

Solutions to the Practice Problems on Equilibrium

$$1. \quad (a) \quad K = \frac{a_{\text{CO}}^2}{(a_{\text{C}})(a_{\text{CO}_2})} = \frac{(P_{\text{CO}}/P^\circ)^2}{(1)(P_{\text{CO}_2}/P^\circ)} = \frac{P_{\text{CO}}^2}{P^\circ P_{\text{CO}_2}}$$

$$(b) \quad K = \frac{a_{\text{H}_2\text{CO}_3}}{(a_{\text{CO}_2})(a_{\text{H}_2\text{O}})} = \frac{[\text{H}_2\text{CO}_3]/c^\circ}{(P_{\text{CO}_2}/P^\circ)X_{\text{H}_2\text{O}}} = \frac{P^\circ[\text{H}_2\text{CO}_3]}{c^\circ P_{\text{CO}_2} X_{\text{H}_2\text{O}}}$$

It is usually the case that the mole fraction of the solvent is very close to 1. It is then a reasonable approximation to write

$$K = \frac{P^\circ[\text{H}_2\text{CO}_3]}{c^\circ P_{\text{CO}_2}}.$$

$$(c) \quad K = \frac{(a_{\text{NH}_3})^2(a_{\text{CO}_2})(a_{\text{H}_2\text{O}})}{a_{(\text{NH}_4)_2\text{CO}_3}} = \frac{(P_{\text{NH}_3}/P^\circ)^2(P_{\text{CO}_2}/P^\circ)(P_{\text{H}_2\text{O}}/P^\circ)}{1} = \frac{P_{\text{NH}_3}^2 P_{\text{CO}_2} P_{\text{H}_2\text{O}}}{(P^\circ)^4}$$

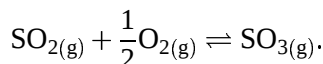
$$(d) \quad K = \frac{(a_{\text{Ba}^{2+}})(a_{\text{OH}^-})^2}{a_{\text{Ba}(\text{OH})_2}} = \frac{([\text{Ba}^{2+}]/c^\circ)([\text{OH}^-]/c^\circ)^2}{1} = \frac{[\text{Ba}^{2+}][\text{OH}^-]^2}{(c^\circ)^3}$$

Because $P^\circ = 1 \text{ atm}$ and $c^\circ = 1 \text{ mol/L}$, we don't normally write down these factors. However, it then becomes essential to remember to express concentrations in mol/L and pressures in atm.

2. The reaction ratio for this reaction is $Q = a_{\text{I}}^2/a_{\text{I}_2}$. According to the measurements, $a_{\text{I}_2} = (0.87 \text{ atm})/(1 \text{ atm}) = 0.87$ and $a_{\text{I}} = 8.2 \times 10^{-7}$. The reaction ratio therefore has the value $Q = 7.7 \times 10^{-13}$. Since this is much smaller than the equilibrium constant, the reaction is not in equilibrium. In fact, the dissociation of iodine molecules is spontaneous under these conditions.

3. The equilibrium constant is $K = \frac{(a_{\text{PCl}_3})(a_{\text{Cl}_2})}{a_{\text{PCl}_5}} = \frac{(0.56)(0.17)}{1.8 \times 10^{-3}} = 53$.

4. We can't do anything in these problems without a balanced reaction. The reaction is



The corresponding equilibrium constant is

$$K = \frac{a_{\text{SO}_3}}{(a_{\text{SO}_2})(a_{\text{O}_2})^{1/2}}.$$

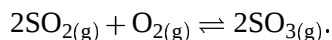
Note that the data are given to us in the wrong form: The activities of gases are computed from the pressure, not from the number of moles in a litre. However, the ideal gas law lets us calculate pressures from these concentrations: $P = RT \left(\frac{n}{V} \right)$. I like to do calculations with the ideal gas law in SI units, because it's less likely that I will make mistakes if I'm completely consistent about this. There are 1000 L in 1 m^3 , so the concentration of (for instance) sulfur dioxide in SI units is 3.77 mol/m^3 . Thus

$$P_{\text{SO}_2} = (8.314510 \text{ J K}^{-1} \text{ mol}^{-1})(1000 \text{ K})(3.77 \text{ mol/m}^3) = 31.3 \text{ kPa} = 0.309 \text{ atm}.$$

Similarly, $P_{\text{SO}_3} = 0.339$ and $P_{\text{O}_2} = 0.353 \text{ atm}$. The equilibrium constant is therefore

$$K = \frac{0.339}{(0.309)(0.353)^{1/2}} = 1.85.$$

Note that we needed the balanced reaction to determine the form of the equilibrium constant. We could have balanced the reaction differently. For instance, we could have avoided the use of fractions by multiplying the reaction by 2:



The equilibrium constant would then have been

$$K = \frac{a_{\text{SO}_3}^2}{(a_{\text{SO}_2})^2(a_{\text{O}_2})} = 3.41.$$

The value of the equilibrium constant depends on how we balance the reaction. In fact, an equilibrium constant not accompanied by a balanced reaction is meaningless. In some cases to be discussed later (e.g. solubility, acid dissociation), there is a convention about how we should write the reaction. Otherwise, you must always give a balanced reaction when stating an equilibrium constant.

5. We need to know the initial pressure of iodine. We can get this from the ideal gas law ($P = nRT/V$), but first we need to know the number of moles.

$$n_{\text{I}_2} = \frac{25 \text{ g}}{253.808 \text{ g/mol}} = 0.098 \text{ mol}.$$

The initial pressure of molecular iodine is therefore

$$P_{\text{I}_2, \text{initial}} = \frac{(0.098 \text{ mol})(8.314510 \text{ J K}^{-1} \text{ mol}^{-1})(1000 \text{ K})}{12 \times 10^{-3} \text{ m}^3} = 68 \text{ kPa} \equiv 0.67 \text{ atm}.$$

We want to determine the stoichiometric relationships among the activities (which enter into the equilibrium ratio). Since pressure is proportional to number and activity is proportional to pressure, we have

	Initial	Final
a_{I_2}	0.67	a_{I_2}
a_{I}	0	$2(0.67 - a_{\text{I}_2})$

The last entry in the table is obtained by stoichiometry: The number of iodine molecules reacted is calculated by subtracting the final amount from the initial. The number of iodine atoms formed is twice as large, by stoichiometry. Using the data in the table, we see that the equilibrium relationship is

$$\begin{aligned} K &= 0.31 = \frac{a_{\text{I}}^2}{a_{\text{I}_2}} = \frac{[2(0.67 - a_{\text{I}_2})]^2}{a_{\text{I}_2}}. \\ \therefore 0.31a_{\text{I}_2} &= 1.80 - 5.36a_{\text{I}_2} + 4a_{\text{I}_2}^2. \end{aligned}$$

$$\begin{aligned}
\therefore 0 &= 4a_{\text{I}_2}^2 - 5.67a_{\text{I}_2} + 1.80. \\
\therefore a_{\text{I}_2} &= \frac{5.67 \pm \sqrt{5.67^2 - 4(4)(1.80)}}{2(4)} \\
&= \frac{5.67 \pm 1.83}{2(4)} \\
&= 0.94 \text{ or } 0.48
\end{aligned}$$

The first solution is wrong: It corresponds to a larger I_2 pressure than we started with. The second solution is the physically correct one. The equilibrium pressures are therefore $P_{\text{I}_2} = 0.48 \text{ atm}$ and $P_{\text{I}} = 2(0.67 - 0.48 \text{ atm}) = 0.38 \text{ atm}$.

6.

$$P_{\text{COBr}_2, \text{initial}} = \frac{(0.015 \text{ mol})(8.314472 \text{ J K}^{-1} \text{ mol}^{-1})(346.15 \text{ K})}{2.5 \times 10^{-3} \text{ m}^3} = 17 \text{ kPa} \equiv 0.17 \text{ atm}.$$

	Initial	Final
a_{COBr_2}	0.17	$0.17 - x$
a_{CO}	0	x
a_{Br_2}	0	x

$$\begin{aligned}
K &= 5.4 = \frac{(a_{\text{CO}})(a_{\text{Br}_2})}{a_{\text{COBr}_2}} = \frac{x^2}{0.17 - x}. \\
\therefore x^2 &= 5.4(0.17 - x). \\
\therefore 0 &= x^2 + 5.4x - 0.92. \\
\therefore a_{\text{CO}} &= a_{\text{Br}_2} = x = \frac{1}{2} \left(-5.4 \pm \sqrt{5.4^2 - 4(-0.92)} \right) \\
&= 0.165. \\
\therefore a_{\text{COBr}_2} &= 0.17 - x = 0.005.
\end{aligned}$$

The total pressure is

$$P = P_{\text{COBr}_2} + P_{\text{CO}} + P_{\text{Br}_2} = 0.005 + 0.165 + 0.165 \text{ atm} = 0.34 \text{ atm}.$$