Chemical Thermodynamics and Equilibrium

Answers and Explanations

1. D

All are characteristics of equilibrium.

2. C

Choice 'C' represents the proper expression of K_c, the equilibrium constant for this reaction. The equilibrium constant is the particular value of the reaction quotient, Q, that reflects the concentrations at equilibrium. Note that stoichiometric coefficients become exponents in reaction quotients and equilibrium constants. You can tell the exponents from the stoichiometry. This is in contrast to rate expressions in chemical kinetics, where the exponents must be found experimentally.

3. A

Le Chatelier's principle tells us that if you disturb a system at equilibrium the system will respond in such a way that opposes the disturbance. One application of the principle is that when the pressure is increased for a chemical reaction, the equilibrium will shift to favor the direction that leads to *lower volume*. The most common framework in which this applies is a reaction involving gases in which there is a difference in the number of moles of gas between reagents and products. Increasing the pressure will cause the equilibrium to shift to favor formation of the fewer moles of gas. In the case of our reaction, there are four moles of gas on the reagent side and two moles of gas on the product side, so increasing pressure will lead to the formation of more product at equilibrium.

Regarding choice 'II', introducing a catalyst will not increase the equilibrium yield of the reaction (though it may increase the practical yield). A catalyst affects the rate of a reaction not the position of equilibrium.

Regarding choice 'III', heating the reaction vessel will not increase the equilibrium yield. One of the situations Le Chatelier's principle helps to predict is what occurs to the position of equilibrium when the temperature of a reaction is changed. *When the temperature of a reaction is increased, equilibrium shifts to favor the endothermic direction*. As indicated by the negative enthalpy change in the given information, the forward direction of our reaction is exothermic. Therefore, it is the reverse direction, the conversion of products to reagents, which is endothermic and which will be promoted by an increase in temperature.

4. A

Increasing the temperature of an endothermic reaction shifts the equilibrium to favor the products. The changing temperature produces an actual change in the equilibrium constant. We can see the temperature dependence of the equilibrium constant in the following equation.

$$K = e^{\frac{-\Delta G^\circ}{RT}}$$

$$K = \left(e^{\frac{-\Delta H^\circ}{RT}}\right)\left(e^{\frac{\Delta S^\circ}{R}}\right)$$

Choice 'II' is not correct, however. Even though increasing the pressure will shift the reaction to favor the products, it will not change the actual value of the equilibrium constant. Changing the total pressure will affect the denominator of the reaction quotient, where there are more moles of gas, more than the numerator, so if the reaction had been at equilibrium, it would no longer be so, not because the actual equilibrium constant has changed but because the reaction quotient describing the state of the system will have changed and will no longer equal the equilibrium constant.

Choice 'III' is not correct, one of the oldest MCAT questions. A catalyst does not change the position of equilibrium. It will have no effect on the standard free energy change of the reaction. It will only affect the rate of the reaction.

5. B

The equilibrium constant, K_c, for a reaction is a particularly important value of the reaction quotient, Q_c. (The 'c' subscript here signifies that the equilibrium constant and reaction quotient are being expressed in terms of concentration rather than partial pressures, which is an issue for gaseous reactions.) There are many possible values of the reaction quotient, Q_c. You might have a lot of reagent and little product, or you might have a lot of product and a little reagent. Reaction quotient gives you a way to capture those different possible states of the system. If the reaction quotient is smaller than the equilibrium constant, it means that the reaction has a greater proportion of reagents than would be present at equilibrium, and the reaction will be spontaneous forward. If the reaction quotient is larger than the equilibrium constant, we have a higher proportion of products at present than the equilibrium state, and the reaction will be spontaneous in the reverse.

For our problem, we are told that 0.01 mol of each gas is present within the 1L reaction vessel, so the concentration of all three gases is 0.01M. From this we can compute the reaction quotient describing the current state of the system.

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

$$Q_c = \frac{(0.01\text{M})^2}{(0.01\text{M})^2\,(0.01\text{M})} = 100\ \text{M}^{-1}$$

The reaction quotient is greater than the equilibrium constant, so the reverse direction is spontaneous.

6. C

The direction of spontaneity for a reaction doesn't only depend on the standard free energy change, $\Delta G°$, which predicts the direction of spontaneity *if the concentrations of reagents and products are all 1M*. The direction of spontaneity also depends on the reaction quotient, Q.

$$\Delta G = \Delta G° + RT\ln Q$$

Even with a negative standard free energy change, the reaction might be going in the reverse if the concentration of products is much greater than reagents.

7. C

The standard free energy change determines the equilibrium constant.

$$K = e^{\frac{-\Delta G°}{RT}}$$

Likewise, you can determine the standard free energy change from the equilibrium constant.

$$\Delta G° = -2.3\,RT\log K$$

$$\Delta G° = (-2.3)(8.3\ \text{J mol}^{-1}\ \text{K}^{-1})(298\text{K})(\log 1/9)$$

$$\sim (-2)(8)(300)(-1)\ \text{J mol}^{-1}$$

$$\sim +5\ \text{kJ mol}^{-1}$$

8. A

A classic in chem 101, you are not likely to run into the full problem like this on the MCAT, where solution of a quadratic equation is necessary. If such a problem were to show up on the MCAT, simplifying assumptions would likely prevail, such as reagent consumed being very small compared to the starting concentration. Nevertheless, it's important to see a full example solved because it's an archetypal problem.

We begin with 1.0 mole of both carbon monoxide and water vapor in a 2 liter container (don't forget to dilute to 0.50 M). Equal in the stoichiometry, let's call the concentrations of carbon dioxide and hydrogen at equilibrium "x" and our remaining concentrations of carbon monoxide and water vapor each "0.50 - x".

$$K = \frac{[x][x]}{[0.5-x][0.5-x]} = 4.05$$

$$\frac{x^2}{0.25 - x + x^2} = 4$$

$$3x^2 - 4x + 1 = (3x-1)(x-1) = 0$$

$$x = 1 \ \ or \ \ 0.33$$

We started with [CO] = 0.5 M, and we will lose 0.33 M, so our answer is 0.17 M.

9. B

Le Chatelier's principle tells us that if product is removed from a reaction vessel, the equilibrium shifts to make more product. That is the fundamental logic here. Because the products in this reaction are gases in an open container, and these are continually dissipating into the surroundings, the reaction keeps moving forward trying to find the equilibrium state which it can never reach.

It is very common in biochemistry to see the product of a reaction in a biochemical pathway as the reagent for the next step. Forward flux is maintained, often in spite of a positive standard free energy change for the reaction, by product removal.

10. A

Remember that you don't always need to be able to see all the way to the end of a problem to be productive in solving it. If you don't know where to begin, write some things down that you know and do your thinking on the page. Let the problem unfold.

Dalton's Law states that in a mixture of non-reacting gases, the total pressure exerted is equal to the sum of the partial pressures of the individual gases, so we can make the following statement about the pressures in the reaction vessel at equilibrium.

$$P_{NH3} + P_{CO2} = 0.117 \text{ atm}$$

We also know from the stoichiometry of the reaction:

$$P_{NH3} = 2P_{CO2}$$

Combining these equations it is easy to show that:

$$P_{CO2} = 0.039 \text{ atm}$$

$$P_{NH3} = 0.078 \text{ atm}$$

The solid reagent has a constant concentration, so it will not appear in K_p.

$$K_p = (P_{NH3})^2(P_{CO2}) = (7.8 \times 10^{-2})^2 (3.9 \times 10^{-2})$$

$$= 2.4 \times 10^{-4}$$

11. C

The forms of elemental sulfur described in the passage are molecular solids. A molecular solid consists of discrete molecules. The forces that bind the molecules together are intermolecular forces, ie. Van der Waals forces, dipole-dipole interactions or hydrogen bonds. For monoclinic and rhombic sulfur, the forces between S_8 molecules are Van der Waals forces. This is because S_8 molecules are nonpolar. The relatively high melting point for these crystals is because S_8 molecules are relatively large.

12. B

Each unit cell will share an S_8 molecule at each vertex with eight neighbors. There are eight vertices, so the unit cell will have eight atoms of sulfur total.

13. B

Notice that for each 10K increase in temperature, the enthalpy of rhombic sulfur increases 200 J. Therefore the molar heat capacity is 20 J mol^{-1} K^{-1}. We were asked for the specific heat so we must convert to J g^{-1} K^{-1}. The molecular weight of S_8 is 257 g/mol.

$$\left(\frac{20 \text{ J}}{\text{mol K}}\right)\left(\frac{1 \text{ mol}}{257 \text{ g}}\right) = \frac{.08 \text{ J}}{\text{g K}}$$

14. C

As the table data in the passage represents, the enthalpy of monoclinic sulfur at a given temperature is greater than the enthalpy of rhombic sulfur. The transformation of rhombic sulfur into monoclinic sulfur is endothermic. As temperature increases, equilibrium shifts to favor the endothermic direction of a reaction process. This is one of the most important applications of Le Chatelier's Principle. Choice 'I' is true.

Choice 'III' is also true. The standard free energy change is determined by both the enthalpy and the entropy. Being the higher entropy form, monoclinic sulfur is endowed with lower relative free energy at higher temperatures compared to rhombic sulfur.

$$\Delta G° = \Delta H° - T\Delta S°$$

15. A

In becoming liquid, both rhombic sulfur and monoclinic sulfur will be transformed into the same state (you can't tell from molten sulfur if it had been monoclinic or if it had been rhombic). Why would rhombic sulfur make the jump at a given temperature, but not monoclinic? The answer lies in their respective free energies. Rhombic sulfur possesses greater free energy at 113°C than monoclinic. Changing from rhombic to liquid represents a negative ΔG at 113°C, while to change from the lower free energy monoclinic sulfur at the temperature, the free energy change is positive, consistent with a non-spontaneous process, so monoclinic sulfur does not melt.

16. C

We must find a temperature where the free energy change from one allotrope to the other is zero.

$$\Delta G = \Delta H - T\Delta S = 0$$

Examining our table, we see that for all temperatures shown, the enthalpy and entropy changes involved in transforming one mole from rhombic to monoclinic sulfur are:

$$\Delta H_{\text{rh › mc}} = 400\ \text{J}$$

$$\Delta S_{\text{rh › mc}} = 1.1\ \text{J K}^{-1}$$

Let's find the temperature where the free energy change is zero.

$$(400\ \text{J}) - T\,(1.1\ \text{J K}^{-1}) = 0$$

$$T = 364\text{K}$$