Activity is a measure of the effective concentration of a species under non-ideal (e.g., concentrated) conditions. This determines the real chemical potential for a real solution rather than an ideal one.

**Introduction**

Activities and concentrations can both be used to calculate equilibrium constants and reaction rates. However, most of the time we use concentration even though activity is also a measure of composition, similar to concentration. It is satisfactory to use concentration for diluted solutions, but when you are dealing with more concentrated solutions, the difference in the observed concentration and the calculated concentration in equilibrium increases. This is the reason that the activity was initially created.

\[ a = e^{\frac{\mu - \mu_0}{RT}} \tag{1} \]

where

- \( a \) = Activity
- \( \mu \) is chemical potential (dependent on standard state) which is Gibbs Energy per mole
- \( \mu_0 \) is the standard chemical potential
- \( R \) is the gas constant
- \( T \) is the absolute Temperature

**Non-ideality in Gases (Fugacity)**

Fugacity is the effective pressure for a non-ideal gas. The pressures of an ideal gas and a real gas are equivalent when the chemical potential is the same. The equation that relates the non-ideal to the ideal gas pressure is:

\[ f = \phi P \tag{2} \]

with

- \( f \) represents fugacity,
- \( P \) is the pressure for an ideal gas, and
- \( \phi \) is the fugacity coefficient.

For an ideal gas, the fugacity coefficient is 1.

**Non-ideality in Solutions**

**pH**

We have become accustomed to using the equation \( pH = -\log[H^+] \), but this equation not accurate at all
concentrations. A better expression for pH is \( \text{pH} = -\log[a_H^+] \) which accounts for the activity, \( a \). The only reason that other indicators may correctly seem to measure the acidity, which was equivalent to \( -\log[H^+] \), is because of the use of Beer’s law, which uses concentration rather than activity.¹

References

3. PAC, 1996, 68, 957

Problems

1. What is the purpose of using activity rather than concentration?
2. If the ratio of fugacity to the pressure of the ideal gas is 1 then what is the activity coefficient?
3. If pH does not = -\log[H^+] then why do the calculations seem to show the correct acidity?
4. If concentration is not accurate does that mean we should start only using activity instead?

Solutions

1. Activity is more accurate in more concentrated solutions
2. The coefficient is one because the gas is in a similar state as an ideal gas.
3. The use of Beer’s law which uses also concentration rather than activity results in the seemingly correct results.
4. Activity is only required highly concentrated solutions.