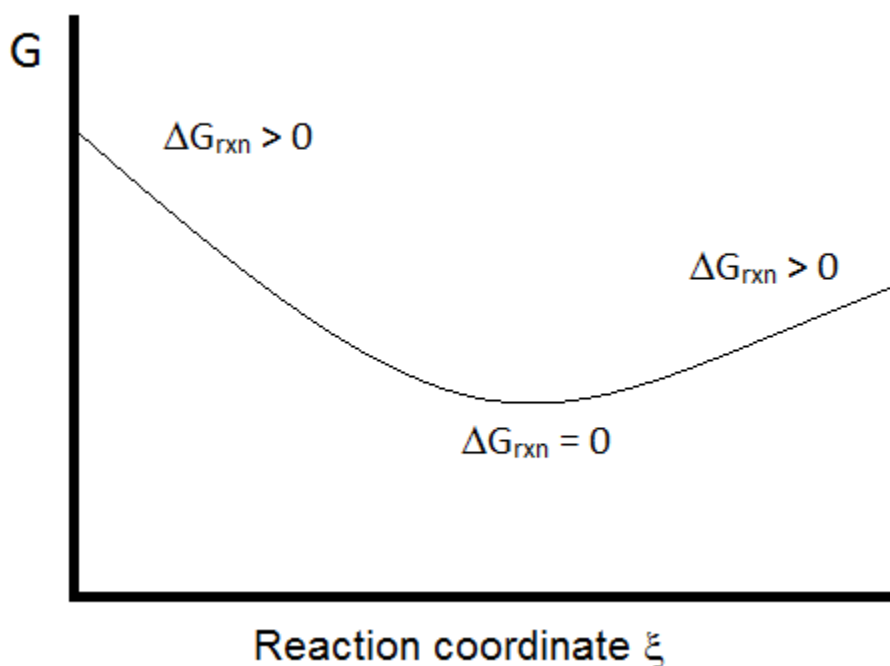


Chapter 9: Chemical Equilibrium

The small is great, the great is small; all is in equilibrium in necessity...

- Victor Hugo in "Les Miserables"

As was discussed in Chapter 6, the natural tendency of chemical systems is to seek a state of minimum Gibbs function. Once the minimum is achieved, movement in any chemical direction will not be spontaneous. It is at this point that the system achieves a state of equilibrium.

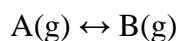


From the diagram above, it should be clear that the direction of spontaneous change is determined by $\left(\frac{\partial G}{\partial \xi}\right)_{p,T}$. If the slope of the curve is negative, the reaction will favor a shift toward products. And if it is positive, the reaction will favor a shift toward reactants. This is a non-trivial point, as it underscores the importance of the composition of the reaction mixture in the determination of the direction of the reaction.

Chemical Potential

Equilibrium can be understood as accruing at the composition of a reaction mixture at which the aggregate chemical potential of the products is equal to that of the reactants. Consider the simple reaction

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The criterion for equilibrium will be

$$\mu_A = \mu_B$$

If the gases behave ideally, the chemical potentials can be described in terms of the mole fractions of A and B

$$\mu_A^o + RT \ln \left(\frac{p_A}{p_{tot}} \right) = \mu_B^o + RT \ln \left(\frac{p_B}{p_{tot}} \right)$$

where Dalton's Law has been used to express the mole fractions.

$$x_i = \frac{p_i}{p_{tot}}$$

The above expression can be simplified by putting all of the μ_i^o terms on the left and the $RT \ln \left(\frac{p_i}{p_{tot}} \right)$ terms on the right.

$$\mu_A^o - \mu_B^o = RT \ln \left(\frac{p_B}{p_{tot}} \right) - RT \ln \left(\frac{p_A}{p_{tot}} \right)$$

Combining the $\ln \left(\frac{p_i}{p_{tot}} \right)$ terms and recognizing that $\mu_A^o - \mu_B^o$ is $-\Delta G^o$ for the reaction, one obtains

$$-\Delta G^o = RT \ln \left(\frac{p_B}{p_A} \right)$$

And since p_A/p_B is K_p for this reaction (assuming perfectly ideal behavior), one can write

$$\Delta G^o = -RT \ln K_p$$

Another way to achieve this result is to consider the Gibbs function change for a reaction mixture in terms of the **reaction quotient**. The reaction quotient can be expressed as

$$Q_p = \frac{\prod_i p_i^{v_i}}{\prod_j p_j^{v_j}}$$

where v_i are the stoichiometric coefficients for the products, and v_j are those for the reactants. Or if the stoichiometric coefficients are defined by expressing the reaction as a sum

$$0 = \sum_i \nu_i X_i$$

Where X_i refers to one of the species in the reaction, and ν_i is then the stoichiometric coefficient for that species, it is clear that ν_i will be negative for a reactant (since its concentration or partial pressure will reduce as the reaction moves forward) and positive for a product (since the concentration or partial pressure will be increasing.) If the stoichiometric coefficients are expressed in this way, the expression for the reaction quotient becomes

$$Q_p = \prod_i p_i^{\nu_i}$$

Using this expression, the Gibbs function change for the system can be calculated from

$$\Delta G_{rxn} = \Delta G_{rxn}^o + RT \ln Q_p$$

And since at equilibrium

$$\Delta G_{rxn} = 0 \quad \text{and} \quad Q_p = K_p$$

It is evident that

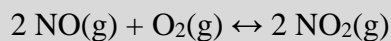
$$\Delta G_{rxn}^o = -RT \ln K_p$$

It is in this simple way that K_p and ΔG^o are related.

It is also of value to note that the criterion for a spontaneous chemical process is that $\Delta G_{rxn} < 0$, rather than ΔG_{rxn}^o , as is stated in many texts! Recall that ΔG_{rxn}^o is a function of all of the reactants and products being in their standard states of unit fugacity or activity. However, the direction of spontaneous change for a chemical reaction is dependent on the composition of the reaction mixture. Similarly, the magnitude of the equilibrium constant is insufficient to determine whether a reaction will spontaneously form reactants or products, as the direction the reaction will shift is also a function of not just the equilibrium constant, but also the composition of the reaction mixture!

Example:

Based on the data below at 298 K, calculate the value of the equilibrium constant (K_p) for the reaction



	NO(g)	NO ₂ (g)
ΔG_f^o (kJ/mol)	86.55	51.53

Solution:

First calculate the value of ΔG_{rxn}^o from the ΔG_f^o data.

$$\Delta G_{rxn}^o = (2) \left(51.53 \frac{\text{kJ}}{\text{mol}} \right) - (2) \left(86.55 \frac{\text{kJ}}{\text{mol}} \right) = -70.04 \frac{\text{kJ}}{\text{mol}}$$

And now use the value to calculate K_p using $\Delta G_{rxn}^o = -RT \ln K_p$.

$$-70040 \frac{\text{J}}{\text{mol}} = - \left(8.314 \frac{\text{J}}{\text{mol K}} \right) (298 \text{ K}) \ln K_p$$

$$K_p = 1.89 \cdot 10^{12}$$

Note: as expected for a reaction with a very large negative ΔG_{rxn}^o , the equilibrium constant is very large, favoring the formation of the products.

Activities and Fugacities

To this point, we have mostly ignored deviations from ideal behavior. But it should be noted that thermodynamic equilibrium constants are not expressed in terms of concentrations or pressures, but rather in terms of activities and fugacities (both being discussed in Chapter 7). Based on these quantities,

$$K_p = \prod_i f_i^{v_i}$$

and

$$K_c = \prod_i a_i^{v_i}$$

And since activities and fugacities are unitless, thermodynamic equilibrium constants are unitless as well.

Further, it can be noted that the activities of solids and pure liquids are unity (assuming ideal behavior) since they are in their standard states at the given temperature. As such, these species never change the magnitude of the equilibrium constant and are generally omitted from the equilibrium constant expression.

K_p and K_c

Oftentimes it is desirable to express the equilibrium constant in terms of concentrations (or activities for systems that deviate from ideal behavior.) In order to make this conversion, the relationship between pressure and concentration from the ideal gas law can be used.

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

And noting that the concentration is given by $\left(\frac{n}{V} \right)$, the expression for the equilibrium constant becomes

$$K_p = \prod_i (RT[X_i])^{\nu_i}$$

And since for a given temperature, RT is a constant and can be factored out of the expression, leaving

$$\begin{aligned} K_p &= \left(\prod_i (RT)^{\nu_i} \right) \left(\prod_i [X_i]^{\nu_i} \right) \\ &= (RT)^{\sum_i \nu_i} \prod_i [X_i]^{\nu_i} \\ &= (RT)^{\sum_i \nu_i} K_c \end{aligned}$$

This conversion works for reactions in which all reactants and products are in the gas phase. Care must be used when applying this relationship to heterogeneous equilibria.

Pressure Dependence of K_p

Since the equilibrium constant K_p is a function of ΔG_{rxn}^o which is defined for a specific composition (all reactants in their standard states and at unit pressure (or fugacity), Changes in pressure have no effect on equilibrium constants for a fixed temperature. However, changes in pressure can have profound effects on the compositions of equilibrium mixtures.

To demonstrate the relationship, one must recall Dalton's law of partial pressures. According to this relationship, the partial pressure of a component of a gas-phase mixture can be expressed

$$p_i = x_i p_{tot}$$

It is the combination of mole fractions that describes the composition of the equilibrium mixture.

Substituting the above expression into the expression for K_p yields

$$K_p = \prod_i (x_i p_{tot})^{v_i}$$

This expression can be factored into two pieces – one containing the mole fractions and thus describing the composition, and one containing the total pressure.

$$K_p = \left(\prod_i x_i^{v_i} \right) \left(\prod_i p_{tot}^{v_i} \right)$$

The second factor is a constant for a given total pressure. If the first term is given the symbol K_x , the expression becomes

$$K_p = K_x (p_{tot})^{\sum_i v_i}$$

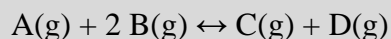
In this expression, K_x has the same form as an equilibrium constant

$$K_x = \prod_i x_i^{v_i}$$

but is not itself a constant. The value of K_x will vary with varying composition, and will *need* to vary with varying total pressure (in most cases) in order to maintain a constant value of K_p .

Example:

Consider the following reaction at equilibrium.



In which direction will the equilibrium shift if the volume of the reaction vessel is decreased?

Solution:

A decrease in the volume will lead to an increase in total pressure. Since the equilibrium constant can be expressed as

$$K_p = \frac{p_C p_D}{p_A p_B^2} = \frac{x_C x_D}{x_A x_B^2} (p_{tot})^{-1}$$

An increase in pressure will lead to an increase in K_x in order to maintain a constant value of K_p . So the reaction will shift to form more of the products C and D.

Note: This should make some sense, since a shift to the side of the reaction with fewer moles of gas will lower the total pressure of the reaction mixture, and thus relieving the stress introduced by increasing the pressure. This is exactly what is expected according to Le Chatelier's principle.

It should be noted that there are several ways one can affect the total pressure of a gas-phase equilibrium. These include the introduction or removal of reactants or products (perhaps through condensation or some other physical process), a change in volume of the reaction vessel, or the introduction of an inert gas that does not participate in the reaction itself. (Changes in the temperature will be discussed in a later section.) The principle of Le Chatlier can be used as a guide to predict how the equilibrium composition will respond to a change in pressure.

Le Chatlier's principle: When a stress is introduced to a system at equilibrium, the system will adjust so as to reduce the stress.

Le Chatlier's principle is fairly clear on how to think about the addition or removal of reactants or products. For example, the addition of a reactant will cause the system to shift to reduce the partial pressure of the reactant. It can do this by forming more products.

An important exception to the rule that increasing the total pressure will cause a shift in the reaction favoring the side with fewer moles of gas occurs when the total pressure is increased by introducing an inert gas to the mixture. The reason is that the introduction of an inert gas will affect the total pressures *and* the partial pressures of each individual species.

Example:

A 1.0 L vessel is charged with 1.00 atm of A, and the following reaction is allowed to come to equilibrium at 298 K.



- What are the equilibrium partial pressures and mole fractions of A and B?
- If the volume of the container is doubled, what are the equilibrium partial pressures and mole fractions of A and B?
- If 1.000 atm of Ar (an inert gas) is introduced into the system described in b), what are the equilibrium partial pressures and mole fractions of A and B once equilibrium is reestablished?

Solution:

First, we can use an ICE¹ table to solve part a).

	A	2 B
Initial	1.00 atm	0
Change	-x	+2x
Equilibrium	1.00 atm - x	2x

So (for convenience, consider K_p to have units of atm)

¹ ICE is an acronym for "Initial, Change, Equilibrium". An ICE table is a tool that is used to solve equilibrium problems in terms of an unknown number of moles (or something proportional to moles, such as pressure or concentration) will shift for a system to establish equilibrium. See (Tro, 2014) or a similar General Chemistry text for more background and information.

$$3.10 \text{ atm} = \frac{(2x)^2}{(1.00 \text{ atm} - x)}$$

Solving for x yields values of

$$x_1 = -1.34935 \text{ atm}, \quad x_2 = 0.57434 \text{ atm}$$

Clearly, x_1 , while a solution to the mathematical problem, is not physically meaningful since the equilibrium pressure of B cannot be negative. So the equilibrium partial pressures are given by

$$p_A = 1.00 \text{ atm} - 0.574 \text{ atm} = 0.426 \text{ atm}$$

$$p_B = 2(0.574 \text{ atm}) = 1.148 \text{ atm}$$

So the mole fractions are given by

$$x_A = \frac{0.426 \text{ atm}}{0.426 \text{ atm} + 1.148 \text{ atm}} = 0.271$$

$$x_B = 1 - 0.271 = 0.729$$

In part b) the volume is doubled. Again, an ICE table is useful. The initial pressures will be half of the equilibrium pressures found in part a).

	A	2 B
Initial	0.213 atm	0.574 atm
Change	-x	+2x
Equilibrium	0.213 atm - x	0.574 atm + 2x

So the new equilibrium pressures can be found from

$$3.10 \text{ atm} = \frac{(0.574 \text{ atm} + 2x)^2}{(0.213 \text{ atm} - x)}$$

And the values of x that solve the problem are

$$x_1 = -1.40775 \text{ atm}, \quad x_2 = 0.0587505 \text{ atm}$$

We reject the negative root (since it would cause both of the partial pressures to become negative. So the new equilibrium partial pressures are

$$p_A = 0.154 \text{ atm}, \quad p_B = 0.692 \text{ atm}$$

And the mole fractions are

$$x_A = 0.182, \quad x_B = 0.818$$

We can see that the mole fraction of A decreased and the mole fraction B increased. This is the result expected by Le Chatlier's principle since the lower total pressure favors the side of the reaction with more moles of gas.

Now for part c). We introduce 1.000 atm of an inter gas. The new partial pressures are

$$p_A = 0.154 \text{ atm}, p_B = 0.692 \text{ atm}, p_{Ar} = 1.000 \text{ atm}$$

And because the partial pressures of A and B are unaffected, the equilibrium does not shift! What *is* affected is the composition, and so the mole fractions will change.

$$x_A = \frac{0.154 \text{ atm}}{0.154 \text{ atm} + 0.692 \text{ atm} + 1.000 \text{ atm}} = 0.08342$$

$$x_B = \frac{0.692 \text{ atm}}{0.154 \text{ atm} + 0.692 \text{ atm} + 1.000 \text{ atm}} = 0.3749$$

$$x_{Ar} = \frac{1.000 \text{ atm}}{0.154 \text{ atm} + 0.692 \text{ atm} + 1.000 \text{ atm}} = 0.5417$$

And since

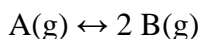
$$K_p = K_x(p_{tot})$$

$$\frac{(0.3749)^2}{0.08342} (1.846 \text{ atm}) = 3.1$$

Within round-off error, the value obtained is the equilibrium constant. So the conclusion is that the introduction of an inert gas, even though it increases the total pressure, does not induce a change in the partial pressures of the reactants and products, so it does not cause the equilibrium to shift.

Degree of Dissociation

Reactions such as the one in the previous example involve the dissociation of a molecule. Such reactions can be easily described in terms of the fraction of reactant molecules that actually dissociate to achieve equilibrium in a sample. This fraction is called the **degree of dissociation**. For the reaction in the previous example



the degree of dissociation can be used to fill out an ICE table. If the reaction is started with n moles of A, and α is the fraction of A molecules that dissociate, the ICE table will look as follows.

	A	2 B
Initial	n	0
Change	$-\alpha n$	$+2n\alpha$
Equilibrium	$n(1 - \alpha)$	$2n\alpha$

The mole fractions of A and B can then be expressed by

$$x_A = \frac{n(1 - \alpha)}{n(1 - \alpha) + 2n\alpha} = \frac{1 - \alpha}{1 + \alpha}$$

$$x_B = \frac{2\alpha}{1 + \alpha}$$

Based on these mole fractions

$$K_x = \frac{\left(\frac{2\alpha}{1 + \alpha}\right)^2}{\left(\frac{1 - \alpha}{1 + \alpha}\right)} = \frac{4\alpha^2}{(1 - \alpha^2)}$$

And so K_p , which can be expressed as

$$K_p = K_x (p_{tot})^{\sum \nu_i}$$

is given by

$$K_p = \frac{4\alpha^2}{(1 - \alpha^2)} (p_{tot})$$

Example:

Based on the ΔG_f° values given below, find the equilibrium constant at 25 °C and degree of dissociation for a system that is at a total pressure of 1.00 atm for the reaction



	$\text{N}_2\text{O}_4(\text{g})$	$\text{NO}_2(\text{g})$
ΔG_f° (kJ/mol)	99.8	51.3

First, the value of K_p can be determined from ΔG_{rxn}° .

$$\Delta G_{rxn}^{\circ} = 2 \left(51.3 \frac{\text{kJ}}{\text{mol}} \right) - 99.8 \frac{\text{kJ}}{\text{mol}} = 2.8 \frac{\text{kJ}}{\text{mol}}$$

So, using $\Delta G_{rxn}^{\circ} = -RT \ln K_p$,

$$2800 \frac{\text{J}}{\text{mol}} = - \left(8.314 \frac{\text{J}}{\text{mol K}} \right) (298 \text{ K}) \ln K_p$$

$$K_p = 0.323 \text{ atm}$$

The degree of dissociation can then be calculated from

$$K_p = \frac{4\alpha^2}{(1 - \alpha^2)} (p_{tot})$$

$$0.323 \text{ atm} = \frac{4\alpha^2}{1 - \alpha^2} (1.00 \text{ atm})$$

Solving for α ,

$$\alpha = 0.273$$

Note: since α represents the fraction of N_2O_4 molecules dissociated, it must be a positive number between 0 and 1.

Example:

Consider the gas-phase reaction



A reaction vessel is initially filled with 1.00 mol of A and 2.00 mol of B. At equilibrium, the vessel contains 0.60 mol C and a total pressure of 0.890 atm at 1350 K.

1. How many mol of A and B are present at equilibrium?
2. What is the mole fraction of A, B, and C at equilibrium?
3. Find values for K_x , K_p , and ΔG_{rxn}°

Solution:

Let's build an ICE table!

	A	2 B	2 C
Initial	1.00 mol	2.00 mol	0
Change	-x	-2x	+2x
Equilibrium	1.00 mol - x	2.00 mol - 2x	2x = 0.60 mol

From the equilibrium measurement of the number of moles of C, $x = 0.30$ mol. So at equilibrium,

	A	2 B	2 C
Equilibrium	0.70 mol	1.40 mol	0.60 mol

The total number of moles at equilibrium is 2.70 mol. From these data, the mole fractions can be determined.

$$x_A = \frac{0.70 \text{ mol}}{2.70 \text{ mol}} = 0.259$$

$$x_B = \frac{1.40 \text{ mol}}{2.70 \text{ mol}} = 0.519$$

$$x_C = \frac{0.60 \text{ mol}}{2.70 \text{ mol}} = 0.222$$

So K_x is given by

$$K_x = \frac{(0.222)^2}{(0.259)(0.519)^2} = 0.7064$$

And K_p is given by $K_p = K_x(p_{tot})^{\sum \nu_i}$, so

$$K_p = 0.7604(0.890 \text{ atm})^{-1} = 0.794 \text{ atm}^{-1}$$

The thermodynamic equilibrium constant is unitless, of course, since the pressures are all divided by 1 atm. So the actual value of K_p is 0.794. This value can be used to calculate ΔG_{rxn}^o using

$$\Delta G_{rxn}^o = -RT \ln K_p$$

So

$$\Delta G_{rxn}^o = -\left(8.314 \frac{\text{J}}{\text{mol K}}\right)(1350 \text{ K}) \ln(0.794) = 2590 \frac{\text{J}}{\text{mol}}$$

Temperature Dependence of K_p

The value of K_p is independent of pressure, although the composition of a system at equilibrium may be very much dependent on pressure. Temperature dependence is another matter. Because the value of ΔG_{rxn}^o is dependent on temperature, the value of K_p is as well. The

form of the temperature dependence can be taken from the definition of the Gibbs function. At constant temperature and pressure

$$\frac{\Delta G_{T_2}^o}{T_2} - \frac{\Delta G_{T_1}^o}{T_1} = \Delta H^o \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Substituting

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

For the two values of ΔG^o and using the appropriate temperatures, yields

$$\frac{-RT_2 \ln K_2}{T_2} - \frac{-RT_1 \ln K_1}{T_1} = \Delta H^o \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

And simplifying the expression so that only terms involving K are on the left and all other terms are on the right results in the **van't Hoff equation**, which describes the temperature dependence of the equilibrium constant.

$$\ln \left(\frac{K_2}{K_1} \right) = -\frac{\Delta H^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Because of the assumptions made in the derivation of the Gibbs-Helmholtz equation, this relationship only holds if ΔH^o is independent of temperature over the range being considered. This expression also suggests that a plot of $\ln(K)$ as a function of $1/T$ should produce a straight line with a slope equal to $-\Delta H^o/R$. Such a plot is known as a **van't Hoff plot**, and can be used to determine the reaction enthalpy.

Example:

A certain reaction has a value of $K_p = 0.0260$ at 25°C and $\Delta H_{rxn}^o = 32.4 \frac{\text{kJ}}{\text{mol}}$. Calculate the value of K_p at 37°C .

Solution:

This is a job for the van't Hoff equation!

$$T_1 = 298 \text{ K}$$

$$K_1 = 0.0260$$

$$\Delta H_{rxn}^o = 32400 \text{ J/mol}$$

$$T_2 = 310 \text{ K}$$

$$K_2 = ?$$

So the equation becomes

$$\ln \left(\frac{K_2}{0.0260} \right) = -\frac{32400 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol K}}} \left(\frac{1}{310 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$

$$K_2 = 0.0431$$

Note: the value of K_2 increased with increasing temperature, which is what is expected for an endothermic reaction. An increase in temperature should result in an increase of product formation in the equilibrium mixture. But unlike a change in pressure, a change in temperature actually leads to a change in the value of the equilibrium constant!

Example:

Given the following average bond enthalpies for P-Cl and Cl-Cl bonds, predict whether or not an increase in temperature will lead to a larger or smaller degree of dissociation for the reaction



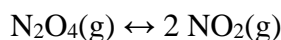
X-Y	D(X-Y) (kJ/mol)
P-Cl	326
Cl-Cl	240

Solution:

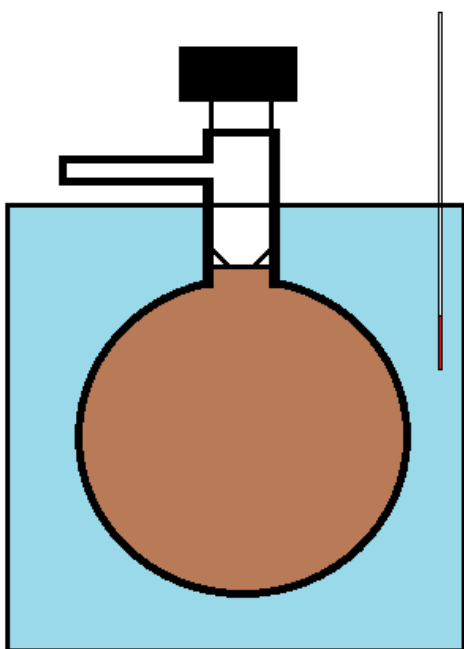
The estimated reaction enthalpy is given by the total energy expended breaking bonds minus the energy recovered by the formation of bonds. Since this reaction involves breaking two P-Cl bonds (costing 652 kJ/mol) and the formation of one Cl-Cl bond (recovering 240 kJ/mol), it is clear that the reaction is endothermic (by approximately 412 kJ/mol). As such, an increase in temperature should increase the value of the equilibrium constant, causing the degree of dissociation to be increased at the higher temperature.

The Dumas Bulb Method for Measuring Decomposition Equilibrium

A classic example of an experiment that is employed in many physical chemistry laboratory courses uses a Dumas Bulb method to measure the dissociation of $\text{N}_2\text{O}_4(\text{g})$ as a function of temperature (Mack & France, 1934). In this experiment, a glass bulb is used to create a constant volume container in which a volatile substance can evaporate, or achieve equilibrium with other gases present. The latter is of interest in the case of the reaction



The reaction is endothermic, so at higher temperatures, a larger degree of dissociation is observed.



The procedure is to first calibrate the internal volume of the Dumas bulb. This is done using a heavy gas (such as SF_6) and comparing the mass of the bulb when evacuated to the mass of the bulb full of the calibrant gas at a particular pressure and temperature.

The Dumas bulb is then charged with a pure sample of the gas to be investigated (such as N_2O_4) and placed in a thermalized bath. It is then allowed to come to equilibrium. Once Equilibrium is established, the stopcock is opened to allow gas to escape until the internal pressure is set to the pressure of the room. The stopcock is then closed and the bulb weighed to determine the total mass of gas remaining inside. The experiment is repeated at higher and higher temperatures (so that at each subsequent measurement, the larger degree of dissociation creates more molecules of gas and an

increase in pressure in the bulb (along with the higher temperature), which then leads to the expulsion of gas when the pressure is equilibrated.

The degree of dissociation is then determined based on the calculated gas density at each temperature.

$$\alpha = \frac{\rho_1 - \rho_2}{\rho_2(n - 1)}$$

where ρ_1 is the measured density and ρ_2 is the theoretical density if no dissociation occurs (calculated from the ideal gas law for the given temperature, pressure, and molar mass of the dissociating gas) and n is the number of fragments into which the dissociating gas dissociates (in the case of $\text{N}_2\text{O}_4 \leftrightarrow 2 \text{NO}_2$, $n = 2$.) The equilibrium constant is then calculated as

$$K = \frac{4\alpha^2}{1 - \alpha^2} \left(\frac{p}{1.00 \text{ atm}} \right)$$

Finally, a van't Hoff plot is generated to determine the reaction enthalpy.

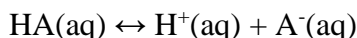
Acid-Base Equilibria

A great many processes involve proton transfer, or acid-base types of reactions. As many biological systems depend on carefully controlled pH, these types of processes are extremely important. The pH is defined by

$$pH \equiv -\log[H^+]$$

where $[H^+]$ is in mol/L.

The dissociation of a weak acid in water is governed by the equilibrium defined by



The equilibrium constant for such a reaction, K_a , takes the form

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

As is the case for all thermodynamic equilibrium constants, the concentrations are replaced by activities and the equilibrium constant is unitless. However, if all species behave ideally (have unit activity coefficients) the units can be used as a very useful guide in solving problems.

Example:

What is the pH of a 0.200 M HOAc (acetic acid) solution? ($K_a = 1.8 \times 10^{-5}$ M)

Solution:

An ICE table will come in very handy here!

	HOAc	H ⁺	OAc ⁻
Initial	0.200 M	0	0
Change	-x	+x	+x
Equilibrium	0.200 M - x	x	x

The equilibrium problem can then be set up as

$$K_a = \frac{[H^+][OAc^-]}{[HOAc]}$$

Substituting the values that are known

$$1.8 \cdot 10^{-5} M = \frac{(x)(x)}{(0.200 M - x)}$$

This produces a quadratic equation, and thus two values of x which satisfy the relationship.

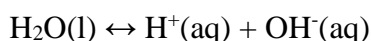
$$\begin{aligned}x_1 &= -0.001906 M \\x_2 &= 0.001888 M\end{aligned}$$

The negative root is not physically meaningful since the concentrations of H^+ and OAc^- cannot be negative. Using the value of x_2 as $[\text{H}^+]$, the pH is calculated to be

$$\text{pH} = -\log(0.001888) = 2.72$$

The Auto-ionization of Water

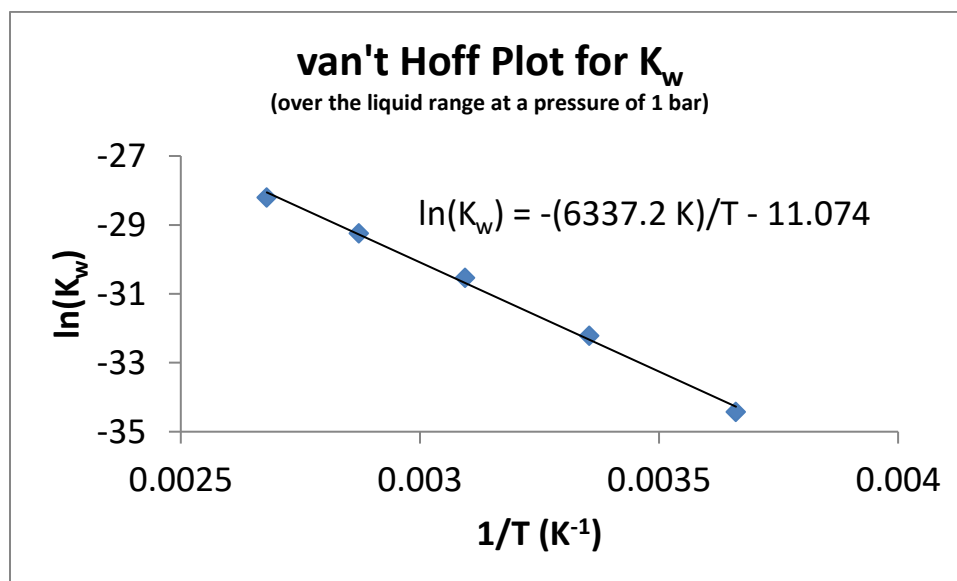
Water is a very important solvent as water molecules have large dipole moments which create favorable interactions with ionic compounds. Water also has a large dielectric constant which damps the electric field generated by ions in solutions, making the comparative interactions with water more favorable than with other ions in solution in many cases. But water also dissociates into ions through the reaction



The equilibrium constant governing this dissociation is highly temperature dependent. The data below are presented by Bandura and Lvov (Bandura & Lvov, 2006)

T (°C)	0	25	50	75	100
pK _w	14.95	13.99	13.26	12.70	12.25

From these data, a van't Hoff plot can be constructed.



There is some curvature to the line, suggesting some (albeit small) temperature dependence for ΔH_{rxn} . However, from the fit of these data, a value of ΔH_{rxn} can be determined to be 52.7 kJ/mol.

Of particular note is that the dissociation is endothermic, so increases in temperature will lead to a greater degree of dissociation.

Example:

What is the pH of neutral water at 37 °C (normal human body temperature)?

Solution:

From the best-fit line in the above van't Hoff plot, the value of K_w can be calculated:

$$\ln(K_w) = -\frac{6337.2 \text{ K}}{(310 \text{ K})} - 11.04$$

$$K_w = 2.12 \cdot 10^{-14} \text{ M}^2$$

Since K_w gives the product of $[H^+]$ and $[OH^-]$ (which must be equal in a neutral solution),

$$[H^+] = \sqrt{2.12 \cdot 10^{-14} \text{ M}^2} = 1.456 \cdot 10^{-7} \text{ M}$$

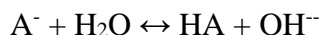
And the pH is given by

$$pH = -\log(1.456 \cdot 10^{-7}) = 6.84$$

Note: This is slightly less than a pH of 7.00, which is normally considered to be “neutral.” But a pH of 7.00 is only neutral at 25 °C! At higher temperatures, neutral pH is a lower value due to the endothermic nature of the auto-ionization water.

The Hydrolysis of a Weak Base

Hydrolysis is defined as a reaction with water that splits a water molecule. The hydrolysis of a weak base defines the equilibrium constant K_b .



For this reaction, the equilibrium constant K_b is given by

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

The concentration (or activity) of the pure compound H_2O is not included in the equilibrium expression because, being a pure compound in its standard state, it has unit activity throughout the process of establishing equilibrium. Further, it should be noted that when K_b is combined with the expression for K_a for the weak acid HA ,

$$K_a K_b = \left(\frac{[H^+][A^-]}{[HA]} \right) \left(\frac{[HA][OH^-]}{[A^-]} \right) = [H^+][OH^-] = K_w$$

As a consequence, if one knows K_a for a weak acid, one also knows K_b for its conjugate base, since the product results in K_w .

Example:

What is the pH of a 0.150 M solution of KF? (For HF, $pK_a = 3.17$ at 25 °C)

Solution:

The problem involves the hydrolysis of the conjugate base of HF, F^- . The hydrolysis reaction is



An ICE table is in order here.

	F^-	HF	OH^-
Initial	0.150 M	0	0
Change	-x	+x	+x
Equilibrium	0.150 M - x	x	x

So the expression for K_b is

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \cdot 10^{-14} M^2}{10^{-3.17} M} = \frac{[x][x]}{[1.50 M - x]}$$

In this case, the small value of K_b insures that the value of x will be negligibly small compared to 0.150 M. In this limit, the value of x (which is equal to $[OH^-]$)

$$x = [OH^-] = 1.49 \cdot 10^{-6} M$$

So $[H^+]$ is given by

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14} M^2}{1.49 \cdot 10^{-6} M} = 6.71 \cdot 10^{-9} M$$

And the pH is given by

$$pH = -\log(6.71 \cdot 10^{-9}) = 8.17$$

Note: The pH of this salt solution is slightly basic. This is to be expected as KF can be thought of being formed in the reaction of a weak acid (HF) with a strong base (KOH). In the competition to control the pH, the strong base ends up winning the battle.

Buffers

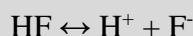
Buffer solutions, which are of enormous importance in controlling pH in various processes, can be understood in terms of acid/base equilibrium. A buffer is created in a solution which contains both a weak acid and its conjugate base. This creates to absorb excess H^+ or supply H^+ to replace what is lost due to neutralization. The calculation of the pH of a buffer is straightforward using an ICE table approach.

Example:

What is the pH of a solution that is 0.150 M in KF and 0.250 M in HF?

Solution:

The reaction of interest is



Let's use an ICE table!

	HF	H^+	F^-
Initial	0.250 M	0	0.150 M
Change	-x	+x	+x
Equilibrium	0.250 M - x	x	0.150 M + x

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

$$10^{-3.17} M = \frac{x(0.150 M + x)}{(0.250 M - x)}$$

This expression results in a quadratic relationship, leading to two values of x that will make it true. Rejecting the negative root, the remaining root of the equation indicates

$$[H^+] = 0.00111 M$$

So the pH is given by

$$pH = -\log(0.00111) = 2.95$$

For buffers made from acids with sufficiently large values of pK_a the buffer problem can be simplified since the concentration of the acid and its conjugate base will be determined by

their pre-equilibrium values. In these cases, the pH can be calculated using the Henderson-Hasselbalch equation.

If one considers the expression for K_a

$$K_a = \frac{[H^+][A^-]}{[HA]} = [H^+] \frac{[A^-]}{[HA]}$$

Taking the log of both sides and multiplying by -1 yields

$$pK_a = pH - \log \frac{[A^-]}{[HA]}$$

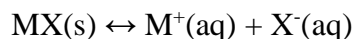
An rearrangement produces the form of the Henderson-Hasselbalch equation.

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

It should be noted that this expression will fail if 1) the pK_a is too small and/or the concentrations $[A^-]$ or $[HA]$ are too small, since the equilibrium concentration will deviate wildly from the pre-equilibrium values under these conditions.

Solubility of Ionic Compounds

The solubility of ionic compounds in water can also be described using the concepts of equilibrium. If you consider the dissociation of a generic salt MX



The equilibrium expression is

$$K_{sp} = [M^+][X^-]$$

K_{sp} is the **solubility product** and is the equilibrium constant that describes the solubility of an electrolyte. And again, the pure solid MX is not included in the expression since it has unit activity throughout the establishment of equilibrium.

Example:

What is the maximum solubility of CuS at 25 °C? ($K_{sp} = 1 \cdot 10^{-36} \text{ M}^2$)

Solution:

Yup – time for an ICE table.

	CuS	Cu ²⁺	S ²⁻
--	-----	------------------	-----------------

Initial		0	0
Change		+x	+x
Equilibrium		x	x

So the equilibrium expression is

$$1 \cdot 10^{-36} M^2 = x^2$$

$$x = 1 \cdot 10^{-18} M$$

Example:

What is the maximum solubility of CuS at 25 °C in 0.100 M NaS? ($K_{sp} = 1 \cdot 10^{-36} M^2$)

Solution:

In this problem we need to consider the existence of $S^{2-}(aq)$ from the complete dissociation of the strong electrolyte NaS. An ICE table will help, as usual.

	CuS	Cu^{2+}	S^{2-}
Initial		0	0.100 M
Change		+x	+x
Equilibrium		x	0.100 M + x

Given the miniscule magnitude of the solubility product, x will be negligibly small compared to 0.100 M. So the equilibrium expression is

$$1 \cdot 10^{-36} M^2 = x(0.100 M)$$

$$x = 1 \cdot 10^{-35} M$$

The huge reduction in solubility is due to the **common ion effect**. The existence of sulfide in the solution due to sodium sulfide greatly reduces the solution's capacity to support additional sulfide due to the dissociation of CuS.

Relating K_{eq} to ΔH° and ΔS°

At constant temperature and pressure

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

Noting that

$$\Delta G^{\circ} = -RT \ln K_p$$

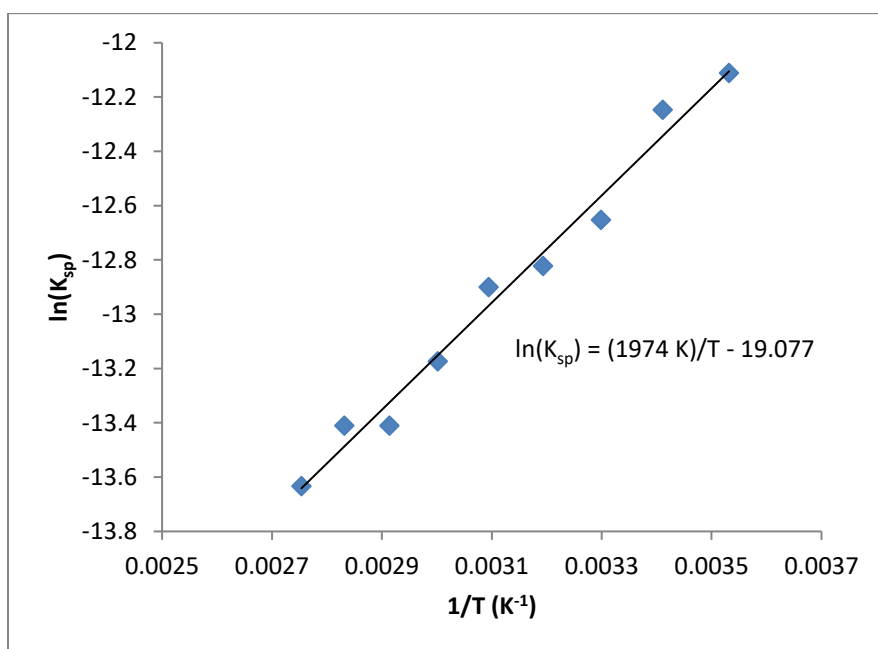
it is evident that

$$-RT \ln K_p = \Delta H^{\circ} - T\Delta S^{\circ}$$

Dividing both sides by $-RT$ produces

$$\ln K_p = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

This result suggests that a plot of $\ln(K)$ as a function of $1/T$ should produce a line with a slope equal to $-\Delta H^{\circ}/R$ and an intercept of $\Delta S^{\circ}/R$. Such a plot using K_{sp} for $\text{Ca}(\text{OH})_2$ is shown below.



The result shows that the dissociation is exothermic.

$$\Delta H_{rxn}^{\circ} = -\text{slope} \cdot R = -(1974 \text{ K}) \left(8.314 \frac{\text{J}}{\text{mol K}} \right) = -16410 \frac{\text{J}}{\text{mol}}$$

It also shows a negative change in entropy upon dissociation, which is counter intuitive.

$$\Delta S_{rxn}^{\circ} = \text{incpt} \cdot R = (-19.077) \left(8.314 \frac{\text{J}}{\text{mol K}} \right) = -158.6 \frac{\text{J}}{\text{mol K}}$$

The explanation for the negative entropy change is that for certain ions in solution that the organization of water molecules within the solvation sphere leads to a large negative entropy change for the solvent – particularly at the saturation point. The negative entropy change for the

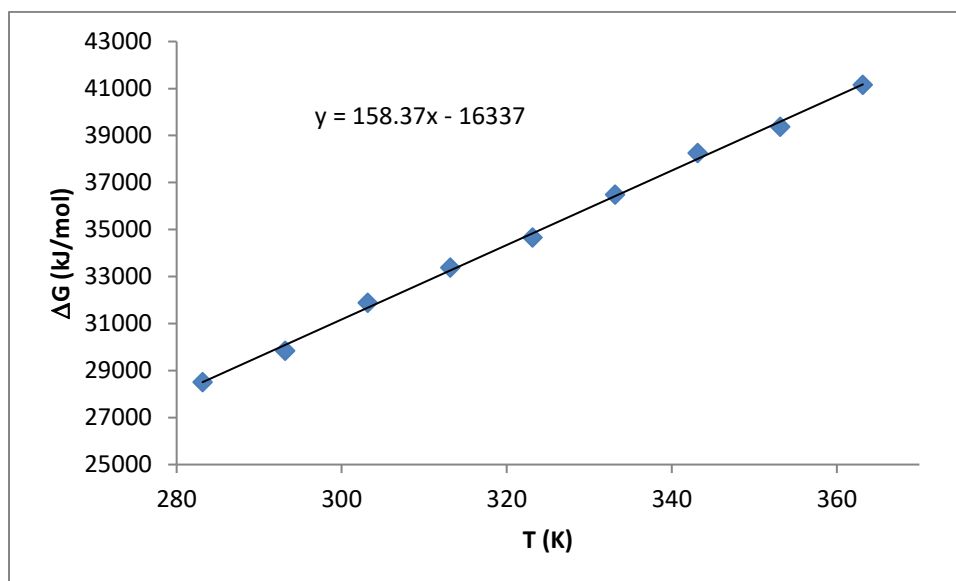
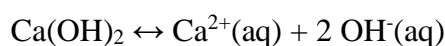
Thermochemistry and Chemical Kinetics: Chemical Equilibrium © 2021 Patrick E. Fleming – Available under Creative Commons Attribution-Noncommercial-Share Alike license 4.0 ([CC BY-NC-SA 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/))

solvent, at least in this case, overcomes the positive entropy change for the solute, leading to a net negative entropy change.

Another approach to determining the entropy change is to recognize

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$$

So a plot of ΔG_{rxn}^o vs. T should yield a curve, where the slope at any point gives ΔS_{rxn}^o . Below is a plot of the data calculated from K_{sp} for $\text{Ca}(\text{OH})_2$ as a function of temperature. The data are fairly linear, meaning that ΔS_{rxn}^o is relatively independent of temperature over this range. The plot also confirms the negative entropy change for the reaction



The magnitude of the entropy change determined in this manner is very similar to that determined from the $\ln(K_{sp})$ vs $1/T$ method, as expected for a system in which ΔS_{rxn}^o is independent of temperature.

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Vocabulary and Concepts

common ion effect	226	reaction quotient.....	206
conjugate base	223	solubility product	225
degree of dissociation	213	thermodynamic equilibrium constant	208
dissociation of a weak acid	220	van't Hoff equation	217
Dumas Bulb	218	van't Hoff plot.....	217
Henderson-Hasselbalch equation.....	225	weak acid	223
Le Chatlier's principle	211		

Learning Objectives

After mastering the material covered in this chapter, one will be able to:

1. Know stuff.
2. Do stuff.
3. Be stuff.

Problems

Oh – I got problems . . .