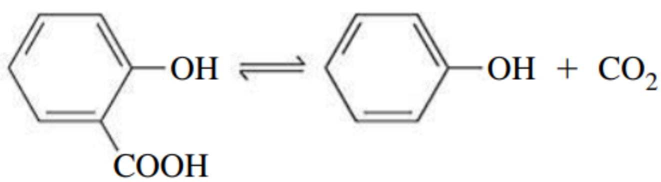
Problems Chapter 15 (Equilibrium)

1. A sample of air with a mole ratio of $N_2$ to $O_2$ of 79:21 is heated to 2500 K. When equilibrium is established in a closed container with air initially at 1.00 atm, the mole percent of NO is found to be 1.8%. Calculate $K_P$ for the reaction.

   $N_2$ (g) + $O_2$ (g) $\Leftrightarrow$ 2 NO (g)

2. The decomposition of salicylic acid to phenol and $CO_2$ was carried out at 200.0 ˚C, a temperature at which the reactant and products are all gaseous. A 0.300 g sample of salicylic acid was introduced into a 50.0 mL reaction vessel, and equilibrium was established. The equilibrium mixture was rapidly cooled to condense salicylic acid and phenol as solids; the $CO_2$ (g) was collected and its volume was measured at 20 ˚C and 730 torr. In two independent experiments, the volumes of $CO_2$ (g) obtained were 48.2 and 48.5 mL, respectively. Calculate $K_P$ for the reaction.




3. One of the key reactions in the gasification of coal is the methanation reaction, in which methane is produced from synthesis gas – a mixture of CO and $H_2$.

   CO (g) + 3 $H_2$ (g) $\Leftrightarrow$ $CH_4$ (g) + $H_2O$ (g)     BH = –230 kJ; $K_c$ = 190 at 1000 K

   a. Is the equilibrium conversion of synthesis gas to methane favored at higher or lower temperatures? Higher or lower pressures?
   b. Assume you have 4.00 mol of synthesis gas with a 3:1 mol ratio of $H_2$ (g) to CO (g) in a 15.0 L flask. What will be the mole fraction of $CH_4$ (g) at equilibrium at 1000 K?

4. A mixture of $H_2S$ (g) and $CH_4$ (g) in the mole ratio 2:1 was brought to equilibrium at 700 ˚C and a total pressure of 1 atm. On analysis, the equilibrium mixture was found to contain $9.54 \times 10^{-3}$ mol $H_2S$. The $CS_2$ present at equilibrium was converted successively to $H_2SO_4$ and then to $BaSO_4$; $1.42 \times 10^{-3}$ mol $BaSO_4$ was obtained. Use these data to determine $K_P$ at 700 ˚C for the reaction

   2 $H_2S$ (g) + $CH_4$ (g) $\Leftrightarrow$ $CS_2$ (g) + 4 $H_2$ (g)

5. The formation of nitrosyl chloride is given by the following equation:

   2 NO (g) + $Cl_2$ (g) $\Leftrightarrow$ 2 NOCl (g)     $K_c = 4.6 \times 10^4$ at 298 K

   In a 1.50 L flask, there are 4.125 mol of NOCl and 0.1125 mol of $Cl_2$ present at equilibrium (298 K).

   a. Determine the partial pressure of NO at equilibrium.
   b. What is the total pressure of the system at equilibrium?

6. Consider the reaction

   $IO_4^-$ (aq) + 2 $H_2O$ (l) $\Leftrightarrow$ $H_4IO_6^-$ (aq)     $K_c = 3.5 \times 10^{-2}$

   If you start with 25.0 mL of a 0.905 M solution of $NaIO_4$, and then dilute it with water to 500.0 mL, what is the concentration of $H_4IO_6^-$ at equilibrium?

7. The reaction

$$PCl_3\ (g) + Cl_2\ (g) \Leftrightarrow PCl_5\ (g)$$

has $K_P$ = 0.0870 at 300 ˚C. A flask is charged with 0.50 atm $PCl_3$, 0.50 atm $Cl_2$, and 0.20 atm $PCl_5$ at this temperature.
   a. Use the reaction quotient to determine the direction the reaction must proceed to reach equilibrium.
   b. Calculate the equilibrium partial pressures of the gases.
   c. What effect will increasing the volume of the system have on the mole fraction of $Cl_2$ in the equilibrium mixture?
   d. The reaction is exothermic. What effect will increasing the temperature of the system have on the mole fraction of $Cl_2$ in the equilibrium mixture?

8. Carbon monoxide replaces oxygen in oxygenated hemoglobin according to the reaction

$$HbO_2\ (aq) + CO\ (aq) \Leftrightarrow HbCO\ (aq) + O_2\ (aq)$$

   a. Use the reactions and associated equilibrium constants at body temperature to find the equilibrium constant for the reaction just shown.

$$Hb\ (aq) + O_2\ (aq) \Leftrightarrow HbO_2\ (aq) \qquad K_c = 1.8$$

$$Hb\ (aq) + CO\ (aq) \Leftrightarrow HbCO\ (aq) \qquad K_c = 306$$

   b. Suppose that an air mixture becomes polluted with CO at a level of 0.10%. Assuming the air contains 20.0% $O_2$, and that the $O_2$ and CO ratios that dissolve in the blood are identical to the ratios in the air, what is the ratio of HbCO to $HbO_2$ in the blood stream? Comment on the toxicity of CO.

9. Consider the exothermic reaction

$$C_2H_4\ (g) + Cl_2\ (g) \Leftrightarrow C_2H_4Cl_2\ (g)$$

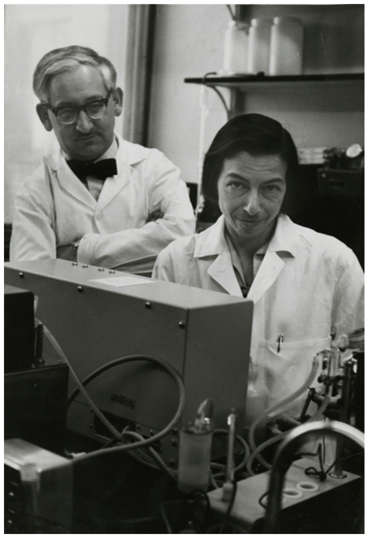
If you were trying to maximize the amount of $C_2H_4Cl_2$ produced, which tactic might you try? Assume that the reaction mixture reaches equilibrium.
   a. Increasing the reaction volume
   b. Removing $C_2H_4Cl_2$ from the reaction mixture as it forms
   c. Lowering the reaction temperature
   d. Adding $Cl_2$

10. Consider the reaction

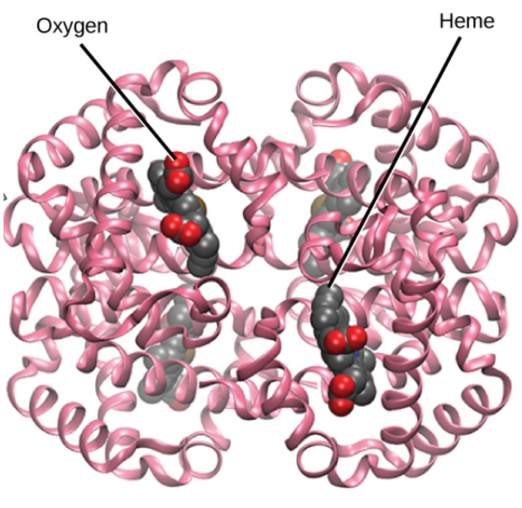
$H_2\ (g) + I_2\ (g) \Leftrightarrow 2\ HI\ (g)$

A reaction mixture at equilibrium at 175 K contains $P_{H2}$ = 0.958 atm, $P_{I2}$ = 0.877 atm, and $P_{HI}$ = 0.020 atm. A second reaction mixture, also at 175 K, contains $P_{H2}$ = $P_{I2}$ = 0.621 atm and $P_{HI}$ = 0.101. Is the second reaction at equilibrium? If not, what will be the partial pressure of HI when the reaction reaches equilibrium at 175 K?

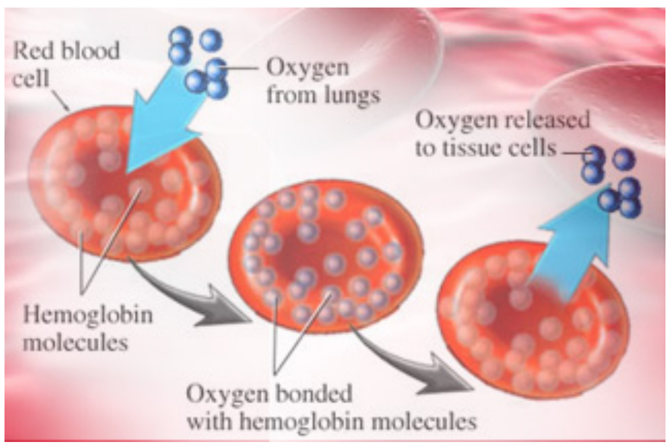
**Ruth Erica Benesch: unraveling the workings of hemoglobin**



Oxygen collected in our lungs needs to be delivered to all the tissues for them to maintain their metabolic functions. Hemoglobin, a protein found in red blood cells, is the vehicle that ferries oxygen molecules to all the cells in our body. It is a large molecule made of four subunits. Each subunit contains a heme group with a $Fe^{2+}$ ion, which is capable of binding an oxygen molecule, carrying it to the cell that needs it and releasing it there, based on the equilibrium reaction below.




(b) Hemoglobin




$$Hb\ (aq) + 4O_2\ (g) \rightleftharpoons Hb\ (O_2)_4\ (aq).$$

Ruth Erica Benesch extensively studied hemoglobin. Benesch was born in a Jewish family and grew up in pre-Second World War Germany. In 1939 she was able to escape with the *Kindertransport* program which rescued Jewish children from Germany to UK. There she met her husband and lifelong scientific partner Reinhold Benesch, who also fled from his native Poland to escape antisemitism. Together they emigrated to USA, obtained their doctorate degrees in biochemistry from Northwestern University and embarked on a forty year-long scientific career dedicated to hemoglobin (on occasion affectionately referring to each other as "R2B2"). When cells use oxygen for metabolism, $CO_2$ is produced. The Benesches found out that high $CO_2$ concentration signals to hemoglobin that oxygen is needed at that area. They also discovered the key role of 2,3-bisphosphoglyceric acid (2,3-BPG) in enabling hemoglobin to release oxygen molecules to cells that need them. 2,3-BPG binds to deoxygenated (oxygen-free) hemoglobin much better than to the oxygenated form, decreasing its affinity for oxygen and promoting oxygen release. This discovery vastly enhanced our knowledge about the respiratory system. Benesch was one of the most cited women in science in the 1970.

**References:**

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