6.16: Problems

Use Le Chatelier's principle to answer questions 1-8.

1. One gram of iodine just dissolves in 2950 mL of water at ambient temperatures. One gram of iodine is added to 1000 mL of pure water and the resulting system is allowed to come to equilibrium. When equilibrium is reached, will all of the iodine have dissolved? What will happen if a small amount of water is added to the equilibrated system?

2. A saturated solution of barium sulfate is in contact with excess solid barium sulfate.

$$BaSO_4\left(s\right)\rightleftharpoons Ba^{2+}+SO_4^{2-}$$

A small amount of a concentrated solution of $BaCl_2$ is added. How does the system respond?

3. In the presence of a catalyst, oxygen reacts with sulfur dioxide to produce sulfur trioxide.

$$SO_2\left(g\right)+½O_2\left(g\right)\rightleftharpoons SO_3\left(g\right)$$

A particular system consists of an equilibrated mixture of these three gases. A small amount of oxygen is added. How does the system respond?

4. A system containing these three gases is at equilibrium.

$$SO_2\left(g\right)+½O_2\left(g\right)\rightleftharpoons SO_3\left(g\right)$$

We suddenly decrease the volume of this system. How does the system respond?

5. In the presence of a catalyst, oxygen reacts with nitrogen to produce nitric oxide.

$$N_2\left(g\right)+O_2\left(g\right)\rightleftharpoons 2NO\left(g\right)$$

A particular system consists of an equilibrated mixture of these three gases. While keeping the temperature constant, we suddenly increase the volume of this system. How does the system respond?

6. Nitric oxide formation

$$N_2\left(g\right)+O_2\left(g\right)\rightleftharpoons 2NO\left(g\right)$$

is endothermic. (At constant temperature, the system absorbs heat as reaction occurs from left to right.) How does the position of equilibrium change when we increase the temperature of this system?

7. Pure water dissociates to a slight extent, producing hydronium, H_3O^+, and hydroxide, OH^-, ions. This reaction is called the autoprotolysis of water.

$$2H_2O\rightleftharpoons H_3O^++OH^-$$

Is the autoprotolysisautoprotolysis reaction endothermic or exothermic? (What happens to the temperature when we mix an acid with a base?) How does the autoprotolysis equilibrium change when we increase the temperature of pure water?

8. At the melting point, most substances are more dense in their solid state than they are in their liquid state. Such a substance is at its melting point at a particular pressure. Suppose that we now increase the pressure on this system. Does the melting point of the substance increase or decrease?

For each of the systems 9 – 20, specify

(a) what phases are present,

(b) the number of phases, P,

(c) the substances that are present,

(d) the number of components*, C, and

(e) the number of degrees of freedom, F.

Assume that the temperature and pressure of each system is constant and that all relevant chemical reactions are at equilibrium.

9. Pure helium gas, He, sealed in a glass bulb.

10. A mixture of helium gas, He, and neon gas, Ne, sealed in a glass bulb.

11. A mixture of N_2O_4 gas and NO_2 gas sealed in a glass bulb. These compounds react according to the equation

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

12. A mixture of N_2O_4 gas, NO_2 gas, and He gas sealed in a glass bulb.

13. A mixture of PCl_5 gas, PCl_3 gas, and Cl_2 gas, sealed in a glass bulb. The proportions of PCl_3 and Cl_2 are arbitrary. These compounds react according to the equation

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

14. A mixture of PCl_5 gas, PCl_3 gas, Cl_2 gas, and He gas sealed in a glass bulb. The proportions of PCl_3 and Cl_2 are arbitrary.

15. A mixture of PCl_5 gas, PCl_3 gas, and Cl_2 gas sealed in a glass bulb. In this particular system, the number of moles of PCl_3 is the same as the number of moles of Cl_2.

16. A saturated aqueous solution of iodine, I_2. The solution is in contact with a quantity of solid I_2.

17. An aqueous solution that contains potassium ion, K^+, iodide ion, I^-, triiodide ion, I_3^-, and dissolved I_2. The solution is in contact with a quantity of solid I_2. Recall that triiodide ion is formed by the reaction

$$I^- + I_2 \rightleftharpoons I_3^-$$

18. An aqueous solution that contains K^+, and I^-. This solution is in contact with a quantity of solid silver iodide, AgI. Recall that AgI is quite insoluble. Neutral molecules of AgI do not exist as such in aqueous solution. The solid substance equilibrates with its dissolved ions according to the reaction

$$AgI\,(s) \rightleftharpoons Ag^+ + I^-$$

19. An aqueous solution that contains K^+, I^-, and chloride ions, Cl^-. This solution is in contact with a mixture of (pure) solid AgI and (pure) solid $AgCl$.

20. An aqueous solution that contains K^+, I^-, Cl^-, and nitrate ions, NO_3^-. This solution is in contact with a mixture of (pure) solid AgI and (pure) solid $AgCl$.

21. A large vat contains oil and water. The oil floats as a layer on top of the water. Orville has another tank with a reserve supply of oil. He also has pipes and pumps that enable him to pump oil between his tank and the vat. Wilbur has a third tank with a reserve supply of water. Wilbur has pipes and pumps that enable him to pump water between his tank and the vat. Their pumps are calibrated to show the volume of oil or water added to or removed from the vat. Normally, Orville and Wilbur work as a team to keep the total mass of liquid in the vat constant. The oil and water have densities of 0.80 kg L^{-1} and 1.00 kg L^{-1}, respectively. Let M_{vat} be the total mass of the liquids in the vat.

(a) If Orville pumps a small volume of oil, dV_{oil}, into or out of the vat, while Wilbur does nothing, what is the change in the mass of liquid in the vat? (i.e., $dM_{vat} = ?$)

(b) If Wilbur pumps a small volume of water, dV_{water}, into or out of the vat, while Orville does nothing, what is the change in the mass of liquid in the vat? (i.e., $dM_{vat} = ?$)

(c) Suppose that Orville and Wilbur make adjustments, dV_{oil} and dV_{water} at the same time, but contrary to their customary practice, they do not coordinate their adjustments with one another. What would be the change in the mass of liquid in the vat? (i.e., $dM_{vat} = ?$)

(d) If Orville and Wilbur make adjustments, dV_{oil} and dV_{water}, at the same time, in such a way as to keep the mass of liquid in the vat constant, what value of dM_{vat} results from this combination of adjustments? (i.e., $dM_{vat} = ?$)

(e) From your answers to (c) and (d), what relationship between dV_{oil} and dV_{water} must Orville and Wilbur maintain in order to keep dM_{vat} constant?

(f) One day, the boss, Mr. Le Chatelier, instructs Orville to add 1.00 L of oil to the vat. Qualitatively, what change does Mr. Le Chatelier impose on the mass of the vat's contents? (That is, what is the direction of the imposed change?)

(g) Quantitatively, what is the change in mass that Mr. Le Chatelier imposes? (That is, what is the equation for the change in the mass in the vat in kg?

(h) Qualitatively, how must Wilbur respond?

(i) Quantitatively, how must Wilbur respond? (That is, what is the equation for the change in the mass in the vat in kg?)

22. Which of the following processes can be carried out reversibly?

(a) Melting an ice cube.

(b) Melting an ice cube at 273.15 K and 1.0 bar.

(c) Melting an ice cube at 275.00 K.

(d) Melting an ice cube at 272.00 K and 1.0 bar.

(e) Frying an egg.

(f) Riding a roller coaster.

(g) Riding a roller coaster and completing the ride in 10 minutes.

(h) Separating pure water from a salt solution at 1 bar and 280.0 K.

(i) Dissolving NaCl in an aqueous solution that is saturated with NaCl.

(j) Compressing a gas.

(k) Squeezing juice from a lemon.

(l) Growing a bacterial culture.

(m) Bending (flexing) a piece of paper.

(n) Folding (creasing) a piece of paper.

Notes

[1] The ordinate (pressure) values for the solid–liquid and liquid–gas equilibrium lines are severely compressed. The ranges of pressure values are so different that the three equilibrium lines cannot otherwise be usefully exhibited on the same graph.

[2] We also use closely related quantities that we call ***fugacities***. We think of a fugacity as a “corrected pressure.” For present purposes, we can consider a fugacity to be a particular type of activity.

[3] G. N. Lewis and M. Randall, ***Thermodynamics and the Free Energy of Chemical Substances***, 1^{st} Ed., McGraw-Hill, Inc., New York, 1923, p. 448.

[4] Ilya Prigogine, ***Introduction to the Thermodynamics of Irreversible Processes***, Second Edition, Interscience Publishers, 1961.

[5] S. R. de Groor and P. Mazur, ***Non-Equilibrium Thermodynamics***, Dover Publications, New York, 1984. (Published originally by North Holland Publishing Company, Amsterdam, 1962.)