

You may need a calculator for number 4 (but you actually don't as long as you're clever about how you approach the problem).

1. You're doing an experiment to see how long an open container with 100mL of methanol will last. You also have a meter handy to tell you the amount of methanol left (and once it is gone), in case you decide to store it as a mixture. To decrease the vapor pressure, and thus maximize how long the methanol will last, you could:

- I. Keep it on your sunny windowsill
  - II. Conduct the experiment in your cabin at the mountains
  - III. Decrease the surface area of the container
  - IV. Add water to it
  - V. Store it in a cool place
  - VI. Pour in some CaO
  - VII. Get some surfing time in between measurements (be at sea level)
- 1) III, IV, V and VII **Correct**
  - 2) IV and V
  - 3) III, V and VI
  - 4) II and III
  - 5) II, IV and VI

Explanation: Keeping the methanol in a warm, sunny place will increase the vapor pressure and the methanol will evaporate faster. Water and methanol are miscible, so the water will mix with the methanol, thus competing for positions at the surface of the mixture (where vapor pressure takes place) and decrease the rate at which it evaporates. Along with surface area, decreasing the surface area of the container will also reduce the rate of evaporation. CaO will not dissolve or contribute to this phenomenon (CaO does not dissolve in water). At the beach there is a full atmosphere of air pushing back down on the liquid, it will evaporate faster in the mountains where the air is thinner (less pressure pushing back on the liquid, making it easier to leave as a gas).

2. A 7.0 molal aqueous solution of (CsF/ methanol/SrI<sub>2</sub>) would have a higher boiling point. What is the boiling point of this solution?  $K_{bwater} = 0.5 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}$ .

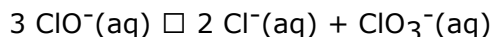
- 1) CsF, 380K
- 2) CH<sub>3</sub>OH, 376.5K
- 3) CsF, 383.5K
- 4) SrI<sub>2</sub>, 380K
- 5) SrI<sub>2</sub>, 383.5K **Correct**
- 6) CH<sub>3</sub>OH, 383.5K
- 7) CsF, 363K

Explanation: An aqueous solution of strontium iodide would have a higher boiling point since when it dissociates, there are three particles. Cesium fluoride only dissociates into two and methanol is one (Van't Hoff factor). Plug the values into the formula for boiling point elevation to get the new boiling point.

3. Sodium hypochlorite (NaOCl), aka bleach, is commercially prepared by adding chlorine gas to a solution of sodium hydroxide.



The hypochlorite ion is the active bleaching agent, but can decompose to chloride and chlorate ions in a competing side reaction:



Set up the equilibrium constant K for the decomposition of hypochlorite:

1.  $K = \frac{[\text{Cl}^-]^2[\text{ClO}_3^-]}{[\text{ClO}^-]^3}$

2.  $K = [\text{Cl}^-]^2[\text{ClO}_3^-]/[\text{ClO}^-]^3$  **Correct**

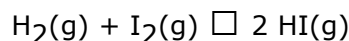
3.  $K = [\text{ClO}^-]^3 / [\text{Cl}^-]^2[\text{ClO}_3^-]$

4.  $K = [\text{Cl}^-][\text{ClO}_3^-]/[\text{ClO}^-]$

5.  $K = [\text{Cl}^-][\text{ClO}^-]/[\text{Cl}_2][\text{OH}^-]^2$

Explanation: Products appear in the numerator, reactants in the denominator, and the coefficients of the balanced reaction become the exponents of each species' term.

4. Suppose  $\text{H}_2$  (g) and  $\text{I}_2$  (g) are sealed in a container at  $T = 400$  K with partial pressures  $P_{\text{H}_2} = 1.32$  atm and  $P_{\text{I}_2} = 1.14$  atm. At this temperature, the gases do not react rapidly to form  $\text{HI}$  (g), although after a long enough time they would produce  $\text{HI}$  (g) at its equilibrium partial pressure. Suppose, instead that the gases are heated in the sealed flask to 600 K, a temperature at which equilibrium is quickly established:



For this reaction at 600K, the equilibrium constant  $K = 92.6$ .

Determine the **change in partial pressure** of hydrogen gas.

1. 1.5044 atm **Correct**

2. 2.3522 atm

Explanation: Using the ideal gas law (constant volume), the initial partial pressures would be:

$$P_{\text{H}_2} = 1.32 \text{ atm} \times (600\text{K}/400\text{K}) = 1.98 \text{ atm}$$

$$\text{and } P_{\text{I}_2} = 1.14 \text{ atm} \times (600/400\text{K}) = 1.71 \text{ atm.}$$

These gases react, and the extent of the reaction can be calculated. Set up a RICE table and equilibrium expression  $K$  to solve for the change in partial pressures of all the gases.

$$K = 92.6 = (2x)^2 / [(1.98-x)(1.71 - x)]$$

Multiply and collect terms to find:

$$88.6x^2 - 341.694x + 313.525 = 0.$$

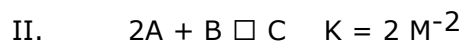
Solve using the quadratic formula. Only one solution will yield a real result.

$$x = 1.5044 \text{ atm or } 2.3522 \text{ atm}$$

Plugging into the equilibrium expressions,  $P_{\text{H}_2} = (1.980 - x)$  and  $P_{\text{I}_2} = (1.71 - x)$ , it is obvious that  $x = 2.3522$  atm gives a non-physical, negative partial pressure. Thus the change in partial pressure of  $\text{H}_2$  (g) must be given by  $x = 1.5044$  atm.

Challenge yourself by solving for the equilibrium partial pressures (NOT JUST THE CHANGES) of each gas.

5. Consider the following two ways to make the product, C:



All other things being equal, at what concentration of A would method I produce more C?

1.  $[A] > 1\text{M}$
2.  $[A] < 1\text{M}$  **Correct**
3. All values of  $[A]$
4. No values of  $[A]$

Explanation: For Method I,  $K_{eq} = [C] / ([A][B])$ , thus  $[C] = 4([A][B])$ . For Method II,  $K_{eq} = [C] / ([A]^2[B])$ , thus  $[C] = 2([A]^2[B])$ . Since the  $K_{eq}$  for Method I is greater, Method I would produce more C under all conditions except when  $[A]$  is very small (since you are squaring that term, and the squares of fractions are less than the fractions themselves). Choice 3 is false because both  $K_{eq}$ 's are greater than 1, thus both reactions are product-favored.

6. Which of the following statements is/are true:

- I. K will slowly approach the value of Q while the reaction reaches equilibrium.
- II. If  $Q > K$ , the reverse reaction is dominant over the forward reaction.
- III. Q will never exceed the value of K.

1. I only
2. II only **Correct**
3. III only
4. I and II
5. I and III

Explanation: Statement I is false because Q approaches the value of K when reaching equilibrium, not vice versa. Statement II is true because when  $Q > K$ , there is an excess of products and thus the reverse reaction is dominant. Statement III is false because Q exceeds the value of K when you add an excess of products. The reaction also reaches equilibrium, not stop at completion, when  $Q=K$ .

7. Which of the followings statements is not true concerning the Le Chatelier Principle?

1. For the reaction  $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$  (called the Haber process), decreasing the volume of the system would cause ammonia to form.
2. For the reaction  $CO(g) + NO_2(g) \rightleftharpoons CO_2(g) + NO(g)$ , changing the volume of the system would have no effect.
3. For the reaction  $CO(g) + 2 H_2(g) \rightleftharpoons CH_3OH(g)$  adding methanol would cause carbon monoxide to form.
4. For the reaction  $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$  ( $\Delta H = -92 \text{ kJ}\cdot\text{mol}^{-1}$ ), increasing the temperature would cause ammonia to form. **Correct**

Explanation: The Haber process is an exothermic reaction ( $\Delta H = -92 \text{ kJ}\cdot\text{mol}^{-1}$ ), allowing us to think of heat as belonging on the right-hand side of the equation. Addition of heat would therefore cause a shift toward the left-hand side of the equation, producing nitrogen and hydrogen gas rather than ammonia.

8. If a given reaction has an equilibrium constant of 10 at 25 °C ( $K = 10$ ,  $T = 302 \text{ K}$ ) and a standard change in enthalpy of  $-10 \text{ kJ}\cdot\text{mol}^{-1}$  ( $\Delta H^\circ = -10 \text{ kJ}\cdot\text{mol}^{-1}$ ), without doing any math, at which of the following temperatures will the reaction most likely be non-spontaneous?

1. 100 °C
2. - 200 °C
3. 500 K **Correct**
4. 250 K

Explanation: Based on the Van't Hoff equation, a negative value of  $\Delta H^\circ$  suggests that raising the temperature at which the reaction is performed will make the reaction less spontaneous. The greatest temperature available is 500 K, and it is therefore the temperature at which the reaction is most likely to be non-spontaneous.