

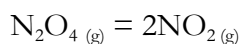
Solving Gas-Phase Equilibria Problems

The following problem is an example of determining the equilibrium partial pressures in a gas-phase equilibrium problem. What is worth pointing out right at the start is that the ‘partial pressure’ of a gas is in effect the ‘concentration of the gas’, as the pressure of a gas is directly proportional to its concentration. A large partial pressure indicates a large concentration, whilst a low partial pressure indicates a lower concentration – recall that concentration is the amount of entities per unit volume. For example, in solution chemistry it is the number of moles per litre of solvent.

Question: What are the equilibrium partial pressures of N_2O_4 and NO_2 when 0.2 mol of each gas are mixed in a 4.0 L flask at 100 °C ($K=11$ atm)

To solve this problem I will take you through the relevant steps, explaining what I am doing at each step and where appropriate why I am doing it. There are many ways to solve these problems, they are in effect simply mathematical treatments, and hence you might not necessarily “like” the method which I use – if you understand the concepts, you will no doubt be able to derive your own methodology to use. I welcome members of the class to use their own methods where appropriate.

STEP ONE: Write the balance chemical equation



STEP TWO: Find the initial partial pressures P_{NO_2} and $P_{\text{N}_2\text{O}_4}$ using the Ideal Gas Law ($pV = nRT$); where R is a constant (it doesn’t change) and T is the absolute temperature (in Kelvin – not degrees celcius!)

$$p = nRT / V$$

$$P_{\text{NO}_2} = P_{\text{N}_2\text{O}_4} = (0.2 \text{ mol} \times 0.0821 \text{ L atm/mol K} \times 373 \text{ K}) / 4.0 \text{ L}$$

The partial pressure of NO_2 = the partial pressure of N_2O_4 because we put the same amount (0.2 mol) of each gas into the reaction vessel, remember that the partial pressure is like the concentration of the gas.

From the calculation above then we find that $P_{\text{NO}_2} = P_{\text{N}_2\text{O}_4} = 1.5$ atm

STEP THREE: Calculate the Reaction Quotient

$$Q = P_{\text{NO}_2}^2 / P_{\text{N}_2\text{O}_4} = (1.5 \text{ atm})^2 / (1.5 \text{ atm}) = 1.5 \text{ atm}$$

In the question we were told that the equilibrium constant (K) is equal to 11 atm. $Q < K$, so the reaction will proceed in a forward direction, until it reaches equilibrium. That is to say, we need to build up a larger product concentration to achieve equilibrium.

STEP FOUR: For each mole of N_2O_4 that reacts, 2 moles of NO_2 are formed. We can construct a “change table” – similar to what we did when calculating the pH of weak acids/bases.

	N_2O_4	NO_2
P_o	1.50 atm	1.50 atm
ΔP	- x atm	+ 2x atm
P_{eq}	(1.50 - x) atm	(1.50 + 2x) atm

P_o = the initial partial pressure (before the reaction begins)

ΔP = the change in partial pressure as a result of chemical reaction

P_{eq} = the newly established equilibrium partial pressure

STEP FIVE: Now we can calculate the equilibrium partial pressure (P_{eq}) using the equilibrium constant expression (K).

$$K_{eq} = 11 = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{(1.50 + 2x)^2}{(1.50 - x)}$$

Rearrangement then follows:

$$\begin{aligned} 11(1.5 - x) &= (1.5 + 2x)^2 \\ 11(1.5 - x) &= 2.25 + 6x + 4x^2 \\ 16.5 - 11x &= 2.25 + 6x + 4x^2 \\ -16.5 + 16.5 - 11x + 11x &= -16.5 + 11x + 6x + 4x^2 + 2.25 \\ 0 &= 4x^2 + 17x - 14.25 \end{aligned}$$

The Rearrangement then gives; $4x^2 + 17x - 14.25 = 0$, which is a quadratic expression – hence ‘x’ can be solved through the use of the quadratic equation (two roots will be given, the real root – a positive value is the one of chemical value, the imaginary root – the negative one, should be ignored.)

Using the quadratic equation we find that $x = 0.717$

STEP SIX: Calculating the equilibrium partial pressures of all species

$$P_{\text{N}_2\text{O}_4} = 1.50 \text{ atm} - 0.717 = 0.783 \text{ atm}$$

$$P_{\text{NO}_2} = 1.50 \text{ atm} + 2(0.717) = 2.93 \text{ atm}$$

CHECK THE CALCULATION BY PUTTING THESE VALUES INTO THE EQUILIBRIUM EXPRESSION AND SEEING IF YOU GET THE SAME VALUE FOR THE EQUILIBRIUM CONSTANT (K = 11)