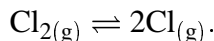


Chemistry 2720 Fall 2003 Quiz 4 Solutions

There are two ways to solve this problem: The easy way and the hard way.

The easy way: The equilibrium is



Note that it doesn't matter how you balanced the reaction, provided everything you do from here on is consistent with your reaction as you wrote it. For this reaction,

$$\Delta\bar{G}^\circ = 2\Delta\bar{G}_{f(\text{Cl})}^\circ = 210.610\text{kJ/mol}.$$

We can therefore calculate the equilibrium constant for the reaction:

$$\begin{aligned} K &= e^{-\Delta\bar{G}^\circ/(RT)} \\ &= \exp\left(\frac{-210610\text{J/mol}}{(8.314472\text{JK}^{-1}\text{mol}^{-1})(298.15\text{K})}\right) \\ &= 1.27 \times 10^{-37}. \end{aligned}$$

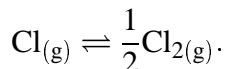
Since

$$K = a_{\text{Cl}}^2/a_{\text{Cl}_2},$$

and since the smallness of the equilibrium constant indicates that extremely little of the Cl_2 will dissociate, we have

$$\begin{aligned} a_{\text{Cl}_2} &= \frac{P_{\text{Cl}_2}}{P^\circ} = \frac{1.3\text{bar}}{1\text{bar}} = 1.3. \\ a_{\text{Cl}}^2 &= Ka_{\text{Cl}_2} = 1.65 \times 10^{-37}. \\ \therefore a_{\text{Cl}} &= \sqrt{1.65 \times 10^{-37}} = 4.06 \times 10^{-19}. \\ \therefore P_{\text{Cl}} &= a_{\text{Cl}}P^\circ = 4.06 \times 10^{-19}\text{bar}. \end{aligned}$$

The hard way: The starting point is roughly the same, namely a balanced reaction. Just to show you that it really doesn't matter how you write the reaction, I'll balance it a different way than in my previous solution:



$$\begin{aligned} \therefore \Delta\bar{G}^\circ &= -\Delta\bar{G}_{f(\text{Cl})}^\circ = -105.305\text{kJ/mol}. \\ \therefore K &= e^{-\Delta\bar{G}^\circ/(RT)} \\ &= \exp\left(\frac{105305\text{J/mol}}{(8.314472\text{JK}^{-1}\text{mol}^{-1})(298.15\text{K})}\right) \\ &= 2.81 \times 10^{18}. \end{aligned}$$

If you don't notice at this point that K is enormous, i.e. that the reaction strongly favors Cl_2 , you might proceed as follows: The total pressure is 1.3 bar, so we have

$$P_{\text{Cl}} + P_{\text{Cl}_2} = 1.3\text{bar}.$$

If we divide this equation by the standard pressure (1 bar), we get

$$a_{\text{Cl}} + a_{\text{Cl}_2} = 1.3,$$

or

$$a_{\text{Cl}_2} = 1.3 - a_{\text{Cl}}.$$

Note that you can't do an initial, change, final table because the pressure rather than the volume is fixed. If the volume is constant, then the number of moles is simply proportional to the pressure and stoichiometric arguments can be applied to the latter quantities. If the pressure is constant on the other hand, the volume will adapt to the number of moles and there isn't a fixed proportionality constant between P and n .

Carrying on, since

$$K = a_{\text{Cl}_2}^{1/2} / a_{\text{Cl}},$$

we have

$$\begin{aligned} K &= \frac{(1.3 - a_{\text{Cl}})^{1/2}}{a_{\text{Cl}}}. \\ \therefore K a_{\text{Cl}} &= (1.3 - a_{\text{Cl}})^{1/2}. \\ \therefore K^2 a_{\text{Cl}}^2 &= 1.3 - a_{\text{Cl}}. \\ \therefore 0 &= (2.81 \times 10^{18})^2 a_{\text{Cl}}^2 + a_{\text{Cl}} - 1.3. \\ \therefore a_{\text{Cl}} &= \frac{-1 \pm \sqrt{1^2 - 4(2.81 \times 10^{18})^2(-1.3)}}{2(2.81 \times 10^{18})^2}. \end{aligned}$$

When solving the quadratic equation, there's always the problem of which root to use. In this case, since the quantity under the square root is enormous, we'll have to use the + root to get a positive answer. I get

$$a_{\text{Cl}} = 4.06 \times 10^{-19},$$

i.e. the same answer as we would have obtained by the easy method of solution. The final answer is thus, as above,

$$P_{\text{Cl}} = 4.06 \times 10^{-19} \text{ bar}.$$

The moral of this story is that it pays to think about the sizes of the numbers in these problems.