

## 6.4: Activity is an Effective Concentration

### Effective Concentrations in Gases

In chemical thermodynamics, activity (symbol  $a$ ) is a measure of the “effective concentration” of a species in a mixture, in the sense that the species' chemical potential depends on the activity of a real solution in the same way that it would depend on concentration for an ideal solution. By convention, activity is treated as a dimensionless quantity, although its value depends on customary choices of standard state for the species. The activity of pure substances in condensed phases (solid or liquids) is normally taken as unity (the number 1). Activity depends on temperature, pressure and composition of the mixture, among other things. For gases, the activity is the effective partial pressure, and is usually referred to as *fugacity*.

The difference between activity and other measures of composition arises because molecules in non-ideal gases or solutions interact with each other, either to attract or to repel each other. The activity of an ion is particularly influenced by its surroundings. The use of activities allows chemists to explain various discrepancies between ideal solutions and real solutions. The mathematical description of an ideal solution must be modified to describe a real solution, just as the law for ideal gases ( $PV = nRT$ ) must be modified to describe real gases.

#### ✓ Example 6.4.1: Ideal vs. Real Gases

Compare the pressures predicted for one mole of ethane at 298.15 K under the following equations of states:

- ethane is an ideal gas or
- ethane is a van der Waal gas

What is the deviation of the two?

#### Solution

a) Ideal gas law equation of state: Calculate the pressure of 1.000 mole of ethane at 298.15 K in a 1.000 L flask using the ideal gas law.

$$\begin{aligned}
 P_{ideal}V &= nRT && (6.4.1) \\
 P_{ideal} &= \frac{nRT}{V} \\
 &= \frac{(1 \text{ mole})(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{1 \text{ L}} \\
 &= 24.47 \text{ atm}
 \end{aligned}$$

b) Van der Waal's equation of state: Calculate the pressure of 1.00 mole of ethane at 298 K in a 1.00 L flask using the van der Waals equation. The van der Waals constants for ethane can be found in [Table A8](#).

- $a = 5.492 \text{ atm} \frac{\text{L}^2}{\text{M}^2}$  and
- $b = 0.06499 \text{ L/m}$

$$\begin{aligned}
 \left( P_{vdW} + \frac{an^2}{V^2} \right) (V - nb) &= nRT && (6.4.2) \\
 P_{vdW} &= \frac{nRT}{V - nb} - \frac{an^2}{V^2} \\
 &= 20.67 \text{ atm}
 \end{aligned}$$

Calculate the percent error between the  $P_{ideal}$  and the  $P_{vdW}$

$$\text{Error} = \frac{P_{vdW} - P_{ideal}}{P_{vdW}} = 18.36\%$$

An error this large is often **too big to ignore** when carrying out a gas-phase reaction or designing a vessel in which to carry out such a reaction.

There are two ways to deal with real systems that deviate appreciably from ideal conditions:

1. Use a more accurate phenomenologically (i.e., real) Equation of State like the van der Waal' (Equation 6.4.2) that models the system more accurately. This must explicitly address **intermolecular forces** and other effects that exist in real system and the concentration used is 1 mol/L (i.e., the real concentration).
2. Use an ideal equation of state like the ideal gas Equation of State in Equation 6.4.1), but use an "effective concentration" of 0.816 mol/L to generate the observed pressure (that is, the gas behaves as if it has a reduced concentration of 100%-18.36% = 81.6% of the real concentration).

## Effective Concentrations in Solutions

In a similar fashion, the difference between the calculated solute concentrations in an ideal solution and in a real solution can lead to wide variations in experimental results. The following three examples compare the results obtained when formal concentrations are used (assuming ideality) and when activities are used (assuming non-ideality). Just like gases, "ideal solutions" have certain predictable physical properties (e.g. **colligative properties**) that real solutions often deviate from. As with the van der Waal equation in Example 1, this deviation originates from solute-solvent, solvent-solvent and solute-solute **interactions**. The magnitude of this non-ideality naturally greater with higher with solute concentrations and with greater **intermolecular interaction** (e.g., ions vs. non-charged species). Lewis introduced idea of 'effective concentration' or 'activity' to deal with this problem by allowing an "ideal solution" description for non-ideal solutions.

Since the Van der Waals equation describes real gases instead of the ideal gases law, **activity** can be used in place of concentration to describe the behavior of real solutions vs. ideal solutions.

The activity of a substance (abbreviated as  $a$ ) describes the effective concentration of that substance in the reaction mixture. Activity takes into account the non-ideality of the reaction mixture, including solvent-solvent, solvent-solute, and solute-solute interactions. Thus, activity provides a more accurate description of how all of the particles act in solution. For very dilute solutions, the activities of the substances in the solution closely approach the formal concentration (what the calculated concentration should be based on how much substance was measured out.) As solutions get more concentrated, the activities of all of the species tend to be smaller than the formal concentration. The decrease in activity as concentration increases is much more pronounced for ions than it is for neutral solutes.

Activities are actually **unitless** ratios that compare an effective pressure or an effective concentration to a standard state pressure or concentration (the correct term for the effective pressure is **fugacity**). There are several ways to define standard states for the different components of a solution, but a common system is

- the standard state for gas pressure,  $P^\circ$ , is 1 bar (often approximated with 1 atm)
- the standard state for solute concentration,  $C^\circ$ , is 1 molal (moles solute/kg solvent) for dilute solutions. Often molality is approximated with molarity (moles solute/Liter solution).
- the standard state for a liquid is the pure liquid
- the standard state for a solid is the pure solid

Thus, when we discuss the activity of a gas, we actually are discussing the ratio of the effective pressure to the standard state pressure:

$$a_{gas} = \frac{P}{P^\circ} \quad (6.4.3)$$

- $a_{gas}$  is a ratio with **no units**.

Likewise, the activity of a solute in solution would be:

$$a_{solute} = \frac{C}{C^\circ} \quad (6.4.4)$$

- $a_{solute}$  is a ratio with **no units**.

For all solids, the activity is a ratio of the concentration of a pure solid to the concentration of that same pure solid

$$a_{solid} = \frac{C_{\text{effective solid}}}{C_{\text{effective solid}}^{\circ}} = 1 \quad (6.4.5)$$

- $a_{solid}$  **always** has a value of 1 with no units.

For all liquids, the activity is a ratio of the concentration of a pure liquid to the concentration of that same pure liquid:

$$a_{liquid} = \frac{C_{\text{effective liquid}}}{C_{\text{effective liquid}}^{\circ}} = 1 \quad (6.4.6)$$

- $a_{liquid}$  **always** has a value of 1 with no units.

For most experimental situations, solutions are assumed to be dilute with respect to the solvent. This assumption implies the solvent can be approximated with pure liquid. According to [Raoult's Law](#), the vapor pressure of the solvent in a solution is equal to the mole fraction of the solvent in the solution times the vapor pressure of the pure solvent:

$$\chi = \frac{P}{P^{\circ}} \quad (6.4.7)$$

The mole fraction of solvent in a dilute solution is approximately 1, so the vapor pressure of the solution is essentially identical to the vapor pressure of the pure solvent. This means that the activity of a solvent in dilute solution will always has a value of 1, with no units.

Activity indicates how many particles "appear" to be present in the solution, which is different from how many actually are present. Hence, activity is a "fudge factor" to ideal solutions that correct the true concentration.

- $a_{gas}$  is a ratio with **no units**.
- $a_{solute}$  is a ratio with **no units**.
- $a_{solid}$  is **always** 1 with no units.
- $a_{liquid}$  is **always** 1 with no units.

## Estimating Activities

The activity of a substance can be estimated from the nominal concentration of that substance ( $C$ ) by using an activity coefficient,  $\gamma$ :

$$a = \gamma \cdot [C] \quad (6.4.8)$$

The value of  $\gamma$  depends upon the substance, the temperature, and the concentration of all solute particles in the solution. The lower the concentration of all solute particles in the solution, the closer the value of  $\gamma$  for each solute approaches 1:

$$\lim_{[C] \rightarrow 0} \gamma \rightarrow 1 \quad (6.4.9)$$

Therefore, as  $\gamma$  approaches 1, the value of  $a$  for the solute approaches  $C$ .

$$\lim_{\gamma \rightarrow 1} a \rightarrow [C] \quad (6.4.10)$$

The activity coefficient for a nonvolatile, neutral solute is often estimated by non-linear curve fitting, taking into account the molality of the solute and the activity of the solvent (usually its vapor pressure). In most situations, it is more practical to look up the values of the activity coefficient for a given solute than it is to carry out the curve fitting.

Table 6.4.1: Activity Coefficients

m/(mol kg <sup>-1</sup> )	HCl	LiCl	NaCl	LiNO <sub>3</sub>	NaNO <sub>3</sub>
0.01	0.904	0.903	0.902	0.903	0.900
0.02	0.875	0.873	0.870	0.872	0.866
0.05	0.830	0.825	0.820	0.825	0.811

m/(mol kg <sup>-1</sup> )	HCl	LiCl	NaCl	LiNO <sub>3</sub>	NaNO <sub>3</sub>
0.10	0.796	0.790	0.778	0.788	0.762
0.2	0.767	0.757	0.735	0.752	0.703
0.4	0.755	0.740	0.693	0.728	0.638
0.6	0.763	0.743	0.673	0.727	0.599
0.8	0.783	0.755	0.662	0.733	0.570
1.0	0.809	0.774	0.657	0.743	0.548
1.2	0.840	0.796	0.654	0.757	0.530
1.4	0.876	0.823	0.655	0.774	0.514
1.6	0.916	0.853	0.657	0.792	0.501
1.8	0.960	0.885	0.662	0.812	0.489
2.0	1.009	0.921	0.668	0.835	0.478
2.5	1.147	1.026	0.688	0.896	0.455
3.0	1.316	1.156	0.714	0.966	0.437
3.5	1.518	1.317	0.746	1.044	0.422
4.0	1.762	1.510	0.783	1.125	0.408
4.5	2.04	1.741	0.826	1.215	0.396
5.0	2.38	2.02	0.874	1.310	0.386

Estimating the activity coefficient of electrolytes (solutes that dissolve or react with the solvent to form ions) depends upon the number of ions formed by the dissociation of the solute in solution or the reaction of the solute with the solution, because each ion formed is dealt with individually. In a theoretical, infinitely dilute ideal solution, an electrolyte would dissociate or react completely to form an integer number of independent ions. For example, 1 mole of NaCl would dissociate to form 2 moles of ions (1 mole of Na<sup>+</sup> ions and 1 mole of Cl<sup>-</sup> ions). In reality, it is found that electrolytes almost always act as if they contain **fewer** moles of ions than expected based on the formal concentration. This non-ideality is attributed to the degree of dissociation/reaction of the solute, to the solute-solvent interactions such as complex ion formation, and to the solute-solute interactions such as ion pairing. An activity coefficient incorporates the particle interactions into a single term that modifies the formal concentration to give an estimate of the effective concentration, or activity, of each ion.

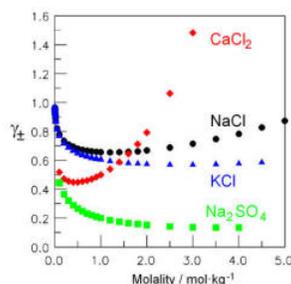


Figure 6.4.1: The dependence of the mean ionic activity coefficient for different salts at 25°C in water as function of concentration.

At infinite dilution, *gamma* is solely determined by the Debye-Hückel limiting law (Equation 6.4.11) and depends only on the number and charges of the cations and anions. This means that the same limiting mean ionic activity coefficient is found for sodium chloride and potassium chloride and that also the values for the 2-1 and 1-2 salts sodium sulfate and calcium chloride are identical. At higher electrolyte concentrations though, these values change very strongly and are usually modeled using empirical parameters regressed to the experimental data.

Electrolytes almost always act as if they contain **fewer** moles of ions than expected based on the formal concentration.

Single ion activity coefficients are calculated using various forms of the [Debye-Hückel equation](#):

$$\log \gamma = \frac{-0.51z^2\sqrt{\mu}}{1 + \frac{\alpha\sqrt{\mu}}{305}} \quad (6.4.11)$$

This equation takes into account the solution environment as well as the individual characteristics of the specific ion of interest. It is not difficult to calculate single ion activity coefficients, but tables of these activity coefficients for many common ions in solutions of various concentrations are available (e.g., Table 6.4.1).

## Applications of Activities

The [law of mass action](#) states that a reaction at a constant temperature will proceed spontaneously and predominantly in one direction until a constant ratio of concentrations of products and reactants is obtained. For the generic reaction



the ratio of concentrations (called the mass action expression or equilibrium constant expression) is

$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = Q \quad (6.4.13)$$

where [ ] represents concentration in

$$\frac{\text{moles of solute}}{\text{Liter of solution}} \quad (6.4.14)$$

This ratio can take on any value greater than zero, depending on the reaction conditions. Thus, it is often called the **instantaneous reaction quotient**,  $Q$ . The term “instantaneous” signifies that the reaction will (and is) proceeding spontaneously to reach a constant ratio of products and reactants. When the reaction attains that constant ratio of products and reactants, it has reached a state of dynamic equilibrium, and the ratio of concentrations can be represented by the symbol  $K$ , the equilibrium constant:

$$\frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b} = K \quad (6.4.15)$$

Laws of mass action and equilibrium constants are discussed in most general chemistry textbooks, but they are often discussed as if they were describing ideal systems. For instance, if all of the substances are gases, partial pressures are used in the mass-action expression. If the substances are in solution, molarities are used in the mass-action expression. To be thermodynamically correct, however, the **activities** of the substances must be compared in the mass-action expression.

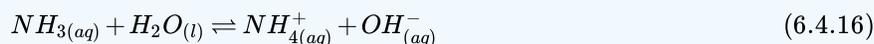
Activities are needed for precise work because, unlike concentrations, activities contain information about the effects of the solvent and other surrounding particles on the behavior of the particles of interest. Using any unit of comparison other than activities will give an incorrect value for  $K$ , but it is assumed that the approximate value is close enough to the true value for most situations. Many [tables](#) list  $K$  values to 2-3 significant digits, but this degree of precision is valid only under the exact experimental conditions used to obtain those values.

## The Derivation of Mass Action Expressions

Given all of the above information on activities, it is now possible to show how a true mass-action equation involving activities can be approximated by a mass-action equation involving molarities. It should be noted that just as the activities were unitless ratios, the molarities and molarities that appear in the following approximations should also be thought of as unitless ratios of concentrations divided by the standard state concentration.

### ✓ Example 6.4.2: A Solution of Ammonia in Water

Starting with the mass action equation in terms of activities, show all the approximations needed to obtain the mass action equation in terms of molar concentrations for the reaction:



#### Solution

$$Q = \frac{a_{NH_4^+} a_{OH^-}}{a_{NH_3} a_{H_2O}} = \frac{a_{NH_4^+} a_{OH^-}}{a_{NH_3} (1)} \quad (6.4.17)$$

- assume  $a_{H_2O} \approx 1$  because water is the solvent in a dilute solution

$$Q = \frac{a_{NH_4^+} a_{OH^-}}{a_{NH_3}} = \frac{\gamma_{NH_4^+} \gamma_{OH^-} m_{NH_4^+} m_{OH^-}}{\gamma_{NH_3} m_{NH_3}} \quad (6.4.18)$$

- assume activity = (activity coefficient)(molality)

$$Q = \frac{\gamma_{NH_4^+} \gamma_{OH^-} m_{NH_4^+} m_{OH^-}}{\gamma_{NH_3} m_{NH_3}} \approx \frac{\gamma_{NH_4^+} \gamma_{OH^-} [NH_4^+][OH^-]}{\gamma_{NH_3} [NH_3]} \quad (6.4.19)$$

- assume molarity [ ]  $\approx$  molality in dilute solutions

$$Q \approx \frac{\gamma_{NH_4^+} \gamma_{OH^-} [NH_4^+][OH^-]}{\gamma_{NH_3} [NH_3]} \approx \frac{[NH_4^+][OH^-]}{[NH_3]} \quad (6.4.20)$$

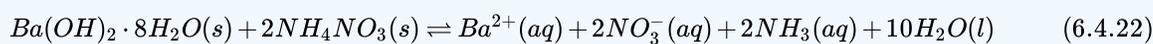
- assume  $\frac{\gamma_{NH_4^+} \gamma_{OH^-}}{\gamma_{NH_3}} \approx 1$  because the solution is dilute

Therefore the final mass action equation typically used for this reaction is

$$Q \approx \frac{[NH_4^+][OH^-]}{[NH_3]} \quad (6.4.21)$$

### ✓ Example 6.4.3: A Reaction of Two Solids that Produces a Solution

Starting with the mass action equation in terms of activities, show all the approximations needed to obtain the mass action equation in terms of molar concentrations for the reaction:



#### Solution

$$Q = \frac{a_{Ba^{2+}} a_{NO_3^-}^2 a_{NH_3}^2 a_{H_2O}^{10}}{a_{Ba(OH)_2 \cdot 8H_2O} a_{NH_4NO_3}^2} = \frac{a_{Ba^{2+}} a_{NO_3^-}^2 a_{NH_3}^2 \cdot (1)}{(1) \cdot (1)} = a_{Ba^{2+}} a_{NO_3^-}^2 a_{NH_3}^2 \quad (6.4.23)$$

- $a = 1$  for solids and for solvent

$$Q = a_{Ba^{2+}} a_{NO_3^-}^2 a_{NH_3}^2 = \gamma_{Ba^{2+}} \gamma_{NO_3^-}^2 \gamma_{NH_3}^2 m_{Ba^{2+}} m_{NO_3^-}^2 m_{NH_3}^2 \quad (6.4.24)$$

- activity = (activity coefficient)(molality)

$$Q = \gamma_{Ba^{2+}} \gamma_{NO_3^-}^2 \gamma_{NH_3}^2 m_{Ba^{2+}} m_{NO_3^-}^2 m_{NH_3}^2 \approx \gamma_{Ba^{2+}} \gamma_{NO_3^-}^2 \gamma_{NH_3}^2 [Ba^{2+}] [NO_3^-]^2 [NH_3]^2 \quad (6.4.25)$$

- molarity [ ]  $\approx$  molality in dilute solutions

$$Q \approx \gamma_{Ba^{2+}} \gamma_{NO_3^-}^2 \gamma_{NH_3}^2 [Ba^{2+}] [NO_3^-]^2 [NH_3]^2 \approx [Ba^{2+}] [NO_3^-]^2 [NH_3]^2 \quad (6.4.26)$$

- $\gamma_{Ba^{2+}} \gamma_{NO_3^-}^2 \gamma_{NH_3}^2 \approx 1$  because the solution is dilute

$$Q \approx [Ba^{2+}] [NO_3^-]^2 [NH_3]^2$$

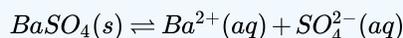
✓ Salt

Determine the molar solubility  $\frac{\text{moles}}{\text{Liter}}$  of the slightly soluble solid,  $\text{BaSO}_4$ , in Pure Water and An Aqueous 0.1 M NaCl Solution?

**Solution**

Pure Water

Barium sulfate is a solid that is slightly soluble in water, with a  $K_{sp}$  value of  $1.1 \times 10^{-10}$ :



This solution is dilute enough that the  $\text{Ba}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{OH}^-$ , and  $\text{H}^+$  ions will not affect each other greatly, thus the activity of the ions closely approaches their formal concentration. In this nearly ideal aqueous solution, the mass action expression would be

$$1.1 \times 10^{-10} = a_{\text{Ba}} \cdot a_{\text{SO}_4} \approx [\text{Ba}^{2+}][\text{SO}_4^{2-}] \quad (6.4.27)$$

Remember that  $\text{BaSO}_4$  is a solid, with an activity equal to 1. At equilibrium, the  $[\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = 1.05 \times 10^{-5}$  M.

An Aqueous 0.1 M NaCl Solution

A saturated aqueous solution of  $\text{BaSO}_4$  that also is 0.1 M in NaCl is no longer near to ideality. The  $\text{Na}^+$  and  $\text{Cl}^-$  ions surround the  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$  ions and prevent these ions from being able to reform solid  $\text{BaSO}_4$  readily as they did in pure water. The activities of the  $\text{Ba}^{2+}$  and the  $\text{SO}_4^{2-}$  ions will be lower than their formal concentrations. However, the product of the activities must still be equal to the true (thermodynamic) equilibrium constant.

$$1.1 \times 10^{-10} = a_{\text{Ba}} \cdot a_{\text{SO}_4} = \gamma_{\text{Ba}}[\text{Ba}^{2+}] \cdot \gamma_{\text{SO}_4}[\text{SO}_4^{2-}] \quad (6.4.28)$$

With the total amount of  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Ba}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{OH}^-$ , and  $\text{H}^+$  ions in the solution,  $\gamma_{\text{Ba}} = 0.38$  and  $\gamma_{\text{SO}_4} = 0.355$ .

$$1.1 \times 10^{-10} = a_{\text{Ba}} \cdot a_{\text{SO}_4} = (0.38)[\text{Ba}^{2+}](0.355)[\text{SO}_4^{2-}] \quad (6.4.29)$$

$$8.2 \times 10^{-10} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \quad (6.4.30)$$

$$[\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = 2.9 \times 10^{-5} \quad (6.4.31)$$

The net result is that more solid  $\text{BaSO}_4$  will dissolve in the 0.1M NaCl solution than in water, and the experimental equilibrium constant will seem to be larger than the thermodynamic equilibrium constant.

### Colligative Properties

The van 't Hoff factor,  $i$ , is a term that often appears in [colligative property](#) calculations to account for the fact that electrolytes will form two or more moles of ions per every mole of electrolyte. In most cases, the solutions are treated as if they are ideal, in which case  $i$  will equal an integer representing the total number of independent ions per one formula unit of the solute (Table 2).

Table 6.4.2: Integer van 't Hoff factors for Colligative Properties

Compound	$i$
Sucrose	1
NaCl	2
MgBr <sub>2</sub>	3
CaCl <sub>2</sub>	3
Na <sub>3</sub> PO <sub>4</sub>	4
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	5

The van 't Hoff factor is actually rarely an integer, and was, in fact, developed to take into account the non-ideality of solutes. Tables listing the  $i$  values for specific compounds in specific solutions are available, but it is also possible to use activities to estimate to effective concentrations of ions in solution for use in colligative property calculations.

✓ Example 6.4.5

What is the freezing point of a 0.1 m BaCl<sub>2</sub> aqueous solution?

**Solution**

The calculation for an ideal solution would be  $\Delta T = mki$ , where  $m = 0.1 \text{ molal}$ ,  $k = 1.86 \frac{^{\circ}\text{C}}{\text{molal}}$ , and  $i = 3$ . The resulting  $\Delta T$  is

$$\Delta T = (0.1 \text{ molal}) \left( 1.86 \frac{^{\circ}\text{C}}{\text{molal}} \right) (3) = 0.558^{\circ}\text{C} \quad (6.4.32)$$

if non-ideality is assumed, the calculation becomes

$$\Delta T = \gamma_{\text{Ba}} \cdot (\gamma_{\text{Cl}})^2 \cdot (m_{\text{Ba}})(m_{\text{Cl}})^2 \quad (6.4.33)$$

Substituting in the estimated  $\gamma$  values of  $\gamma_{\text{Ba}} = 0.38$  and  $\gamma_{\text{Cl}} = 0.755$ , the ion activities are

- $a_{\text{Ba}} = (0.38)(0.1) = 0.038$
- $a_{\text{Cl}} = (0.755)(0.2) = 0.151$

and the  $\Delta T$  is

$$\Delta T = (0.038 + 0.151)(1.86^{\circ}\text{C}) = 0.351^{\circ}\text{C} \quad (6.4.34)$$

The  $\Delta T$  obtained using activities is lower than the  $\Delta T$  obtained when using an integer value for  $i$  because the activity values take into account the fact that the ions in the solution are not able to act as free and independent particles because of their interactions with each other and with the solvent,

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