Chemistry 1A, Spring 2010

Midterm 3 Solutions

Apr 12, 2010

Problems

1. A 1.00 mol sample of CO_2 gas is confined in a 20.0 liter container at 25 °C. If 1.00 mol of H_2 gas is added, holding the volume and temperature constant, the average kinetic energy of the system will _____?

   A) Increase
   B) Decrease
   C) Remain the Same
   D) Not enough information to answer the question.
   Kinetic energy depends only on the temperature, so it will remain the same as temperature is held constant.

2. The average kinetic energy of the particles of a gas is directly proportional to _____?

   A) the rms speed
   B) the square of the rms speed
   C) the square root of the rms speed
   D) the square of the particle mass

$$\frac{3}{2}RT = E_{kin} = \frac{1}{2}mv_{rms}^2$$

3. According to the kinetic-molecular theory, in which of the following gases with the root-mean-square speed of the molecules be the highest at 200°C?

   A) HCl   B) Cl_2 **C) H_2O**   D) SF_6
   E) None. The molecules of all gases have the same root-mean-squared speed at any given temperature.

   Water is the lightest of the choices. Since they will all have the same kinetic energy (as they are at the same temperature), the lightest gas must have the highest velocity, as $v_{rms} \propto \sqrt{\frac{T}{M}}$

4. According to the kinetic-molecular theory, if the temperature of a gas is raised from 100°C to 200°C, the average kinetic energy of the gas will _____?
   A) double
   B) increase by a factor of 1.27
   C) increase by a factor of 100
   D) decrease by half
   E) decrease by a factor of 100

Kinetic energy depends only on temperature. However, we must use the Kelvin scale, as it is an absolute scale, and we know that kinetic energy cannot be below zero.

$$100°C + 273 = 373K$$
$$200°C + 273 = 473K$$

$$
\begin{aligned}
\frac{E_{kin,f}}{E_{kin,i}} &= \frac{\frac{3}{2}\cancel{R}T_f}{\frac{3}{2}\cancel{R}T_i} \\
&= \frac{T_f}{T_i} \\
&= \frac{473\,\cancel{K}}{373\,\cancel{K}} \\
&= 1.27
\end{aligned}
$$

Therefore, $E_{kin,f}$ is 1.27 times larger than $E_{kin,i}$

5. Which of the following is NOT part of the kinetic-molecular theory?

A) Atoms are neither created nor destroyed by ordinary chemical reactions.
B) Attractive and repulsive forces between gas molecules are negligible.
C) Gases consist of molecules in continuous, random motion.
D) Collisions between gas molecules do not result in the loss of energy.
E) The volume occupied by all of the gas molecules in a container is negligible compared to the volume of the container.

Kinetic-molecular theory has only to do with gases, not chemical reactions.

6. Which of the following statements is true for ideal gases, but it <u>not always</u> true for real gases? Mark all that apply.

A) Collisions between molecules are elastic
B) The size of molecules is unimportant compared to the distance between them.
C) The volume occupied by the molecules is negligible compared to the volume of the container.
D) Average molecular kinetic energy increases with temperature.

A,B, and C are all true for ideal gases. However, for real gases, collisions are inelastic (due to intermolecular interactions), the size and volume of the molecules do matter (especially for phase transitions).

7. By what percent does the pressure calculated using the van der Waal's equation differ from the ideal gas law pressure for a 9.99 mole sample of xenon gas in a 0.828 L container at 496 K?
For Xe gas, $a = 4.19$ L^{2}atm/mol^2 and $b = 0.0510$ L/mol. The van der Waal's equation is given below.

$$\left(P + a\frac{n^2}{V^2}\right)\,(V - nb)\ = nRT$$

$$\left(P_{vdW} + a\frac{n^2}{V^2}\right)(V - nb) = nRT$$

$$P_{vdW} + a\frac{n^2}{V^2} = \frac{nRT}{(V - nb)}$$

$$P_{vdW} = \frac{nRT}{(V - nb)} - a\frac{n^2}{V^2}$$

$$= \frac{(9.99\ \text{mol})\left(0.08206\frac{\text{L atm}}{\text{mol K}}\right)(496\ K)}{0.828\ \text{L} - 9.99\ \text{mol} \times .0510\frac{\text{L}}{\text{mol}}} - 4.19\frac{\text{L}^2\text{atm}}{\text{mol}^2}\left(\frac{9.99\ \text{mol}}{0.828\ \text{L}}\right)^2$$

$$= \frac{406.6\ \text{L atm}}{.3185\ \text{L}} - 4.19\frac{\text{L}^2\text{atm}}{\text{mol}^2}\left(145.6\frac{\text{mol}^2}{\text{L}^2}\right)$$

$$= 1277\ \text{atm} - 609.9\ \text{atm}$$

$$P_{vdW} = 667\ \text{atm}$$

Use the ideal gas law to calculate P_{ideal}

$$P_{ideal}V = nRT$$

$$P_{ideal} = \frac{nRT}{V}$$

$$= \frac{9.99\ \text{mol} \times 0.08206\frac{\text{L atm}}{\text{mol K}} \times 496\ K}{0.828\ \text{L}}$$

$$P_{ideal} = 491\ \text{atm}$$

Now, we want to calculate the percent that P_{vdW} differs from P_{ideal}

$$\%diff = \frac{|P_{ideal} - P_{vdW}|}{P_{ideal}} \times 100\%$$

$$= \frac{|491\ \text{atm} - 667\ \text{atm}|}{491\ \text{atm}} \times 100\%$$

$$= 35.8\%$$

So, the pressure from the van der Waals equation is **A) 35.8%** larger than what we would expect from the ideal gas law.

The following two questions refer to the phase diagram for water shown below.

H_2O

Liquid

Solid

P

Gas

Temperature   Tc
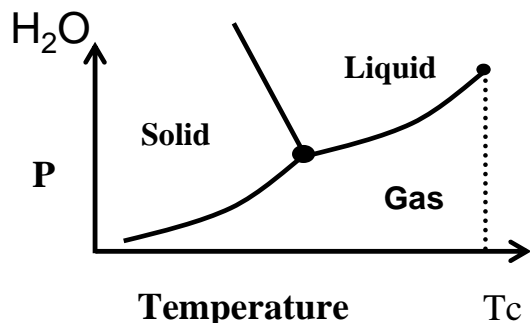
8. Which of the following statements is NOT true:
   A) A Solid to Gas transition is possible by increasing only T.
   B) A Solid to Liquid transition is possible by increasing only T.
   C) A Liquid to Gas transition is possible by increasing only T.
   D) A Solid to Liquid transition is possible by increasing only P.
   E) A Solid to Gas transition is possible by increasing only P.
   The only way to go from Solid to Gas is by increasing temperature or decreasing pressure.

9. The critical point (above which there is no gas/liquid phase transition) of water occurs at 375 °C and 218.0 atm. the liquid vaporizes to gas at 1.00 atm and 100 °C At what pressure are water liquid and vapor at equilibrium at 250 °C?

   D) 185.00 atm.
   If we follow the liquid/gas equilibrium line for water, we see that as temperature decrease, so does the pressure for liquid/gas equilibrium. Therefore, at 250 °C, the pressure for equilibrium must be less that that of the critical point, but greater than that of 100 °C. 185.00 atm as the only answer which is between 1.00 atm and 218.00 atm of pressure.
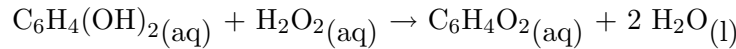
10. 2.0 moles of a monatomic ideal gas are compressed in a cylinder at a constant pressure of 10 atm from 10 L to 5.0 L. What is the work done on the gas for this process, in kJ?

$$
\begin{aligned}
w &= -P_ext\Delta V \\
w &= -P_ext\left(V_f - V_i\right) \\
&= -\left(10 \text{ atm}\right)\left(5.0 \text{ L} - 10 \text{ L}\right) \\
&= 50 \, \text{L atm} \times \frac{100 \, \text{J}}{1 \, \text{L atm}} \times \frac{1 \text{ kJ}}{1000 \, \text{J}} = 5.0 \text{ kJ}
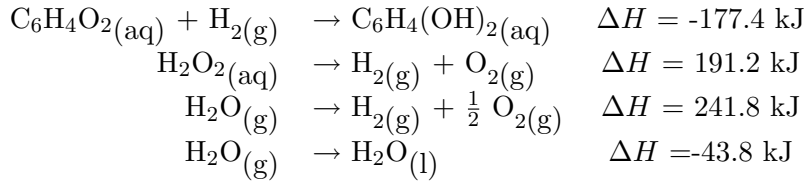\end{aligned}
$$

D) 5.0 kJ of work is done on the gas. The sign of the work should be positive, since for compression, positive work is done on the system, and negative work is done by the surroundings.
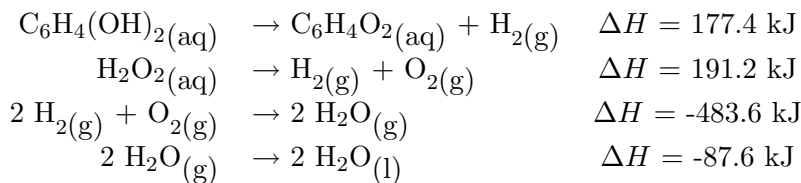
11. The internal energy of a system is always increased by _____?
    A) adding heat to the system
    B) having the system do work on the surroundings
    C) withdrawing heat from the system
    D) adding heat to the system and having the system do work on the surroundings
    E) a volume compression

12. Which one of the following is an exothermic process?
    A) ice melting
    B) water evaporating
    C) boiling soup
    D) condensation of water vapor
    E) Ammonium thiocyanate and barium hydroxide are mixed at 25 °C: the temperature of the surrounding water drops.

13. Which of the following is a statement of the first law of thermodynamics?
    A) $E_k = \frac{mv^2}{2}$
    B) A negative ΔH corresponds to an exothermic process
    C) $\Delta E = E_{final} - E_{initial}$
    D) Energy lost by the system must be gained by the surroundings.
    E) 1 cal = 4.184 J

14. Propanol (pro) burns cooler than isopropanol (iso). What can you conclude about the isomerization of propanol to isopropanol?

propanol   isopropanol

    B) $\Delta H° > 0$
    Propanol burns cooler than isopropanol, which means that isopropanol has a higher $\Delta H_f°$ than propanol. Therefore, to go from propanol to isopropanol, $\Delta H°$ would have to be positive.

15. The value of $\Delta H°$ for the reaction below is -790 kJ. The enthalpy change accompanying the reaction of 0.95 g of S is _____ kJ.

$$2 \text{ S}_{(s)} + 3 \text{ O}_{2(g)} \rightarrow 2 \text{ SO}_{3(g)}$$

$$0.95 \text{ g S} \times \frac{1 \text{ mol S}}{32 \text{ g S}} \times \frac{-790 \text{ kJ}}{2 \text{ mol S}} = \textbf{C)} \ -12 \text{ kJ}$$

16. Δ H for the reaction:

$$C_6H_4(OH)_{2(aq)} + H_2O_{2(aq)} \rightarrow C_6H_4O_{2(aq)} + 2\ H_2O_{(l)}$$

is _____ kJ, given the data below.

$$
\begin{array}{lll}
C_6H_4O_{2(aq)} + H_{2(g)} & \rightarrow C_6H_4(OH)_{2(aq)} & \Delta H = \text{-177.4 kJ} \\
H_2O_{2(aq)} & \rightarrow H_{2(g)} + O_{2(g)} & \Delta H = \text{191.2 kJ} \\
H_2O_{(g)} & \rightarrow H_{2(g)} + \frac{1}{2}\ O_{2(g)} & \Delta H = \text{241.8 kJ} \\
H_2O_{(g)} & \rightarrow H_2O_{(l)} & \Delta H = \text{-43.8 kJ}
\end{array}
$$

To get the correct equation, reverse the first reaction, multiply the third reaction by 2 and reverse, and double the fourth reaction, as follows:

$$
\begin{array}{lll}
C_6H_4(OH)_{2(aq)} & \rightarrow C_6H_4O_{2(aq)} + H_{2(g)} & \Delta H = \text{177.4 kJ} \\
H_2O_{2(aq)} & \rightarrow H_{2(g)} + O_{2(g)} & \Delta H = \text{191.2 kJ} \\
2\ H_{2(g)} + O_{2(g)} & \rightarrow 2\ H_2O_{(g)} & \Delta H = \text{-483.6 kJ} \\
2\ H_2O_{(g)} & \rightarrow 2\ H_2O_{(l)} & \Delta H = \text{-87.6 kJ}
\end{array}
$$

So, when we add these together, we get **C) Δ H = -202.6 kJ**

17. Which one of the following statements is true?
A) Enthalpy is an intensive property.
B) The enthalpy change for a reaction is independent of the state of the reactants and products.
C) Enthalpy is a state function.
D) H is the value of q measured under conditions of constant volume.
E) The enthalpy change of a reaction is the reciprocal of the ?H of the reverse reaction.

18. A 46.2 g sample of copper is heated to 95.4 °C and placed in a calorimeter containing 75.0 g of water at 19.6 °C. The final temperature of the water is 21.8 °C. Assuming the calorimeter does not absorb any heat, what is the heat capacity of copper, in $\frac{J}{g\ K}$? The heat capacity of water is 4.184 $\frac{J}{g\ K}$.

since the calorimeter is ideal, we have:
heat lost by copper = heat gained by water

$$
\begin{aligned}
-q_{Cu} &= q_W \\
-m_{Cu}C_{Cu}\Delta T_{Cu} &= m_W C_W \Delta T_W \\
C_{Cu} &= \frac{m_W C_W \Delta T_W}{-m_{Cu}\Delta T_{Cu}} \\
&= \frac{75.0\ \text{g water} \times 4.184\frac{J}{g\ °C} \times (21.8°C - 19.6°C)}{-46.2\ \text{g Cu} \times (21.8°C - 95.4°C)} \\
&= \frac{75.0\ \cancel{g} \times 4.184\frac{J}{\cancel{g}\ \cancel{°C}} \times (2.2\cancel{°C})}{-46.2\ \text{g} \times (-73.6°C)}
\end{aligned}
$$

6

$$= \frac{690 \text{ J}}{3400 \text{ g}°\text{C}}$$

$$C_{Cu} = \textbf{B)} \ 0.203 \frac{\text{J}}{\text{g}°\text{C}}$$

19. The ΔH for the solution process when solid sodium hydroxide dissolves in water is -44.4 kJ/mol. When a 13.9 g sample of NaOH dissolves in 250.0 g of water in a coffee-cup calorimeter, the temperature increases from 23.0 °C to _____ °C. Assume that the solution has the same specific heat as liquid water, i.e., $\frac{\text{J}}{\text{g K}}$. (*note: on the exam, the ΔH was listed as +44.4 J/mol. This would have caused the water to decrease in temperature. Therefore, everyone was given credit for this problem)

heat given off by reaction = heat absorbed by water solution (since water increases in temperature)

$$-q_{rxn} = q_{sol}$$

$$-q_{rxn} = -\left(13.9 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40 \text{ g NaOH}} \times \frac{-44.4 \text{ kJ}}{1 \text{ mol NaOH}} \times \frac{1000 \text{ J}}{1 \text{ kJ}}\right) = 15430 \text{ J}$$

$$15430 \text{ J} = q_{sol}$$

$$15430 \text{ J} = m_{sol}C_{sol}\Delta T_{sol}$$

$$15430 \text{ J} = (250.0 \text{ g water} + 13.9 \text{ g NaOH}) \times 4.18\frac{\text{J}}{\text{g K}} \times (T_f - (23.0 + 273) \text{ K})$$

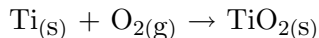$$15430 \text{ J} = 263.9 \text{ g sol} \times 4.18\frac{\text{J}}{\text{g K}} \times (T_f - 296 \text{ K})$$

$$15430 \text{ J} = 1103\frac{\text{J}}{\text{K}} \times (T_f - 296 \text{ K})$$

$$15430 \text{ J} = 1103\frac{\text{J}}{\text{K}} \times T_f - 326500 \text{ J}$$

$$1103\frac{\text{J}}{\text{K}} \times T_f = 311070 \text{ J}$$

$$T_f = 310 \text{ K} - 273 = \textbf{D)} \ 37.0°\text{C}$$

20. The combustion of titanium with oxygen produces titanium dioxide:

$$\text{Ti}_{(s)} + \text{O}_{2(g)} \rightarrow \text{TiO}_{2(s)}$$

When 2.060 g of titanium is combusted in a bomb calorimeter, the temperature of the calorimeter increases from 25.00 °C to 91.60 °C. In a separate experiment, the heat capacity of the calorimeter is measured to be 9.84 kJ/K. The heat of reaction for the combustion of Ti in this calorimeter is _____ kJ/mol.

heat given off by combustion = heat gained by water + heat gained by calorimeter

$$-q_{rxn} = q_{cal}$$

$$
\begin{aligned}
&= K_{cal}\Delta T_{cal} \\
&= 9.84\frac{\text{kJ}}{\text{°C}}\,(91.60\text{°C} - 25.00\text{°C}) \\
&= 9.84\frac{\text{kJ}}{\text{°C}}\,(66.60\text{°C}) \\
-q_{rxn} &= 9.84\frac{\text{kJ}}{\cancel{\text{°C}}}\,(66.60°\cancel{C}) \\
q_{rxn} &= -655.3\ \text{kJ}
\end{aligned}
$$

$$
2.060\ \cancel{\text{g Ti}} \times \frac{1\ \text{mol Ti}}{47.87\ \cancel{\text{g Ti}}} = 0.04303\ \text{mol Ti}
$$

$$
\frac{-655.3\ \text{kJ}}{0.04303\ \text{mol Ti}} = q_{rxn} = \textbf{E)}\ -15200\frac{\text{kJ}}{\text{mol}}
$$

21. The following process of bond-breaking → bond formation corresponds to the combustion of which compound?

$$
3\ \text{C-H} + \text{O-H} + \text{C-O} + \tfrac{3}{2}\ \text{O=O} \rightarrow 2\ \text{C=O} + 4\ \text{O-H}
$$

A) Ethanol   B) Ethane   C) Methanol   D) Methane   E) Formaldehyde

C) Methanol

The combustion of methanol has the following equation:

$$
\text{CH}_3\text{OH} + \tfrac{3}{2}\text{O}_2 \rightarrow \text{CO}_2 + 2\ \text{H}_2\text{O}
$$

Which matches the bonds broken and bonds formed from the question

22. Methane can react with a fluorine atom to produce a methyl radical and hydrogen fluoride.

$\Delta H°_{rxn} = $ -153 kJ/mol

Based on the ΔH°_{rxn} , which of the following is true?
A) Breaking chemical bonds releases energy.
B) All reactions involving bond-breaking and bond formation are exothermic.
C) The H-F bond is stronger than the C-H bond.
D) The H-F bond is weaker than the C-H bond.
E) The heat of the reactants is absorbed by the products.

23. Three balloons were filled with the following mixtures. Which balloons looses the most heat when the contents undergo combustion reactions?
A) 2 moles C_8H_{18}
B) 3 moles C_8H_{18}
C) 2 moles C_8H_{18} and 2 moles O_2

B) has the most moles of hydrocarbon, so it will have the most heat released upon combustion.

24. Which process is accompanied by the largest increase in entropy?
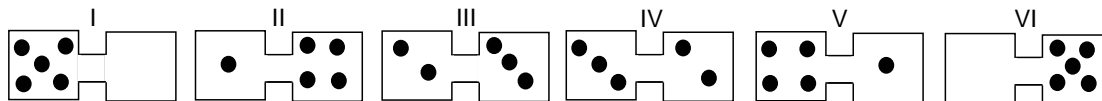
A) I → II
B) I → III
C) II → III
D) III → IV
E) V → VI
I has the most order, so the largest change in entropy would be from I to III, as III has the most disorder.

25. Which of the following processes have a $\Delta S > 0$
A) $CH_3OH_{(l)} \rightarrow CH_3OH_{(s)}$
B) $N_{2\ (g)} + 3\ H_{2\ (g)} \rightarrow 2\ NH_{3\ (g)}$
C) $CH_{4\ (g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3\ H_{2\ (g)}$
D) $Na_2CO_{3\ (s)} + H_2O_{(g)} + CO_{2\ (g)} \rightarrow 2\ NaHCO_{3\ (s)}$
E) All of the above processes have a $\Delta S > 0$.

C) is the only reaction where the number of moles of gas increase, so it is the only one with a positive ΔS

26. Calculate ΔS_{rxn} (J/K) for the reaction of 2.30 moles of NH_3 at standard conditions. The S° for each species is shown below the reaction.
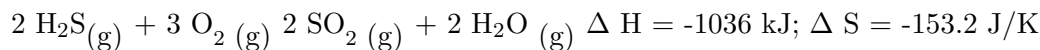
$$4\ NH_{3\ (g)} + 5\ O_{2\ (g)} \rightarrow 4\ NO_{(g)} + 6\ H_2O_{(g)}$$

9
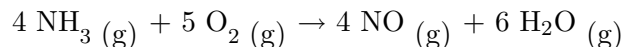
$$S^\circ \left(\frac{\text{J}}{\text{mol K}} \right) \quad 192.5 \qquad 205.1 \qquad 210.8 \qquad 188.8$$

$$
\begin{aligned}
\Delta S^\circ_{rxn} &= \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{reactants}} \\
&= 4S^\circ_{\text{NO}_{(g)}} + 6S^\circ_{\text{H}_2\text{O}_{(g)}} - 4S^\circ_{\text{NH}_{3\ (g)}} - 5S^\circ_{\text{O}_{2\ (g)}} \\
&= 4\left(210.8\frac{\text{J}}{\text{mol K}}\right) + 6\left(\frac{188.8\text{J}}{\text{mol K}}\right) - 4\left(192.5\frac{\text{J}}{\text{mol K}}\right) - 5\left(205.1\frac{\text{J}}{\text{mol K}}\right) \\
&= 843.2\frac{\text{J}}{\text{mol K}} + 1132.8\frac{\text{J}}{\text{mol K}} - 770\frac{\text{J}}{\text{mol K}} - 1025.5\frac{\text{J}}{\text{mol K}} \\
\Delta S^\circ_{rxn} &= 180.5\frac{\text{J}}{\text{mol K}}
\end{aligned}
$$

So, for 2.30 moles of NH_3

$$2.30 \ \text{mol NH}_3 \times \frac{180.5\frac{\text{J}}{\text{mol K}}}{4 \ \text{mol NH}_3} = \textbf{C) } 103.8\frac{\text{J}}{\text{mol K}}$$

27. Above what temperature does the following reaction become non spontaneous?

$$2\ \text{H}_2\text{S}_{(g)} + 3\ \text{O}_{2\ (g)} \ 2\ \text{SO}_{2\ (g)} + 2\ \text{H}_2\text{O}_{(g)} \quad \Delta\,\text{H} = \text{-1036 kJ}; \ \Delta\,\text{S} = \text{-153.2 J/K}$$

$$
\begin{aligned}
\Delta G &= \Delta H - T\Delta S \\
0 &= \Delta H - T\Delta S \\
T &= \frac{\Delta H}{\Delta S} \\
&= \frac{-1036\ \text{kJ} \times \frac{1000\ \text{J}}{1\ \text{kJ}}}{-153.2\frac{\text{J}}{\text{k}}} \\
T &= 6762\ \text{K}
\end{aligned}
$$

This is the temperature at which $\Delta G = 0$. When the temperature is above this, the $T\Delta S$ term, which is positive, will dominate. This will make the reaction non spontaneous ($\Delta G > 0$) above
A) 6.762×10^3 K.

28. Calculate ΔG_{rxn} (kJ) at 298 K under the conditions shown below for the following reaction.

$$\text{SO}_{3\ (g)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{H}_2\text{SO}_{4\ (l)} \qquad \Delta G^\circ = -90.5\ \text{kJ at 298 K}$$
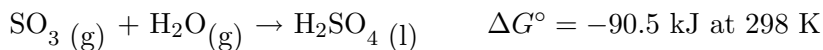
$P_{SO_3} = 0.20$ atm, $P_{H_2O} = 0.88$ atm

$$
\begin{aligned}
\Delta G &= \Delta G^\circ + RT \ln Q \\
&= -90.5 \text{ kJ} + 8.3145 \frac{\cancel{J}}{\text{mol } \cancel{K}} \times \frac{1 \text{ kJ}}{1000 \cancel{J}} \times 298 \cancel{K} \times \ln \frac{1}{P_{SO_3} P_{H_2O}} \\
&= -90.5 \text{ kJ} + 2.48 \frac{\text{kJ}}{\text{mol}} \times \ln \frac{1}{(0.20 \text{ atm}) (0.88 \text{ atm})} \\
&= -90.5 \text{ kJ} + 2.48 \text{ kJ} \times \ln 5.682 \\
&= -90.5 \text{ kJ} + 4.30 \text{ kJ} \\
\Delta G &= \textbf{D)} \ -86.2 \text{ kJ}
\end{aligned}
$$

29. The reaction between carbon tetrachloride and water to form carbon dioxide and hydrogen chloride has a ΔG° value of -232 kJ/mol, and so it is thermodynamically favored. But when you mix carbon tetrachloride with water, no change is observed. Which one of the following can best explain this?
A) The reaction is not favored thermodynamically.
B) It is a slow reaction kinetically.
C) The activation energy of the reaction is too small.
D) The reaction is not spontaneous.

30. At equilibrium, _____.
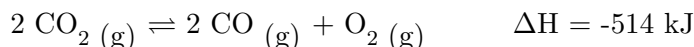A) all chemical reactions have ceased
B) the rates of the forward and the reverse reactions are equal
C) the rate constants of the forward and reverse reactions are equal
D) the value of the equilibrium constant is 1
E) the limiting reagent has been consumed

31. Consider the following reaction at equilibrium:

$$2 \text{ CO}_{2 \text{ (g)}} \rightleftharpoons 2 \text{ CO}_{\text{(g)}} + \text{O}_{2 \text{ (g)}} \qquad \Delta H = \text{-514 kJ}$$

Le Chatelier's principle predicts that an increase in temperature will _____.
A) increase the partial pressure of O2(g)
B) decrease the partial pressure of CO2(g)
**C) decrease the value of the equilibrium constant**
D) increase the value of the equilibrium constant
E) increase the partial pressure of CO

The reaction is exothermic, so heat can be treated as a product. Therefore, increasing the temperature will cause the reaction to shift towards the reactants, decreasing the value of the equilibrium constant (as changing temperature will change the equilibrium constant).

32. Consider the following reaction at equilibrium:

$$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2\,(g)}$$
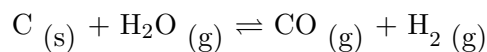
Which of the following conditions will increase the partial pressure of CO?
A) decrease the partial pressure of $H_2O_{(g)}$
B) removing $H_2O_{(g)}$ from the system
C) decreasing the volume of the reaction vessel
D) decreasing the pressure in the reaction vessel
E) increasing the amount of carbon in the system

To see this effect, consider the effect of halving the pressure of all gases on Q

$$K = \frac{P_{CO}P_{H_2}}{P_{H_2O}}$$

$$Q = \frac{\frac{1}{2}P_{CO} \times \frac{1}{2}P_{H_2}}{\frac{1}{2}P_{H_2O}}$$

$$= \frac{\frac{1}{4}P_{CO}P_{H_2}}{\frac{1}{2}P_{H_2O}}$$

$$= \frac{1}{2}\frac{P_{CO}P_{H_2}}{P_{H_2O}}$$

$$Q = \frac{1}{2}K$$

Therefore, since Q < K, the equilibrium must shift towards the products to re-establish equilibrium, which will increase P_{CO}.

33. The effect of a catalyst on an equilibrium is to _____.
A) increase the rate of the forward reaction only
B) increasing the equilibrium constant so that products are favored
C) slow the reverse reaction only
D) increase the rate at which equilibrium is achieved without changing the composition of the equilibrium mixture
E) shift the equilibrium to the right

A catalyst will make the reactions occur more quickly, without affecting the thermodynamics.

34. Choose the statement below that is true.
A) If K > 1, ΔG°_{rxn} is positive.
B) If K < 1, ΔG°_{rxn} is negative.
C) If $\Delta G^\circ_{rxn} = 0$, the reaction is at equilibrium.
D) If $\Delta G_{rxn} = 0$, the reaction is at equilibrium.
E) None of the above statements are true.

35. Use the free energy of formation given below to calculate the equilibrium constant K for the following reaction at 298 K.

$$2\ \text{HNO}_{3\ (aq)} + \text{NO}_{(g)} \rightleftharpoons 3\ \text{NO}_{2(g)} + \text{H}_2\text{O}_{(l)}$$
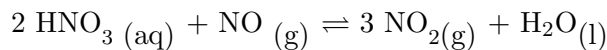
ΔG_f° (kJ/mol)   -110.9   87.6   51.3   -237.1

$$
\begin{aligned}
\Delta G_{rxn}^\circ &= \sum \Delta G_{f,\ \text{products}}^\circ - \sum \Delta G_{f,\ \text{reactants}}^\circ \\
&= 3\Delta G_{f,\ \text{NO}_2}^\circ + \Delta G_{f,\ \text{H}_2\text{O}}^\circ - 2\Delta G_{f,\ \text{HNO}_3}^\circ - \Delta G_{f,\ \text{NO}}^\circ \\
&= 3\,\text{mol}\left(51.3\frac{\text{kJ}}{\text{mol}}\right) + 1\,\text{mol}\left(-237.1\frac{\text{kJ}}{\text{mol}}\right) - 2\,\text{mol}\left(-110.9\frac{\text{kJ}}{\text{mol}}\right) - 1\,\text{mol}\left(87.6\frac{\text{kJ}}{\text{mol}}\right) \\
&= 153.9\ \text{kJ} - 237.1\ \text{kJ} + 221.8\ \text{kJ} - 87.6\ \text{kJ} \\
\Delta G_{rxn}^\circ &= 51.0\,\text{kJ} \times \frac{1000\ \text{J}}{1\text{kJ}} = 51000\ \text{J}
\end{aligned}
$$

$$
\begin{aligned}
\Delta G_{rxn}^\circ &= -RT \ln K_{eq} \\
K_{eq} &= \exp - \frac{\Delta G_{rxn}^\circ}{RT} \\
&= \exp - \frac{51000\ \text{J}}{8.3145\frac{\text{J}}{\text{mol K}} \times 298\ \text{K}} \\
&= e^{-20.58} \\
K_{eq} &= \textbf{C) } 1.15 \times 10^{-9}
\end{aligned}
$$

36. Consider the following equilibria and equilibrium constants:

$$
\begin{aligned}
\text{X} &\rightleftharpoons \text{Y} & K_1 &= 5.0 \\
\text{Y} &\rightleftharpoons \text{Z} & K_2 &= 5.0
\end{aligned}
$$

What is the equilibrium constant, K, for X$\rightleftharpoons$Z?

$$
\begin{aligned}
K_1 &= \frac{[Y]}{[X]} = 5.0 \\
K_2 &= \frac{[Z]}{[Y]} = 5.0 \\
K &= \frac{[Z]}{[X]} \\
&= \frac{[Z]}{[Y]}\frac{[Y]}{[X]} \\
&= K_1 \times K_2 = \textbf{E) } 25.0
\end{aligned}
$$

13

37. At 22°C, $K_p = 0.070$ for the equilibrium:

$$NH_4HS_{(s)} \rightleftharpoons NH_{3\ (g)} + H_2S_{(g)}$$

A sample of solid NH_4HS is placed in a closed vessel and allowed to equilibrate. Calculate the equilibrium partial pressure (atm) of ammonia, assuming that some solid NH_4HS remains.

$$
\begin{aligned}
K_p &= P_{NH_3} \cdot P_{H_2S} \\
0.070 &= P_{NH_3} \cdot P_{H_2S}
\end{aligned}
$$

Now, for every 1 mol of NH_4HS that reacts, there is 1 mole of NH_3 and 1 mole of H_2S produced. Therefore, for every x moles of NH_3, there are x moles of H_2S

$$
\begin{aligned}
0.070 &= P_{NH_3} \cdot P_{H_2S} \\
0.070 &= x^2 \\
x &= \sqrt{0.070} \\
x &= 0.26 \text{ atm}
\end{aligned}
$$

So, ammonia will have a partial pressure of **A)** 0.26 atm.

38. In the experiment "'How Hot is that Flame"', 100.0 g of room temperature water (25.0°C) was put in a calorimeter. 60.0 g of cold water (3.0°C) was added. When the temperature of the entire setup is constant, it was 17.5°C. The specific heat of water is 4.184 $\frac{J}{g\ °C}$. What is the heat capacity of the calorimeter, K_{cal}?

heat lost by room temperature water + heat lost by calorimeter = heat gained by cold water

$$
\begin{aligned}
-q_{RT} - q_{cal} &= q_{CW} \\
q_{cal} &= -q_{CW} - q_{RT} \\
m_{cal}C_{cal}\Delta T_{cal} &= -q_{CW} - q_{RT} \\
K_{cal} &= m_{cal}C_{cal} \text{ since the mass and heat capacity of the calorimeter are both constants} \\
K_{cal}\Delta T_{cal} &= -q_{CW} - q_{RT} \\
K_{cal} &= \frac{-q_{CW} - q_{RT}}{\Delta T_{cal}} \\
K_{cal} &= \frac{-m_{CW}C_w\Delta T_{CW} - m_{RT}C_w\Delta T_{RT}}{\Delta T_{cal}} \\
K_{cal} &= \frac{-\left(60.0\ \cancel{g}\right)\left(4.184\frac{J}{\cancel{g}\ °C}\right)(17.5°C - 3.0°C) - (100.0\ \cancel{g})\left(4.184\frac{J}{\cancel{g}\ °C}\right)(17.5°C - 25.0°C)}{(17.5°C - 25.0°C)} \\
K_{cal} &= \frac{-\left(251.0\frac{J}{\cancel{°C}}\right)(14.5°\cancel{C}) - \left(418.4\frac{J}{\cancel{°C}}\right)(-7.5°\cancel{C})}{(-7.5°C)}
\end{aligned}
$$

$$
\begin{aligned}
K_{cal} &= \frac{-3639.5 \text{ J} + 3138.0 \text{ J}}{(-7.5^{\circ}\text{C})} \\
K_{cal} &= \frac{-501.5 \text{ J}}{(-7.5^{\circ}\text{C})} \\
K_{cal} &= \textbf{B) } 67 \frac{\text{J}}{^{\circ}\text{C}}
\end{aligned}
$$

39. A student explored the thermodynamic properties of the dissolution of borax using titrations at different temperatures. The following plot was obtained. What is ΔS° in $\frac{\text{J}}{\text{mol K}}$ for the dissolution of borax?

Van't Hoff Plot for the Dissolution of Borax

$y = -16870x + 53.727 \quad R^2 = 0.9978$
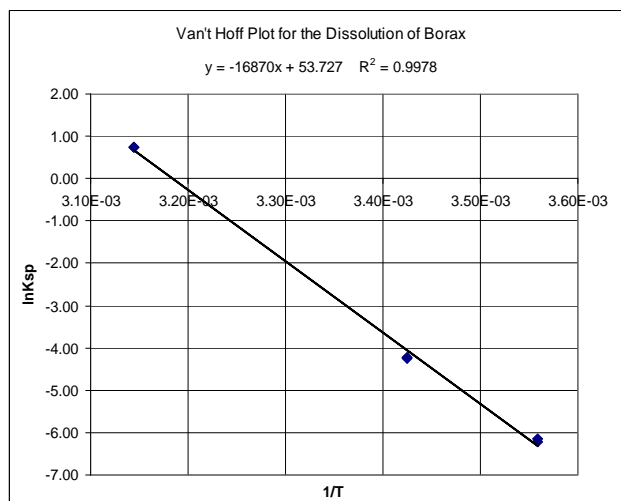
We can use the Van't Hoff equation:

$$
\ln K = -\frac{\Delta H^{\circ}}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^{\circ}}{R}
$$

which shows that the y intercept will be $\dfrac{\Delta S^{\circ}}{R}$ for a plot of $\ln K$ vs. $\dfrac{1}{T}$. Therefore:
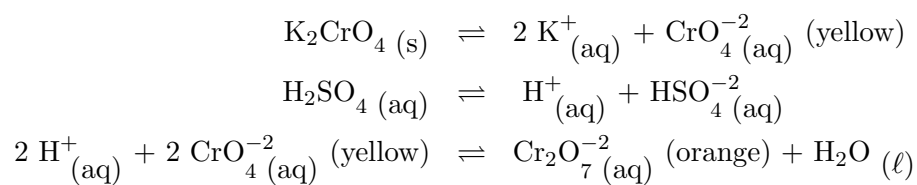
$$
\begin{aligned}
\frac{\Delta S^{\circ}}{R} &= 53.727 \\
\Delta S^{\circ} &= 53.727 \cdot R \\
\Delta S^{\circ} &= 53.727 \cdot 8.314 \frac{\text{J}}{\text{mol K}} \\
\Delta S^{\circ} &= \textbf{C) } 446.69 \frac{\text{J}}{\text{mol K}}
\end{aligned}
$$

40. A student has a solution of potassium chromate (K_2CrO_4) in a test tube. The solution is yellow. To this test tube, several drops of a solution of sulfuric acid are added. Given the reactions below, predict what changes will occur after the addition of acid and why the changes occur.

$$K_2CrO_{4\ (s)} \rightleftharpoons 2\ K^+_{(aq)} + CrO^{-2}_{4\ (aq)} \ (\text{yellow})$$

$$H_2SO_{4\ (aq)} \rightleftharpoons H^+_{(aq)} + HSO^{-2}_{4\ (aq)}$$

$$2\ H^+_{(aq)} + 2\ CrO^{-2}_{4\ (aq)} \ (\text{yellow}) \rightleftharpoons Cr_2O^{-2}_{7\ (aq)} \ (\text{orange}) + H_2O_{(\ell)}$$

A) The solution remains yellow because sulfuric acid is colorless

B) The solution remains yellow because no additional reactions take place

C) The solution turns a lighter yellow because it is more dilute after adding acid

D) The solution turns orange because the acid reacts with the chromate to convert it to dichromate which is orange.