[...]” expression indicates explicitly *equilibrium* concentration of a reactant or product.

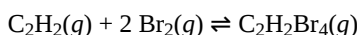
As a reaction approaches equilibrium, concentrations of reactants and products need to change until the rates of forward and reverse reactions are equal. Therefore, only substances whose concentrations can change as a reaction occurs are included in an equilibrium constant expression. For example, consider the following reaction at equilibrium:



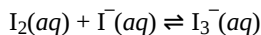
Because HgO is a pure solid, the number of HgO formula units in a given volume of HgO is the same throughout the reaction; it depends only on the density of HgO at the temperature of the reaction. Similarly, the number of Hg atoms per unit volume of pure Hg(l) is constant throughout the reaction. Thus, these concentrations are not included in the  $K_c$  expression. It is necessary for *some* HgO(s) and *some* Hg(l) to be present for the equilibrium to be maintained, but the quantity of each does not matter.

In general,  $K_c$  expressions do not contain terms for pure solids or pure liquids. In addition, for dilute solutions, the concentration of solvent remains constant throughout an equilibrium reaction and is also not included in the  $K_c$  expression, even though the solvent may appear in the reaction equation.

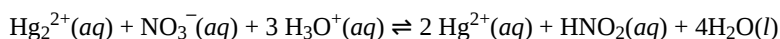
A **homogeneous equilibrium** is one in which *all of the reactants and products are present in a single phase*. Examples of homogeneous equilibria are reactions in the gas phase and reactions in liquid solutions. For example:



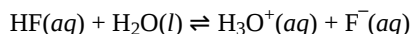
$$K_c = \frac{[\text{C}_2\text{H}_2\text{Br}_4]_e}{[\text{C}_2\text{H}_2]_e [\text{Br}_2]_e^2}$$



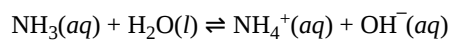
$$K_c = \frac{[\text{I}_3^-]_e}{[\text{I}_2]_e [\text{I}^-]_e}$$



$$K_c = \frac{[\text{Hg}^{2+}]_e^2 [\text{HNO}_2]_e}{[\text{Hg}_2^{2+}]_e [\text{NO}_3^-]_e [\text{H}_3\text{O}^+]_e^3}$$



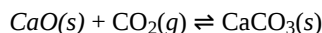
$$K_c = \frac{[\text{H}_3\text{O}^+]_e [\text{F}^-]_e}{[\text{HF}]_e}$$



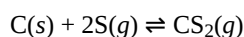
$$K_c = \frac{[\text{NH}_4^+]_e [\text{OH}^-]_e}{[\text{NH}_3]_e}$$

In the aqueous equilibrium systems,  $\text{H}_2\text{O}(l)$  is the solvent. Its concentration does not appear in the  $K_c$  expression.

A **heterogeneous equilibrium** is a system in which *reactants and products are found in two or more phases*. Some heterogeneous equilibria involve chemical changes, for example:

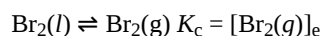


$$K_c = \frac{1}{[\text{CO}_2]_e}$$



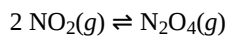
$$K_c = \frac{[\text{CS}_2]_e}{[\text{S}]_e^2}$$

Other heterogeneous equilibria involve phase changes, for example:

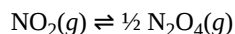


### Working with $K_c$

When all the coefficients in a balanced chemical equation are multiplied by some factor  $n$ , then the new  $K_c$  is the original  $K_c$  raised to the  $n^{\text{th}}$  power. For example:

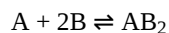


$$K_{c,1} = \frac{[\text{N}_2\text{O}_4]_e}{[\text{NO}_2]_e^2}$$

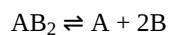


$$K_{c,2} = \frac{[\text{N}_2\text{O}_4]_e^{1/2}}{[\text{NO}_2]_e} = (K_{c,1})^{1/2}$$

When a reaction's direction is reversed, the  $K_c$  for the new reaction is the reciprocal (inverse) of the original reaction  $K_c$ . For example:

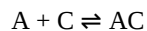


$$K_{c,1} = \frac{[\text{AB}_2]_e}{[\text{A}]_e [\text{B}]_e^2}$$

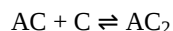


$$K_{c,2} = \frac{[\text{A}]_e [\text{B}]_e^2}{[\text{AB}_2]_e} = \frac{1}{K_{c,1}}$$

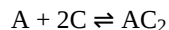
When two reactions occur sequentially to yield a new overall reaction, the  $K_c$  for the overall reaction is the product of the  $K_c$  values for the individual steps. For example:



$$K_{c,1} = \frac{[\text{AC}]_e}{[\text{A}]_e [\text{C}]_e}$$



$$K_{c,2} = \frac{[\text{AC}_2]_e}{[\text{AC}]_e[\text{C}]_e}$$



$$K_{c,3} = \frac{[\text{AC}_2]_e}{[\text{A}]_e[\text{C}]_e^2} = K_{c,1} \times K_{c,2}$$

## D29.4 Equilibrium Constant and Partial Pressure

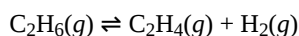
Reactions in which all reactants and products are in the gas phase are another class of homogeneous equilibria. In these cases, the partial pressure of each gas can be used instead of its concentration in the equilibrium constant equation. At constant temperature, the partial pressure of a gas is directly proportional to its molar concentration ( $c$ ), which is the amount of a substance (moles) per unit volume (liters):  $c = n/V$ . This proportionality of pressure and concentration can be derived from the ideal gas equation:

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) RT$$

$$P = cRT$$

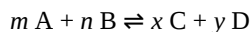
For an example, consider the following reaction:



We can write the equilibrium constant,  $K_p$ , using the equilibrium partial pressures of the gases, by following the same guidelines as for  $K_c$  expressions:

$$K_p = \frac{P_{\text{C}_2\text{H}_4} P_{\text{H}_2}}{P_{\text{C}_2\text{H}_6}}$$

The two equilibrium constants,  $K_c$  and  $K_p$ , are directly related to each other. For the generic gas-phase reaction:

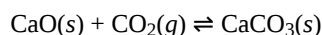


$$\begin{aligned} K_p &= \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n} \\ &= \frac{([\text{C}] \times RT)^x ([\text{D}] \times RT)^y}{([\text{A}] \times RT)^m ([\text{B}] \times RT)^n} \\ &= \frac{[\text{C}]^x [\text{D}]^y}{[\text{A}]^m [\text{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} \\ &= K_c (RT)^{(x+y) - (m+n)} \\ K_p &= K_c (RT)^{\Delta n} \end{aligned}$$

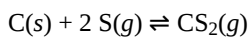
where  $\Delta n$  is the difference between the sum of the coefficients of the gaseous products and the sum of the coefficients of the gaseous reactants in the reaction (that is, the change in amount of gas between the reactants and the products).

Note that the gas constant,  $R$ , can be expressed in different units. Use the  $R$  value and associated units that match the partial pressure units used in the  $K_p$  expression.

For heterogeneous equilibria that involve gases, equilibrium constants can also be expressed using partial pressures instead of concentrations. Two examples are:



$$K_p = \frac{1}{P_{CO_2}}$$



$$K_p = \frac{P_{CS_2}}{(P_S)^2}$$

## D29.5 Calculations Involving Equilibrium Constants

One way to determine the value for an equilibrium constant is to measure the concentrations (or partial pressures) of all reactants and all products at equilibrium.

### Exercise 5: Calculating an Equilibrium Constant

Calculate the equilibrium constant  $K_c$  for the decomposition of  $PCl_5$  at 250 °C.



At equilibrium,  $[PCl_5]_e = 4.2 \times 10^{-5} \text{ M}$ ,  $[PCl_3]_e = 1.3 \times 10^{-2} \text{ M}$ ,  $[Cl_2]_e = 3.9 \times 10^{-3} \text{ M}$

A known equilibrium constant can be used to calculate an unknown equilibrium concentration, provided the equilibrium concentrations of all other reactants and products are known.

## D29.6 Equilibrium Constants and Product-favored Reactions

The magnitude of an equilibrium constant is a measure of the yield of a reaction when it reaches equilibrium. A very large value for  $K_c$  ( $K_c \gg 1$ ) indicates that product concentrations are much larger than reactant concentrations when equilibrium has been achieved: nearly all reactants have been converted into products. If  $K_c$  is large enough, the reaction has gone essentially to completion when it reaches equilibrium.

Earlier we defined a product-favored reaction as one that proceeds spontaneously in the forward direction when all concentrations (or partial pressures) have the standard-state value of 1 M. If  $K_c > 1$ , so that the concentrations of products are greater than the concentrations of reactants, then when all concentrations are 1 M the reaction needs to produce greater concentrations of products to reach equilibrium. That is, the reaction needs to proceed in the forward direction. Thus,  **$K_c > 1$  (or  $K_p > 1$ ) means that a reaction is product-favored.**

A very small value of  $K_c$ , ( $K_c \ll 1$ ) indicates that equilibrium is achieved when only a small fraction of the reactants has been converted into products. Such a reaction is reactant-favored. If  $K_c$  is small enough, essentially no reaction has occurred when equilibrium is reached. When  $K_c \approx 1$ , both reactant and product concentrations are significant and it is necessary to use the equilibrium constant to calculate equilibrium concentrations.

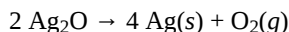
By an argument similar to the one in the next to last paragraph above,  **$K_c < 1$  (or  $K_p < 1$ ) means that a reaction is reactant-favored.**

### Podia Question

One way to remove silver oxide tarnish from silver is to heat the silver to a high temperature.

[https://mediaspace.wisc.edu/id/0\\_p9myzb11](https://mediaspace.wisc.edu/id/0_p9myzb11)

The reaction is:



At 298 K, the reaction is reactant-favored. Obtain data from the [Appendix](#) and determine at what temperature the reaction becomes product-favored. What assumptions need to be made to solve this problem?

*Two days before the next whole-class session, this Podia question will become live on [Podia](#), where you can submit your answer.*

**Comments.** If you found any inconsistencies, errors, or other things you would like to report about this module, please use [this link](#) to report them. A similar link will be included in each day's material. We appreciate your comments.

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