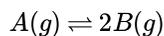


9.5: Degree of Dissociation

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	$2B$
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

$$\begin{aligned}\chi_A &= \frac{n(1-\alpha)}{n(1-\alpha) + 2n\alpha} \\ &= \frac{1-\alpha}{1+\alpha} \\ \chi_B &= \frac{2\alpha}{1+\alpha}\end{aligned}$$

Based on these mole fractions

$$K_x = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2}{\frac{1-\alpha}{1+\alpha}} \quad (9.5.1)$$

$$= \frac{4\alpha^2}{1-\alpha^2} \quad (9.5.2)$$

And so K_p , which can be expressed as

$$K_p = K_x (p_{tot})^{\sum \nu_i} \quad (9.5.3)$$

is given by

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

✓ Example 9.5.1

Based on the 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



	$N_2O_4(g)$	$NO_2(g)$
ΔG_f° (kJ/mol)	99.8	51.3

Solution

First, the value of K_p can be determined from ΔG_{rxn}° via an application of Hess' Law.

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

So, using the relationship between thermodynamics and equilibria

$$\begin{aligned}\Delta G_f^{\circ} &= -RT \ln K_p \\ 2800 \text{ kJ/mol} &= -(8.314 \text{ J/(mol K)})(298 \text{ K}) \ln K_p \\ K_p &= 0.323 \text{ atm}\end{aligned}$$

The degree of dissociation can then be calculated from the ICE tables at the top of the page for the dissociation of $N_2O_4(g)$:

$$\begin{aligned}K_p &= \frac{4\alpha^2}{1-\alpha^2}(p_{tot}) \\ 0.323 \text{ atm} &= \frac{4\alpha^2}{1-\alpha^2}(1.00 \text{ atm})\end{aligned}$$

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 9.5.2

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.

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

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

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

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 Equation 9.5.3, so

$$K_p = 0.7604(0.890 \text{ atm})^{-1} = 0.792 \text{ atm}^{-1}$$

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

$$\begin{aligned}\Delta G_{rxn}^o &= -(8.314 \text{ J}/(\text{mol K}))(1350 \text{ K}) \ln(0.792) \\ &= 2590 \text{ J}/\text{mol}\end{aligned}$$

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