- 1. D All are characteristics of equilibrium.
- 2. **C C** is the proper expression of K_c , the equilibrium constant, for this reaction. (K_c is one value among all the possible Q's (reaction quotients) describing all possible states of our system. K_c is the reaction quotient reflecting the concencentrations at equilibrium.) Note that the stoichiometric coefficients unproblematically become exponents in reaction quotients. This is in contrast to the rate expression in chemical kinetics, where the exponents must be found experimentally.
- A In our reaction, stoichiometrically, we are going from four moles of gas to two, so our system has more volume if equilibrium at a given pressure favors reactant. Increasing the pressure gives free energy to the reactants by increasing the stakes of the pressure volume work performed on the system in going to the right. The system expends this free energy in doing just that.

A simpler way of looking at this would be to apply *Le Chatelier's principle*, which states that when an equilibrium state is disturbed (as in this case when we increased pressure) the system compensates in such a way as to undo the disturbance (in this case, increased pressure, undone by decreasing volume).

4. B When the temperature of an equilibrium system is altered, the system seeks a new equilibrium characterized by a new equilibrium constant. Model what happens by means of the relationship between the temperature and equilibrium concentrations posited by the following equation:

$$\Delta G^0 = -2.303 \ RT \log K$$

Remember that the above equation is for the equilibrium state, existing when there is no free energy in the system. The equation above is one version of the following (for when $\Delta G = 0$):

$$\Delta G = \Delta G^0 + 2.303 RT \log Q$$

When we altered the temperature, one side of the reaction gains free energy, which is expended until a new equilibrium is attained with a new equilibrium constant *K*. Therefore the equilibrium constant does change when the temperature is altered.

However, when the pressure is changed in a gas-phase equilibrium, even though, if the number of moles of gas on each side is different, we are adding free energy to the side with more moles of gas, and even though, therefore, the system is now in motion, seeking to reestablish equilibrium, when it does so, we will characterize the equilibrium with the same equilibrium constant as before. To understand why, examine the following data regarding a system of two gases at equilibrium at 5 atm pressure (with A having 1 atm partial pressure and B the other 4 atm), when we disturb the equilibrium by doubling the total pressure:



Notice that the same proportionate distributions of partial pressure (4:1) are no longer described by the equilibrium constant ($K_p = 16$). Our system is now off equilibrium, and will spontaneously work toward a new proportionate distribution to return to K_p .

5. B The initial concentrations point to a reaction quotion greater than K_c :

$$Q = \frac{[SO_3]^2}{[SO_2]^2[O_3]} = \frac{(25)^2}{(25)^2(25)} = 4$$

Examine the equation below. Can you see why the fact that we have a reaction quotient greater than our equilibrium constant means that our reaction will be on the move toward forming more reactant (leftwards)?

$$\Delta G = \Delta G^0 + 2.303 \ RT \log Q$$

 C The first thing to do in this kind of problem (classic equilibrium plug-and-chug) is state what we know about the equilibrium concentrations:

$$K = \frac{[OO_{i}][H_{i}]}{[OO][H_{i}O]} = 4.05$$

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). Let's call the concentrations of carbon dioxide and hydrogen product formed at equilibrium "x" (they are equal here (stoichiometry)), and our remaining concentrations of carbon monoxide and water vapor each "0.50 - x". Now we can say that at equilibrium:

$$\zeta = \frac{[\hat{x}][\hat{x}]}{[0.5 - \hat{x}][0.5 - \hat{x}]} = \frac{x^2}{[0.5 - \hat{x}]^2} = \frac{x^2}{.25 - x + x^2} = 4.05$$
$$3x^2 - 4x + 1 = [3x - 1][[x - 1]] = 0$$
$$x = 1 \text{ or } \frac{[\hat{x}]}{[\hat{x}]}.$$

We started with [CO] = 0.5 M, and we will lose 0.33 M, so our answer is .17 M.

7. D Review in the light of:

$$\Delta G^0 = -2.303 \ RT \log K$$

- 8. B The system cannot reach equilibrium because we are carrying it out in an open container. The entropy of mixture for the gas (with the rest of the earth's atmosphere) is too great a temptation.
- 9. A This question gives good practice in MCAT style approximations, as in:

$$\log \frac{1}{9} = \log \frac{1}{10} = -1$$

Notice in the equation

$$\Delta G^0 = -2.303 \ RT \log K$$

how a small number for the equilibrium constant (meaning that at equilibrium you have more reactant) points to a positive standard free energy change.

- C Molecules in a crystal are held there by intermolecular forces (London forces, dipole-dipole, or hydrogen bonding). S₈ molecules are not polar, nor do they have hydrogens.
- B Each unit cell will share an S₈ molecule at each vertex with eight neighbors. There are eight vertices, so the unit cell will have eight atoms of sulfur total.
- 12. C Notice that for each 10 K 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 grams.

13. C I is true because, when we disturb an equilibrium by increasing the temperature, the endothermic process will be favored in going to the new higher temperature equilibrium, because, as predicted by Le Chatelier's principle, the process restoring equilibrium will seek to ameliorate the disturbance.

> The truth of **III** can be seen in the following relationship between the free energy change, enthalpy change, and entropy change:

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

At the higher temperature, the greater entropy of the monoclinic form will cause there to be more free energy favoring its formation.

- 14. A To understand this question, one must realize that in becoming liquid, both rhomic sulfur and monoclinic sulfur will be transformed into the same state (you can't tell from molten sulfur if it was once monoclinic or if it used to be 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 would have greater free energy at 113 °C than monoclinic. When compared to the free energy of the liquid, changing from rhombic to liquid would represent a negative ΔG, while with the lower free energy monoclinic, the free energy change is positive, consistent with a nonspontaneous process.
- 15. 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:

$$\Delta H_{\text{th-rec}} = 400 \text{ J}$$

 $\Delta S_{\text{th-rec}} = 1.1 \frac{\text{J}}{\text{K}}$

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

$$\begin{split} [400 \ J] = T \Big(1.1 \ \frac{J}{K} \Big) = 0 \\ T = 364 \ \mathrm{K} \end{split}$$