Name ___________________________ AP CHEM ___/___/___

Collected AP Exam Essay Answers for Chapter 16

1980 - #7

(a) State the physical significance of entropy. **Entropy (S) is a measure of randomness or disorder in a system.**

(b) From each of the following pairs of substances, choose the one expected to have the greater absolute entropy. Explain your choice in each case. Assume 1 mole of each substance.

(1) Pb(s) or C(graphite) at the same temperature and pressure

Pb(s); Pb has metallic bonding and is soft; atoms have large amplitude of vibration; C has atoms more localized by strong covalent bonds and is a more ordered element.

(2) He(g) at 1 atmosphere or He(g) at 0.05 atmosphere, both at the same temperature

He (0.05 atm) At lower pressure (greater volume) atoms have more space in which to move.

(3) $H_2O(l)$ or $CH_3CH_2OH(l)$ at the same temperature and pressure

$CH_3CH_2OH(l)$; Ethanol is a molecule with more atoms and thus more vibrations; water has fewer atoms and is more localized by hydrogen-bonding.

(4) Mg(s) at 0°C or Mg(s) at 150°C, both at the same pressure.

Mg (150°); At higher temperature, atoms have more kinetic energy and vibrate faster and further, i.e., greater randomness occurs.

1983 - #2

$$CO(g) + 2\ H_2(g) <===> CH_3OH(l)\ \Delta H° = -128.1 \text{ kilojoules}$$

Substance	$\Delta H_f°$ (kJ mol^{-1})	$\Delta G_f°$ (kJ mol^{-1})	S° (J mol^{-1} K^{-1})
CO(g)	-110.5	-137.3	+197.9
$CH_3OH(l)$	-238.6	-166.2	+126.8

The data in the table above were determined at 25°C.

(a) Calculate ΔG° for the reaction above at 25°C. **-28.9 KJ/mol**

(b) Calculate K_{eq} for the reaction above at 25°C. **K = 1.17 x 10^5**

(c) Calculate ΔS° for the reaction above at 25°C. **-333 J / mol-K**

(d) In the table above, there is no data for H_2. What are the values of $\Delta H_f°$, $\Delta G_f°$, and of the absolute entropy, S°, for H_2 at 25°C? **$\Delta H_f°$ (H_2) = 0; $\Delta G_f°$ (H_2) = 0; S° = 131 J / mol-K**

1984 - #3

Substance	Standard Heat of Formation, $\Delta H_f°$ (kJ mol^{-1})	Absolute Entropy, S° (J mol^{-1} K^{-1})
C(s)	0.00	5.69
$CO_2(g)$	-393.5	213.6
$H_2(g)$	0.00	130.6
$H_2O(l)$	-285.85	69.96
$O_2(g)$	0.00	205.0
$C_3H_7COOH(l)$	?	226.3

The enthalpy change for the combustion of butyric acid at 25°C, $\Delta H°_{comb}$, is -2,183.5 kilojoules per mole. The combustion reaction is:

$$C_3H_7COOH(l) + 5O_2(g) <===> 4CO_2(g) + 4H_2O(l)$$

(a) From the data above, calculate the standard heat of formation, $\Delta H_f°$, for butyric acid at 25°C. **- 533.8 kJ**

(b) Write a correctly balanced equation for the formation of butyric acid from its elements.

$4\ C(s) + 4\ H_2(g) + O_2(g) \rightarrow C_3H_7COOH$

(c) Calculate the standard entropy change, $\Delta S_f°$, for the formation of butyric acid at 25°C. The entropy change, ΔS°, for the combustion reaction above is -117.1 J K^{-1} at 25°C**. - 523.9 joules/K**

(d) Calculate the standard free energy of formation, $\Delta G_f°$, for butyric acid at 25°C. **- 377.7 kJ**

1985 - #6

(a) When liquid water is introduced into an evacuated vessel at 25 °C, some of the water vaporizes. Predict how the enthalpy, entropy, free energy, and temperature change in the system during this process. Explain the basis for each of your predictions.

$\Delta H > 0$ since heat is required to change liquid water to vapor.

$\Delta S > 0$ since randomness increases when a liquid changes to vapor.

$\Delta G < 0$ since the evaporation takes place in this situation.

$\Delta T < 0$ since the more rapidly moving molecules leave liquid first. The liquid remaing is cooler.

(b) When a large amount of ammonium chloride is added to water at 25 °C, some of it dissolves and the temperature of the system decrease. Predict how the enthalpy, entropy, and free energy change in the system during this process. Explain the basis for each of your predictions.

$\Delta H > 0$. The system after the dissolving has a lower temperature and so the change is endothermic.

$\Delta S > 0$. Since the solution is less ordered than the separate substances are.

$\Delta G < 0$. The solution occurred and so is spontaneous.

(c) If the temperature of the aqueous ammonium chloride system in part (b) were to be increased to 30°C, predict how the solubility of the ammonium chloride would be affected. Explain the basis for your prediction.

Solubility increases. The added heat available pushes the endothermic process toward more dissolving.

1988 - #2

Substance	Enthalpy of Combustion $\Delta H°$ Kilojoules/mole	Absolute Entropy, S° Joules/mole-K
C(s)	-393.5	5.740
$H_2(g)$	-285.8	130.6
$C_2H_5OH(l)$	-1366.7	160.7
$H_2O(l)$	------------	69.91

(a) Write a separate, balanced chemical equation for the combustion of each of the following: C(s), $H_2(g)$, and $C_2H_5OH(l)$. Consider the only products to be $CO_2(g)$ and/or $H_2O(l)$.

$C + O_2 \rightarrow CO_2$

$2\ H_2 + O_2 \rightarrow 2\ H_2O$

$C_2H_5OH + 3\ O_2 \rightarrow 2CO_2 + 3\ H_2O$

(b) In principle, ethanol can be prepared by the following reaction.

$2\ C(s) + 2\ H_2(g) + H_2O(l) \rightarrow C_2H_5OH(l)$

Calculate the standard enthalpy change, $\Delta H°$, for the preparation of ethanol, as shown in the reaction above.

$2\ C + 2\ O_2 \rightarrow 2\ CO_2$ $\quad \Delta H° = 2\ (-\ 393.5) = -\ 787.0$ kJ

$2\ H_2 + O_2 \rightarrow 2\ H_2O$ $\quad \Delta H° = 2(-\ 285.8) = -\ 571.6$ kJ

$2\ CO_2 + 3\ O_2 \rightarrow C_2H_5OH + 3O_2$ $\quad \Delta H° = -\ (-\ 1366.7) = 1.366.7$ kJ

Sum of three equations above

$2\ C + 2\ H_2 + H_2O \rightarrow C_2H_5OH$ $\quad \Delta H° = 8.1$ kJ

(c) Calculate the standard entropy change, $\Delta S°$, for the reaction given in part (b) **- 181.9 J / mol K**

(d) Calculate the value of the equilibrium constant at 25°C for the reaction represented by the equation in part (b).

K = within range 1.1×10^{-11} - 1.3×10^{-11}

1989 - #3

$Br_2\ (l) \rightarrow Br_2\ (g)$

At 25°C the equilibrium constant, K_p, for the reaction above is 0.281 atmosphere.

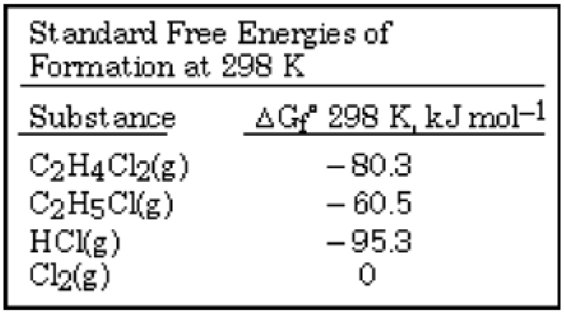
(a) What is $\Delta G°_{298}$ for this reaction? **3.14×10^3 J/mol**

(b) It takes 193 joules to vaporize 1.00 gram of $Br_2(l)$ at 25°C and 1.00 atmosphere pressure. What are the values of $\Delta H°_{298}$ and of $\Delta S°_{298}$ for this reaction? **$\Delta H°_{298} = 30.8$ kJ/mol K; $\Delta S°_{298} = 92.9$ J/mol K**

(c) Calculate the normal boiling point of bromine. Assume that $\Delta H°$ and $\Delta S°$ remain constant as the temperature is changed. **332 K**

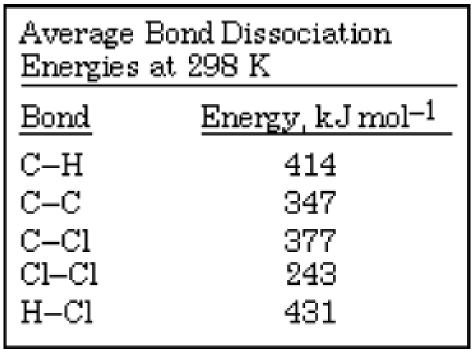
(d) What is the equilibrium vapor pressure of bromine at 25°C? **0.281 atm**

1990 - #3



Standard Free Energies of Formation at 298 K

Substance	ΔG_f° 298 K, kJ mol^{-1}
$C_2H_4Cl_2(g)$	−80.3
$C_2H_5Cl(g)$	−60.5
$HCl(g)$	−95.3
$Cl_2(g)$	0



Average Bond Dissociation Energies at 298 K

Bond	Energy, kJ mol^{-1}
C–H	414
C–C	347
C–Cl	377
Cl–Cl	243
H–Cl	431

The tables above contain information for determining thermodynamic properties of the reaction below.

$C_2H_5Cl(g) + Cl_2(g) <===> C_2H_4Cl_2\ (g) + HCl(g)$

(a) Calculate ΔH° for the reaction above, using the table of average bond dissociation energies. **-151 kJ/mol**
(b) Calculate ΔS° for the reaction at 298 K, using data from either table as needed. **-0.120 kJ/mol K**
(c) Calculate the value for K_{eq} for the reaction at 298 K. **1.50×10^{20}**
(d) What is the effect of an increase in temperature on the value of the equilibrium constant? Explain.
K_{eq} will decrease with an increase in T because the reverse (endothermic) reaction will be favored with addition of heat

1991 - #5

$BCl_3(g) + NH_3(g) \rightleftharpoons Cl_3BNH_3(s)$

The reaction represented above is a reversible reaction.
(a) Predict the sign of the entropy change, ΔS, as the reaction proceeds to the right. Explain your prediction.
ΔS will be negative. The system becomes more ordered as two gases form a solid.
(b) If the reaction spontaneously proceeds to the right, predict the sign of the enthalpy change, ΔH. Explain your prediction. **ΔH must be negative. For the reaction to be spontaneous, ΔG must be negative, so ΔH must be more negative than -TΔS is positive.**
(c) The direction in which the reaction spontaneously proceeds changes as the temperature is increased above a specific temperature. Explain. **As T increases, -TΔS increases. Since ΔS is negative, the positive -TΔS term will eventually exceed ΔH (which is negative), making ΔG positive.**
(d) What is the value of the equilibrium constant at the temperature referred to in (c); that is, the specific temperature at which the direction of the spontaneous reaction changes? Explain.
The equilibrium constant is 1. The system is at equilibrium at this temperature with an equal tendancy to go in either direction.

1992 - #3

$Cl_2(g) + 3F_2(g) \rightarrow 2ClF_3(g)$

ClF_3 can be prepared by the reaction represented by the equation above. For ClF_3 the standard enthalpy of formation, ΔH_f° is - 163.2 kilojoules/mole and the standard free energy of formation, ΔG_f°, is - 123.0 kilojoules/mole.

(a) Calculate the value of the equilibrium constant for the reaction at 298 K. **1.31×10^{43}**
(b) Calculate the standard entropy change, ΔS°, for the reaction at 298 K. **-270 J/K**
(c) If ClF_3 were produced as a liquid rather than as a gas, how would the sign and magnitude of ΔS for the reaction be affected? Explain. **ΔS is a larger negative number ClF_3 (liquid) is more ordered (less disordered) than ClF_3 (gas)**
(d) At 298 K the absolute entropies of $Cl_2(g)$ and $ClF_3(g)$ are 222.96 joules per mole-Kelvin and 281.50 joules per mole-Kelvin, respectively.
  (i) Account for the larger entropy of $ClF_3(g)$ relative to that of $Cl_2(g)$. **ClF_3 is a more complex molecule (i.e. more atoms) with more vibrational and rotational degrees of freedom than Cl_2**
  (ii) Calculate the value of the absolute entropy of $F_2(g)$ at 298 K. **203 J/mol K**

1993 - #8

$2\ C_4H_{10}(g) + 13\ O_2(g) \rightarrow 8\ CO_2(g) + 10\ H_2O(l)$

The reaction represented above is spontaneous at 25°C. Assume that all reactants and products are in their standard states.

(a) Predict the sign of $\Delta S°$ for the reaction and justify your prediction. **$\Delta S < 0$ The number of moles of gaseous products is less than the number of moles of gaseous reactant**

(b) What is the sign of $\Delta G°$ for the reaction? How would the sign and magnitude of $\Delta G°$ be affected by an increase in temperature to 50°C? Explain your answer. **$\Delta G < 0$; ΔG becomes less negative as the temperature is increased since $\Delta S < 0$ and $\Delta G = \Delta H - T\Delta S$. The term $- T\Delta S$ adds a positive number to ΔH.**

(c) What must be the sign of $\Delta H°$ for the reaction at 25°C? How does the total bond energy of the reactants compare to that of the products? **$\Delta H < 0$; The bond energy of the reactants is less than the bond energy of the products.**

(d) When the reactants are placed together in a container, no change is observed even though the reaction is known to be spontaneous. Explain this observation. **The reaction has a high activation energy.**

1994 - #6

$2\ H_2S(g) + SO_2(g) <===> 3\ S(s) + 2\ H_2O(g)$

At 298 K, the standard enthalpy change, $\Delta H°$, for the reaction represented above is -145 kilojoules.

(a) Predict the sign of the standard entropy change, $\Delta S°$, for the reaction. Explain the basis for your prediction. **Statement that $\Delta S°$ is negative; 3 moles of gas → 2 moles of gas plus solid**

(b) At 298 K, the forward reaction (i.e., toward the right) is spontaneous. What change, if any, would occur in the value of $\Delta G°$ for this reaction as the temperature is increased? Explain your reasoning using thermodynamic principles. **$\Delta G°$ is less negative, goes to 0, goes positive, gets larger; Explanation using $\Delta G° = \Delta H° - T\Delta S°$**

(c) What change, if any, would occur in the value of the equilibrium constant, K_{eq}, for the situation described in (b)? Explain your reasoning. **K_{eq} goes from > 1, to 1, to < 1, as T increases. Correct explanation using the equation $\Delta G° = - RT \ln K$ OR higher T favors the reverse reaction (Le Châtelier) because the forward reaction is exothermic.**

(d) The absolute temperature at which the forward reaction becomes nonspontaneous can be predicted.
Write the equation that is used to make the prediction. Why does this equation predict only an approximate value for the temperature? **Since $\Delta G° = 0$ at this point, the equation is $T = \Delta H° / \Delta S°$; Prediction is not exact since $\Delta H°$ and/or $\Delta S°$ vary with T.**

1995 - #8

Lead iodide is a dense, golden yellow, slightly soluble solid. At 25°C, lead iodide dissolves in water forming a system represented by the following equation.

$PbI_2(s) <===> Pb^{2+} + 2\ I^- \quad \Delta H = +46.5$ kilojoules

The solubility-product constant, K_{sp}, for PbI_2 is 7.1×10^{-9} at 25°C.

(a) How does the entropy of the system $PbI_2(s) + H_2O(l)$ change as $PbI_2(s)$ dissolves in water at 25°C? Explain. **ΔS increases; Dissolving converts highly organized solid to less organized hydrated ions OR dissociates, break down, etc. OR less particles => more particles**

(b) If the temperature of the system were lowered from 25°C to 15°C, what would be the effect on the value of K_{sp}? Explain. **K_{sp} decreases lowering T decreases the solubility since the reaction is endothermic**

(c) If additional solid PbI_2 were added to the system at equilibrium, what would be the effect on the concentration of I^- in the solution? Explain. **There is no effect on $[I^-]$; PbI_2 is a solid; its concentration does NOT change on addition of more PbI_2 OR $PbI_2(s)$ is NOT included in the expression for K_{sp} or Q OR the solution is saturated so no more solid will dissolve**

(d) At equilibrium, $\Delta G = O$. What is the initial effect on the value of ΔG of adding a small amount of $Pb(NO_3)_2$ to the system at equilibrium? Explain. **ΔG becomes more positive (increases, gets larger, etc.) due to the common ion effect; the increase in $[Pb^{2+}]$ shifts the equilibrium to the left. OR the reverse reaction becomes more spontaneous as $[Pb^{2+}]$ increases due to the common ion effect**

1997 - #7

For the gaseous equilibrium represented below, it is observed that greater amounts of PCl_3 and Cl_2 are produced as the temperature is increased.

$PCl_5(g) <===> PCl_3(g) + Cl_2(g)$

(a) What is the sign of $\Delta S°$ for the reaction? Explain. **$\Delta S°$ is positive (or "+", or ">0"). Moles products > moles reactants**

(b) What change, if any, will occur in ΔG° for the reaction as the temperature is increased? Explain your reasoning in terms of thermodynamic principles. **ΔG° will decrease (or become more negative, or become smaller). ΔG° = ΔH° - TΔS° and since ΔS° is positive, TΔS° is positive (> 0). Thus increasing T will result in a larger term being subtracted from ΔH°, or, ΔG° = -RT ln K and K is going up in value since T is increasing.)**
(c) If He gas is added to the original reaction mixture at constant volume and temperature, what will happen to the partial pressure of Cl_2? Explain. **no change; P_{He} is not part of the reaction (He is not involved) or equilibrium constant expression; hence altering P_{He} has no effect on the position at equilibrium.**
(d) If the volume of the original reaction is decreased at constant temperature to half the original volume, what will happen to the number of moles of Cl_2 in the reaction vessel? Explain. **moles of Cl_2 will decrease; The decrease in volume leads to an increase in pressure (concentration), therefore the reaction shifts to the left because: $Q > K_{sp}$, the rate of the reverse reaction increase more than the rate of the forward reaction, or, the reaction shifts toward the lesser moles of gas.**

1998 - #3

$C_6H_5OH(s) + 7O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$

When a 2.000-gram sample of pure phenol, $C_6H_5OH(s)$, is completely burned according to the equation above, 64.98 kilojoules of heat is released. Use the information in the table below to answer the questions that follow.

Substance	Standard Heat of Formation, ΔH°$_f$, at 25°C (kJ/mol)	Absolute Entropy, S°, at 25°C (J/mol-K)
C (graphite)	0.00	5.69
$CO_2(g)$	-395.5	213.6
$H_2(g)$	0.00	130.6
$H_2O(l)$	-285.85	69.91
$O_2(g)$	0.00	205.0
C_6H_5OH (s)	?	144.0

(a) Calculate the molar heat of combustion of phenol in kilojoules per mole at 25°C. **ΔH_{comb} = - 3,058 kJ/mol**
(b) Calculate the standard heat of formation, ΔH°$_f$, of phenol in kilojoules per mole at 25°C. **ΔH°$_f$ = - 173 kJ**
(c) Calculate the value of the standard free-energy change, ΔG° for the combustion of phenol at 25°C.
ΔG° = -3,032 kJ
(d) If the volume of the combustion container is 10.0 liters, calculate the final pressure in the container when the temperature is changed to 110°C. (Assume no oxygen remains unreacted and that all products are gaseous.)
0.601 atm

1999 - #6

Answer the following questions in terms of thermodynamic principles and concepts of kinetic molecular theory.
(a) Consider the reaction represented below, which is spontaneous at 298 K.

$CO_2(g) + 2\ NH_3(g) \rightarrow CO(NH_2)_2(s) + H_2O(l)\ \Delta H^\circ_{298} = -134$ kJ

(i) For the reaction, indicate whether the standard entropy change, ΔS°_{298}, is positive, or negative, or zero. Justify your answer. **ΔS° is negative (−) OR ΔS° < 0 OR entropy is decreasing. 3 moles of gaseous particles are converted to 2 moles of solid/liquid.**
(ii) Which factor, the change in enthalpy, ΔH°_{298}, or the change in entropy, ΔS°_{298}, provides the principal driving force for the reaction at 298 K? Explain. **ΔH° drives the reaction. The decrease in entropy (ΔS° < 0) cannot drive the reaction, so the decrease in enthalpy (ΔH° < 0) MUST drive the reaction. OR ΔG° = ΔH° − TΔS°; for a spontaneous reaction ΔG° < 0, and a negative value of ΔS° causes a positive ΔG°.**
(iii) For the reaction, how is the value of the standard free energy change, Δ*G*°, affected by an increase in temperature? Explain. **Given that ΔG° = ΔH° − TΔS° and ΔS° < 0, an increase in temperature causes an increase in the value of ΔG° (ΔG° becomes less negative).**

(b) Some reactions that are predicted by their sign of Δ*G*° to be spontaneous at room temperature do not proceed at a measurable rate at room temperature.
(i) Account for this apparent contradiction. **The reaction rate depends on the reaction kinetics, which is determined by the value of the activation energy, E_{act}. If the activation energy is large, a reaction that is thermodynamically spontaneous may proceed very slowly (if at all).**

(ii) A suitable catalyst increases the rate of such a reaction. What effect does the catalyst have on Δ*G*° for the reaction? Explain. **The catalyst has no effect on the value of ΔG°. The catalyst reduces the value of E_{act}, increasing the rate of reaction, but has no effect on the values of ΔH° and ΔS°, so it cannot affect the thermodynamics of the reaction.**

2001 - #2

$$2\ NO(g) + O_2(g) \rightarrow 2NO_2(g)\ \Delta H_f^\circ = -114.1\ kJ,\ \Delta S^\circ = -146.5\ J\ K^{-1}$$

The reaction represented above is one that contributes significantly to the formation of photochemical smog.

(a) Calculate the quantity of heat released when 73.1 g of $NO(g)$ is converted to $NO_2(g)$. **139 kJ**

(b) For the reaction at 25°C, the value of the standard free-energy change, Δ*G*° is -70.4 kJ.

(i) Calculate the value of the equilibrium constant, K_{eq} , for the reaction at 25°C. **2.2 x10^{12}**

(ii) Indicate whether the value of Δ*G*° would become more negative, less negative, or remain unchanged as the temperature is increased. Justify your answer. **As the temperature increases, *T* Δ*S*° will decrease (Δ*S*° is negative) −*T* Δ*S*° will increase, therefore Δ*G*° will become less negative.**

(c) Use the data in the table below to calculate the value of the standard molar entropy, *S*° for $O_2(g)$ at 25°C.

Substance	Standard Molar Entropy, S° ($J\ K^{-1}\ mol^{-1}$)
NO(g)	210.8
NO_2(g)	240.1

205.1 J K^{-1}

(d) Use the data in the table below to calculate the bond energy, in kJ mol^{-1}, of the nitrogen-oxygen bond in NO_2. Assume that the bonds in the NO_2 molecule are equivalent (i.e., they have the same energy).

456 kJ/mol

Bond	Bond Energy (kJ mol^{-1})
Nitrogen-oxygen bond in NO	607
Oxygen-oxygen bond in O_2	495
Nitrogen-oxygen bond in NO_2	?

2002 - #8

$$C(s) + CO_2(g) \rightleftharpoons 2\ CO(g)$$

Carbon (graphite), carbon dioxide, and carbon monoxide form an equilibrium mixture, as represented by the equation above.

(a) Predict the sign for the change in entropy, Δ*S*, for the reaction. Justify your prediction.

Δ*S* = + There is more disorder in a gas than in a solid, so the product is more disordered than the reactants. The change in entropy is therefore positive. OR There is 1 mole of gas in the reactants and 2 moles of gas in the product.

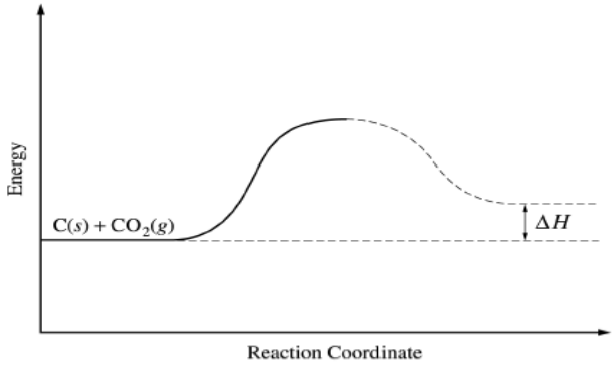
(b) In the table below are data that show the percent of CO in the equilibrium mixture at two different temperatures. Predict the sign for the change in enthalpy, Δ*H*, for the reaction. Justify your prediction.

Temperature	% CO
700°C	60
850°C	94

Δ*H* = + More CO at the higher temperature indicates that the reaction shifts to the right with increasing temperature. For this to occur, the reaction must be endothermic.

(c) Appropriately complete the potential energy diagram for the reaction by finishing the curve on the graph below. Also, clearly indicate Δ*H* for the reaction on the graph.

(d) If the initial amount of C(*s*) were doubled, what would be the effect on the percent of CO in the equilibrium mixture? Justify your answer. **An increase in the amount of C(*s*) has no effect. Solids do not appear in the equilibrium expression, so adding more C(*s*) will not affect the percent of CO in the equilibrium mixture.**



2002B - #3

Nitrogen monoxide, NO(g), and carbon monoxide, CO(g), are air pollutants generated by automobiles. It has been proposed that under suitable conditions these two gases could react to form $N_2(g)$ and $CO_2(g)$, which are components of unpolluted air.

(a) Write a balanced equation for the reaction described above. Indicate whether the carbon in CO is oxidized or whether it is reduced in the reaction. Justify your answer.

$2\ NO(g) + 2\ CO(g) \rightarrow N_2(g) + 2\ CO_2(g)$; CO is oxidized. Carbon in CO has an oxidation number of +2 and in CO_2 carbon has an oxidation number of +4. The oxidation number increases.

(b) Write the expression for the equilibrium constant, K_p, for the reaction.

$$K_p = \frac{(P_{N_2})(P_{CO_2})^2}{(P_{NO})^2(P_{CO})^2}$$

(c) Consider the following thermodynamic data.

	NO	CO	CO_2
$\Delta G_f°$(kJ mol^{-1})	+86.55	−137.15	−394.36

(i) Calculate the value of $\Delta G°$ for the reaction at 298 K. **–687.52 kJ**

(ii) Given that $\Delta H°$ for the reaction at 298 K is −746 kJ per mole of $N_2(g)$ formed, calculate the value of $\Delta S°$ for the reaction at 298 K. Include units with your answer. **– 0.196 kJ K^{-1}**

(d) For the reaction at 298 K, the value of K_p is 3.3 x 10^{120}. In an urban area, typical pressures of the gases in the reaction are $P_{NO} = 5.0 \times 10^{-7}$ atm, $P_{CO} = 5.0 \times 10^{-5}$ atm, $P_{N2} = 0.781$ atm, and $P_{CO2} = 3.1 \times 10^{-4}$ atm.

(i) Calculate the value of ΔG for the reaction at 298 K when the gases are at the partial pressures given above. **–607 kJ**

(ii) In which direction (to the right or to the left) will the reaction be spontaneous at 298 K with these partial pressures? Explain. **The reaction is spontaneous (→ right) because ΔG is negative. (Reference must be according to ΔG, not $\Delta G°$)**

2003 - #7

Answer the following questions that relate to the chemistry of nitrogen.

(a) Two nitrogen atoms combine to form a nitrogen molecule, as represented by the following equation.

$2\ N(g) \rightarrow N_2(g)$

Using the table of average bond energies below, determine the enthalpy change, ΔH, for the reaction.

Bond	Average Bond Energy (kJ mol^{-1})
N — N	160
N = N	420
N ≡ N	950

$\Delta H = -950$ kJ

(b) The reaction between nitrogen and hydrogen to form ammonia is represented below.

$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)\ \Delta H° = -92.2$ kJ

Predict the sign of the standard entropy change, $\Delta S°$, for the reaction. Justify your answer.

$\Delta S°$ is negative. There are fewer moles of product gas (2 mol) compared to reactant gases (4 mol), so the reaction is becoming more ordered.

(c) The value of $\Delta G°$ for the reaction represented in part (b) is negative at low temperatures but positive at high temperatures. Explain. **$\Delta G° = \Delta H° - T\Delta S°$; $\Delta H°$ and $\Delta S°$ are negative. At low temperatures, the $T\Delta S°$ term is smaller than $\Delta H°$, and $\Delta G°$ is negative. At high temperatures, the $T\Delta S°$ term is higher than $\Delta H°$, and $\Delta G°$ is positive.**

(d) When $N_2(g)$ and $H_2(g)$ are placed in a sealed container at a low temperature, no measurable amount of $NH_3(g)$ is produced. Explain. **Even though the reaction is spontaneous at low temperature, the reaction is very slow. The speed of a reaction depends on the fraction of colliding molecules with energy that exceeds the activation energy for the reaction. At low temperature, few reactant particles collide with an energy greater than the activation energy.**

2004 - #2

$2\ \mathrm{Fe}(s) + \frac{3}{2}\ \mathrm{O_2}(g) \rightarrow \mathrm{Fe_2O_3}(s)\ \Delta H_f^\circ = -824\ \mathrm{kJ\ mol^{-1}}$

Iron reacts with oxygen to produce iron(III) oxide, as represented by the equation above. A 75.0 g sample of Fe(*s*) is mixed with 11.5 L of O_2(*g*) at 2.66 atm and 298 K.

(a) Calculate the number of moles of each of the following before the reaction begins.

(i) Fe(*s*) **1.34 moles**

(ii) O_2(*g*) **1.25 moles**

(b) Identify the limiting reactant when the mixture is heated to produce Fe_2O_3(*s*). Support your answer with calculations. **Fe is the limiting reagent**

(c) Calculate the number of moles of Fe_2O_3(*s*) produced when the reaction proceeds to completion.
0.670 moles Fe_2O_3

(d) The standard free energy of formation, ΔG_f°, of Fe_2O_3(*s*) is −740. kJ mol^{-1} at 298 K.

(i) Calculate the standard entropy of formation, ΔS_f°, of Fe_2O_3(*s*) at 298 K. Include units with your answer.
– 0.28 kJ/mol

(ii) Which is more responsible for the spontaneity of the formation reaction at 298 K, the standard enthalpy of formation, ΔH_f°, or the standard entropy of formation, ΔS_f°? Justify your answer. **ΔH_f° is the more important factor. The reaction is exothermic, which favors spontaneity. $\Delta S_f^\circ$is negative, which means the system becomes more ordered as the reaction proceeds. Greater order will not increase the spontaneity of the reaction.**

The reaction represented below also produces iron(III) oxide. The value of ΔH° for the reaction is −280. kJ per mole of Fe_2O_3(*s*) formed.

$2\ \mathrm{FeO}(s) + ½\ \mathrm{O_2}(g) \rightarrow \mathrm{Fe_2O_3}(s)$

(e) Calculate the standard enthalpy of formation, ΔH_f°, of FeO(*s*). **ΔH_f° = - 272 kJ mol^{-1}**

2004B - #7

$\mathrm{N_2}(g) + 2\ \mathrm{H_2}(g) \rightleftharpoons \mathrm{N_2H_4}(g)\ \Delta H_{298}^\circ = +95.4\ \mathrm{kJ\ mol^{-1}};\ \Delta S_{298}^\circ = -176\ \mathrm{J\ K^{-1}\ mol^{-1}}$

Answer the following questions about the reaction represented above using principles of thermodynamics.

(a) On the basis of the thermodynamic data given above, compare the sum of the bond strengths of the reactants to the sum of the bond strengths of the product. Justify your answer. **Bond energy (B.E.) of reactants is greater than bond energy of products. Reaction is endothermic, so more energy is required to break bonds of reactants than is given off when new bonds form in products:**
$\Delta H = \sum(\mathrm{B.E.})_{reactants} - \sum(\mathrm{B.E.})_{products} > 0$

(b) Does the entropy change of the reaction favor the reactants or the product? Justify your answer. **Entropy change favors reactants. Since there are three moles of reactants in gas phase compared to only one mole of products, there are more possible arrangements of reactant molecules compared to product molecules.**

(c) For the reaction under the conditions specified, which is favored, the reactants or the product? Justify your answer. **Reactants are favored because ΔG° for reaction is positive. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, so a positive ΔH° and a negative ΔS° means ΔG° is always positive, independent of temperature.**

(d) Explain how to determine the value of the equilibrium constant, K_{eq}, for the reaction. **(Do not do any calculations.) Solve formula $\Delta G^\circ = -RT \ln K_{eq}$ for K_{eq} and plug in value of ΔG° calculated in part (c), value of temperature (298 K), and value of R (8.31 J mol^{-1} K^{-1}).**

(e) Predict whether the value of K_{eq} for the reaction is greater than 1, equal to 1, or less than 1. Justify your answer. **K_{eq} value is less than 1 for the reaction as written. $\Delta G^\circ = -RT \ln K_{eq}$, and since ΔG° is positive, $\ln K_{eq}$ will be a negative number which means that Keq is less than one. OR $\Delta H^\circ > 0$ and $S^\circ < 0$, thus $\Delta G^\circ > 0$, which means that $K_{eq} < 1$.**

2005 - #8

$\mathrm{AgNO_3}(s) \rightarrow \mathrm{Ag^+}(aq) + \mathrm{NO_3^-}(aq)$

The dissolving of $AgNO_3$(*s*) in pure water is represented by the equation above.

(a) Is ΔG for the dissolving of $AgNO_3$(*s*) positive, negative, or zero? Justify your answer. **ΔG for the dissolving of $AgNO_3$(s) is negative. Because $AgNO_3$(s) is known to be soluble in water, the solution process must be spontaneous, therefore ΔG is negative.**

(b) Is ΔS for the dissolving of $AgNO_3$(*s*) positive, negative, or zero? Justify your answer. **ΔS is positive because the solid reactant $AgNO_3$(s) is more ordered than the aqueous ion products, Ag^+(aq) and NO_3^-(aq).**

(c) The solubility of $AgNO_3(s)$ increases with increasing temperature.

(i) What is the sign of Δ*H* for the dissolving process? Justify your answer. **The sign of ΔH must be positive for the solubility of $AgNO_3$ to increase with increasing temperature. Solubility is an equilibrium process, and since increasing temperature (accomplished by adding heat) shifts the equilibrium towards the products side in the chemical equation, heat must be absorbed during the solution process. Therefore, the solution process is endothermic, and $\Delta H > 0$.**

(ii) Is the answer you gave in part (a) consistent with your answers to parts (b) and (c) (i)? Explain. **Yes. Although ΔH is positive, ΔS is also positive; thus ΔG can be negative because the value of the TΔS term in the equation $\Delta G = \Delta H - T\Delta S$ is positive and can be greater than the value of the ΔH term. A positive number minus a greater positive number yields a negative number for the value of ΔG.**

2005B - #7

Answer the following questions about thermodynamics.

Substance	Combustion Reaction	Enthalpy of Combustion, ΔH°_{comb}, at 298 K (kJ mol^{-1})
$H_2(g)$	$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$	−290
$C(s)$	$C(s) + O_2(g) \rightarrow CO_2(g)$	−390
$CH_3OH(l)$	$\mathbf{CH_3OH + \frac{3}{2} O_2 \rightarrow CO_2 + 2H_2O}$	−730

(a) In the empty box in the table above, write a balanced chemical equation for the complete combustion of one mole of $CH_3OH(l)$. Assume products are in their standard states at 298 K. Coefficients do not need to be whole numbers.

(b) On the basis of your answer to part (a) and the information in the table, determine the enthalpy change for the reaction $C(s) + H_2(g) + H_2O(l) \rightarrow CH_3OH(l)$. **ΔH = 50 kJ**

(c) Write the balanced chemical equation that shows the reaction that is used to determine the enthalpy of formation for one mole of $CH_3OH(l)$. $\mathbf{2C + 4H_2 + O_2 \rightarrow 2CH_3OH}$

(d) Predict the sign of Δ*S*° for the combustion of $H_2(g)$. Explain your reasoning. **ΔS° for the combustion of $H_2(g)$ is negative. Both reactants are in the gas phase and the product is in the liquid phase. The liquid phase is much more ordered than the gas phase, so the product is more ordered compared to the reactants, meaning that ΔS° is negative. (Note: There are fewer moles of products than reactants, which also favors a more ordered condition in the products, but the difference in phases is the more important factor.)**

(e) On the basis of bond energies, explain why the combustion of $H_2(g)$ is exothermic. **On the basis of bond energies, explain why the combustion of $H_2(g)$ is exothermic. The combustion of $H_2(g)$ is exothermic ($\Delta H^\circ < 0$) because more energy is released during the formation of two moles of O–H bonds than is required to break one mole of H–H bonds and one-half of a mole of O–O bonds.**

2006 - #2

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

The combustion of carbon monoxide is represented by the equation above.

(a) Determine the value of the standard enthalpy change, ΔH_{rxn}, for the combustion of $CO(g)$ at 298 K using the following information. $\mathbf{\Delta H_{rxn} = -283.0}$ **kJ mol^{-1}**

$C(s) + \frac{1}{2} O_2(g) \rightarrow$ □$CO(g)$ $\Delta H_{298} = -110.5$ kJ mol^{-1}

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_{298} = -393.5$ kJ mol^{-1}

(b) Determine the value of the standard entropy change, ΔS_{rxn}, for the combustion of $CO(g)$ at 298 K using the information in the following table.

Substance	S_{298} (J mol^{-1} K^{-1})
$CO(g)$	197.7
$CO_2(g)$	213.7
$O_2(g)$	205.1

-86.5 J mol^{-1} K^{-1}

(c) Determine the standard free energy change, ΔG_{rxn}, for the reaction at 298 K. Include units with your answer.

$\mathbf{\Delta G_{rxn} = -257.2}$ **kJ mol^{-1}**

(d) Is the reaction spontaneous under standard conditions at 298 K? Justify your answer. **Yes, the reaction is spontaneous because the value of ΔG_{rxn} for the reaction is negative (-257.2 kJ mol^{-1}).**
(e) Calculate the value of the equilibrium constant, K_{eq}, for the reaction at 298 K. **$K_{eq} = 1.28 \times 10^{45}$**

2006B - #3

Answer the following questions about the thermodynamics of the reactions represented below.
Reaction X: $\frac{1}{2}I_2(s) + \frac{1}{2}Cl_2(g) \rightleftharpoons ICl(g)$ $\quad \Delta H_f° = 18$ kJ mol^{-1}, $\Delta S_{298}° = 78$ J K^{-1} mol^{-1}
Reaction Y: $\frac{1}{2}I_2(s) + \frac{1}{2}Br_2(l) \rightleftharpoons IBr(g)$ $\quad \Delta H_f° = 41$ kJ mol^{-1}, $\Delta S_{298}° = 124$ J K^{-1} mol^{-1}
(a) Is reaction X, represented above, spontaneous under standard conditions? Justify your answer with a calculation.
Reaction is spontaneous because $\Delta G° < 0$
(b) Calculate the value of the equilibrium constant, K_{eq}, for reaction X at 25°C. **$K_{eq} = 8$**
(c) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer. **Since $\Delta H°$ is positive, an increase in T will cause $-\Delta H°/RT$ to become a smaller negative number, therefore K_{eq} will increase. *OR* The reaction is endothermic ($\Delta H = +18$ kJ mol^{-1}); an increase in temperature shifts the reaction to favor more products relative to the reactants, resulting in an increase in the value of K_{eq}.**
(d) Explain why the standard entropy change is greater for reaction Y than for reaction X. **Both reaction X and reaction Y have solid iodine as a reactant, but the second reactant in reaction X is chlorine gas whereas the second reactant in reaction Y is liquid bromine. Liquids have lower entropies than gases, thus in reaction Y the reactants are more ordered (and have lower entropies) than in reaction X. The products of both reaction X and reaction Y have about the same disorder, so the change in entropy from reactants to products is greater in reaction Y than in reaction X.**
(e) Above what temperature will the value of the equilibrium constant for reaction Y be greater than 1.0? Justify your answer with calculations. **T > 330 K Must show work in order to receive credit.**
(f) For the vaporization of solid iodine, $I_2(s) \rightarrow I_2(g)$, the value of $\Delta H_{298}°$ is 62 kJ mol^{-1}. Using this information, calculate the value of $\Delta H_{298}°$ for the reaction represented below.

$$I_2(g) + Cl_2(g) \rightleftharpoons 2\,ICl(g)$$

$\Delta H = -26$ kJ mol^{-1}

2007 - #2

$$N_2(g) + 3\,F_2(g) \rightarrow 2\,NF_3(g) \qquad \Delta H°_{298} = -264 \text{ kJ mol}^{-1};\ \Delta S°_{298} = -278 \text{ J K}^{-1}\text{ mol}^{-1}$$

The following questions relate to the synthesis reaction represented by the chemical equation in the box above.
(a) Calculate the value of the standard free energy change, $\Delta G_{298}°$, for the reaction. **−181 kJ mol^{-1}**
(b) Determine the temperature at which the equilibrium constant, K_{eq}, for the reaction is equal to 1.00. (Assume that $\Delta H°$ and $\Delta S°$ are independent of temperature.) **950. K**
(c) Calculate the standard enthalpy change, $\Delta H°$, that occurs when a 0.256 mol sample of $NF_3(g)$ is formed from $N_2(g)$ and $F_2(g)$ at 1.00 atm and 298 K. **−33.8 kJ**
The enthalpy change in a chemical reaction is the difference between energy absorbed in breaking bonds in the reactants and energy released by bond formation in the products.
(d) How many bonds are formed when two molecules of NF_3 are produced according to the equation in the box above? **There are six N–F bonds formed.**
(e) Use both the information in the box above and the table of average bond enthalpies below to calculate the average enthalpy of the F - F bond.

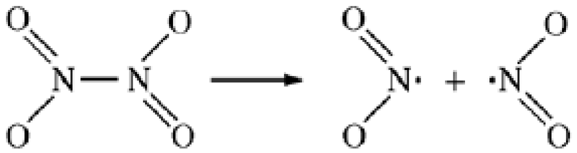
Bond	Average Bond Enthalpy (kJ mol^{-1})
N≡N	946
N–F	272
F–F	?

141 kJ mol^{-1}

2008B - #6a&b

Use principles of thermodynamics to answer the following questions.

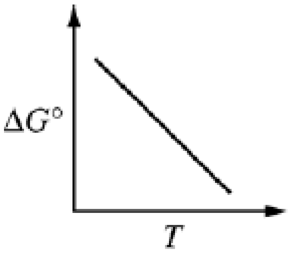
(a) The gas N_2O_4 decomposes to form the gas NO_2 according to the equation below.

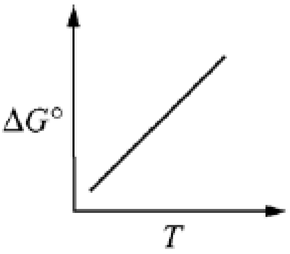


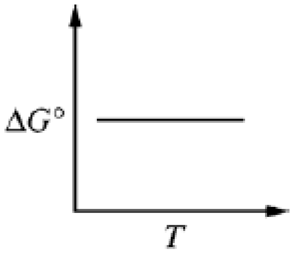
(i) Predict the sign of $\Delta H°$ for the reaction. Justify your answer. **Bonds are broken when NO_2 molecules form from N_2O_4 molecules. Energy must be absorbed to break bonds, so the reaction is endothermic and the sign of $\Delta H°$ is positive.**

(ii) Predict the sign of $\Delta S°$ for the reaction. Justify your answer. **There are two gaseous product molecules for each gaseous reactant molecule, so the product has more entropy than the reactant. The entropy increases as the reaction proceeds, so the sign of $\Delta S°$ is positive.**

(b) One of the diagrams below best represents the relationship between $\Delta G°$ and temperature for the reaction given in part (a). Assume that $\Delta H°$ and $\Delta S°$ are independent of temperature.







Draw a circle around the correct graph. Explain why you chose that graph in terms of the relationship $\Delta G° = \Delta H° - T\Delta S°$.

The leftmost graph should be circled. $\Delta S°$ is positive, so as T increases, $T\Delta S°$ becomes a larger positive number. At higher temperatures, you are subtracting larger positive numbers from $\Delta H°$ to get $\Delta G°$, so $\Delta G°$ decreases with increasing temperature

2009 - #5d-f

Reaction	Equation	ΔH°_{298}	ΔS°_{298}	ΔG°_{298}
X	$C(s) + H_2O(g) \rightleftarrows CO(g) + H_2(g)$	+131 kJ mol^{-1}	+134 J mol^{-1} K^{-1}	+91 kJ mol^{-1}
Y	$CO_2(g) + H_2(g) \rightleftarrows CO(g) + H_2O(g)$	+41 kJ mol^{-1}	+42 J mol^{-1} K^{-1}	+29 kJ mol^{-1}
Z	$2\,CO(g) \rightleftarrows C(s) + CO_2(g)$	?	?	?

Answer the following questions using the information related to reactions X, Y, and Z in the table above.

(d) For reaction Y at 298 K, which is larger: the total bond energy of the reactants or the total bond energy of the products? Explain. **The total bond energy of the reactants is larger. Reaction Y is endothermic (ΔH_{298} = + 41 kJ mol^{-1} > 0), so there is a net input of energy as the reaction occurs. Thus, the total energy required to break the bonds in the reactants must be greater than the total energy released when the bonds are formed in the products.**

(e) Is the following statement true or false? Justify your answer.

> "On the basis of the data in the table, it can be predicted that reaction Y will occur more rapidly than reaction X will occur."

The statement is false. Thermodynamic data for an overall reaction have no bearing on how slowly or rapidly the reaction occurs.

(f) Consider reaction Z at 298 K.

(i) Is $\Delta S°$ for the reaction positive, negative, or zero? Justify your answer. **$\Delta S°$ for reaction Z is negative. In reaction Z, two moles of gas with relatively high entropy are converted into one mole of solid and one mole of gas, a net loss of one mole of gas and thus a net loss in entropy. OR Reaction Z can be obtained by reversing reactions X and Y and adding them together. Thus $\Delta S°$ for reaction Z is the sum of two negative numbers and must itself be negative.**

(ii) Determine the value of $\Delta H°$ for the reaction. **-172 kJ mol^{-1}**

(iii) A sealed glass reaction vessel contains only $CO(g)$ and a small amount of $C(s)$. If a reaction occurs and the temperature is held constant at 298 K, will the pressure in the reaction vessel increase, decrease, or remain the same over time? Explain. **The pressure in the flask decreases. The reaction would proceed to the right, forming more $C(s)$ and $CO_2(g)$. Because two moles of $CO(g)$ would be consumed for every mole of $CO_2(g)$ that is produced, the total number of moles of gas in the flask would decrease, thereby causing the pressure in the flask to decrease.**

2009B – #5b-e

(b) Calculate the standard free-energy change, $\Delta G°$, that occurs when 12.0 g of $H_2(g)$ reacts with excess $N_2(g)$ at 298 K according to the reaction represented below. **– 68 kJ**

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta G_{298} = -34$ kJ mol^{-1}

(c) Given that ΔH_{298} for the reaction is -92.2 kJ mol^{-1}, which is larger, the total bond dissociation energy of the reactants or the total bond dissociation energy of the products? Explain.

$\Delta H_{298} = \Sigma$ (bond energy of the reactants) $-\ \Sigma$ (bond energy of the products)

Based on the equation above, for ΔH_{298} to be negative, the total bond energy of the products must be larger than the total bond energy of the reactants. OR More energy is released as product bonds are formed than is absorbed as reactant bonds are broken.

(d) The value of the standard entropy change, ΔS_{298}, for the reaction is -199 J mol^{-1}K^{-1}. Explain why the value of ΔS_{298} is negative.

All of the reactants and products in the reaction are in the gas phase, so the sign of the entropy change will depend on the number of moles of particles in the reactants and products. There are more moles of reactants (four) compared with moles of products (two), so there is a greater number of microstates in the reactants than in the products. Therefore the entropy decreases as the reaction proceeds (fewer possible microstates), and the sign of the entropy change is negative.

(e) Assume that $\Delta H°$ and $\Delta S°$ for the reaction are independent of temperature.

(i) Explain why there is a temperature above 298 K at which the algebraic sign of the value of $\Delta G°$ changes. **$\Delta G° = \Delta H° - T\Delta S°$ As the temperature increases $|T\Delta S°|$ will at some point exceed $|\Delta H°|$. Because both $\Delta H°$ and $\Delta S°$ are negative, the sign of $\Delta G°$ will then change from negative to positive.**

(ii) Theoretically, the best yields of ammonia should be achieved at low temperatures and high pressures. Explain. **Low temperatures: The reaction is exothermic. By Le Chatelier's principle, decreasing the temperature drives the reaction to the right to produce more heat energy, and thus more ammonia is produced.**

High pressures: For this reaction, higher pressure is achieved by decreasing the volume of the container. As pressure increases, the reaction equilibrium shifts in the direction that reduces the total number of particles (by Le Chatelier's principle). In this case, the product has fewer moles of particles than the reactants; thus product would be favored. Higher pressure therefore results in an increase in the amount of ammonia.