



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

- Predict the sign of  $\Delta S^\circ$  for the reaction and justify your prediction.
- What is the sign of  $\Delta G^\circ$  for the reaction? How would the sign and magnitude of  $\Delta G^\circ$  be affected by an increase in temperature to 50°C? Explain your answer.
- What must be the sign of  $\Delta H^\circ$  for the reaction at 25°C? How does the total bond energy of the reactants compare to that of the products?
- 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.

a) ~~ALTHOUGH~~ THE NUMBER OF PRODUCTS IS GREATER THAN THE NUMBER OF REACTANTS... 15 PARTICLES ARE CHANGED INTO 18 PARTICLES. SOME WOULD ARGUE THAT THE NUMBER OF GAS PARTICLES HAS BEEN REDUCED... SOMETHING TO THINK ABOUT.

•  $\Delta S = +$  MORE PARTICLES AFTER REACTION IS COMPLETED.

b)  $\Delta G = -$  (NEGATIVE). THIS REACTION IS A COMBUSTION REACTION. AS THE TEMPERATURE IS INCREASED TO 50°C (323 K) WOULD CAUSE  $\Delta G$  TO BECOME MORE NEGATIVE...  $\Delta G = \Delta H - T\Delta S$ .  
 $\uparrow$   
 INCREASED.

c)  $\Delta H = -$  (NEGATIVE), EXOTHERMIC... THE REACTION IS A COMBUSTION REACTION. THE BOND ENERGY FOR THE PRODUCTS IS GREATER THAN THE REACTANTS:

$$\Delta H_{\text{BOND ENERGY}} = \sum_{\text{REACTANTS}} - \sum_{\text{PRODUCTS}}$$

d) IF THERE IS NO REACTION, THEN THE REACTANTS DO NOT HAVE SUFFICIENT ACTIVATION ENERGY. NEED A SPARK OR LIT MATCH TO START THE REACTION.

For the gaseous equilibrium represented below it is observed that greater amounts of  $\text{PCl}_3$  and  $\text{Cl}_2$  are produced as the temperature is increased.



- (a) What is the sign of  $\Delta S^\circ$  for the reaction? Explain.
- (b) What change, if any, will occur in  $\Delta G^\circ$  for the reaction as the temperature is increased. Explain your reasoning in terms of thermodynamic principles.
- (c) If He gas is added to the original reaction mixture at constant volume and temperature, what will happen to the partial pressure of  $\text{Cl}_2$ ? Explain.
- (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  $\text{Cl}_2$  in the reaction vessel? Explain.

- a)  $\Delta S = +$  (POSITIVE). THE NUMBER OF PARTICLES INCREASE AS THE REACTION OCCURS. ONE REACTANT PARTICLE VS. 2 (TWO) PRODUCT PARTICLES.
- b)  $\Delta G$  SHOULD BECOME MORE NEGATIVE. BASED ON THE INITIAL INFORMATION PROVIDED (ABOVE THE REACTION) MAKES ME BELIEVE THAT  $\Delta H$  HAS A POSITIVE VALUE, REACTION IS ENDOTHERMIC. IF THE TEMPERATURE WAS TOO LOW, THE REACTION WOULD NOT PRODUCE AS MUCH  $\text{PCl}_3$  OR  $\text{Cl}_2$ .  $\Delta G = \Delta H - T\Delta S$   
 (-)      (+)      ↑ (+) HIGHER!
- c) THERE WILL BE NO CHANGE TO THE PARTIAL PRESSURE OF  $\text{Cl}_2$ . He IS AN INERT GAS AND WILL NOT AFFECT THE PRESSURES (PARTIAL PRESSURES) OF EITHER REACTANTS OR PRODUCTS.
- d) LE CHATLIER! DECREASING THE VOLUME FOR A SYSTEM AT EQUILIBRIUM WILL CAUSE A SHIFT TO FORM FEWER GAS PARTICLES. THEREFORE  $\text{Cl}_2$  WILL DECREASE.

1999

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.



$\Delta G = \text{NEGATIVE}$

- (i) For the reaction, indicate whether the standard entropy change,  $\Delta S^\circ_{298}$ , is positive, or negative, or zero. Justify your answer.
- (ii) Which factor, the change in enthalpy,  $\Delta H^\circ_{298}$ , or the change in entropy,  $\Delta S^\circ_{298}$ , provides the principal driving force for the reaction at 298 K? Explain.
- (iii) For the reaction, how is the value of the standard free energy change,  $\Delta G^\circ$ , affected by an increase in temperature? Explain.
- (b) Some reactions that are predicted by their sign of  $\Delta G^\circ$  to be spontaneous at room temperature do not proceed at a measurable rate at room temperature.
- (i) Account for this apparent contradiction.
- (ii) A suitable catalyst increases the rate of such a reaction. What effect does the catalyst have on  $\Delta G^\circ$  for the reaction? Explain.

a) i)  $\Delta S = -$  (NEGATIVE), THE NUMBER OF REACTANT PARTICLES IS GREATER THAN THE NUMBER OF PRODUCT PARTICLES... THE REACTION BECOMES MORE ORGANIZED.

ii)  $\Delta H$  MUST DRIVE THIS REACTION AND MUST HAVE A NEGATIVE VALUE. SINCE  $\Delta S$  IS NEGATIVE, THE " $-T\Delta S$ " PORTION OF  $\Delta G = \Delta H - T\Delta S$  IS POSITIVE. FOR  $\Delta G$  TO HAVE A NEGATIVE VALUE (SPONTANEOUS IN FORWARD DIRECTION).

iii) INCREASING THE TEMPERATURE WILL CAUSE THE VALUE OF  $\Delta G$  WILL BECOME MORE POSITIVE.  $\Delta S$  IS NEGATIVE CAUSING THE " $-T\Delta S$ " TO BECOME MORE POSITIVE WHILE THE VALUE FOR  $\Delta H$  REMAINS CONSTANT.

# 1999 (THERM) CON'T

b) "AT A MEASURABLE RATE"

- i) REACTION RATES DEAL WITH KINETICS. IF A REACTION IS SPONTANEOUS IN THE FORWARD DIRECTION, THE REACTION MAY NOT HAVE ENOUGH ACTIVATION ENERGY TO START THE REACTION. IF THE ACTIVATION ENERGY IS HIGH, THE REACTION MAY BE VERY SLOW.
- ii) A CATALYST WILL NOT CHANGE THE VALUE OF  $\Delta G$ . A CATALYST WILL LOWER THE ACTIVATION ENERGY AND SPEED UP THE REACTION. A CATALYST WILL NOT CHANGE (ALTER) THE VALUES FOR  $\Delta H$  OR  $\Delta S$ .

2003

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

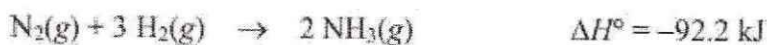
(a) Two nitrogen atoms combine to form a nitrogen molecule, as represented by the following equation.



Using the table of average bond energies below, determine the enthalpy change,  $\Delta H$ , for the reaction.

Bond	Average Bond Energy ( $\text{kJ mol}^{-1}$ )
N - N	160
N = N	420
N $\equiv$ N	950

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



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

(c) The value of  $\Delta G^\circ$  for the reaction represented in part (b) is negative at low temperatures but positive at high temperatures. Explain.

(d) When  $\text{N}_2(g)$  and  $\text{H}_2(g)$  are placed in a sealed container at a low temperature, no measurable amount of  $\text{NH}_3(g)$  is produced. Explain.



$$\Delta H_{\text{B.E.}} = \sum_{\text{REACTANTS}} - \sum_{\text{PRODUCTS}}$$

$$\Delta H_{\text{B.E.}} = (0) - \left( 950 \frac{\text{kJ}}{\text{mol}} \right) = \boxed{-950 \frac{\text{kJ}}{\text{mol}} = \Delta H}$$

No BONDS WERE BROKEN!

b)  $\Delta S = -$  (NEGATIVE). MORE REACTANT PARTICLES (4) THAN PRODUCT PARTICLES (2). THE REACTION BECOMES MORE ORGANIZED AS REACTANTS FORM PRODUCTS.

- c) IF  $\Delta G$  IS NEGATIVE AT LOW TEMPERATURES WHERE  $\Delta S$  IS ALSO NEGATIVE (FOR THE REACTO THIS REACTION) WHICH INDICATES THAT  $\Delta H$  MUST BE NEGATIVE OR EXOTHERMIC. USING THE EQUATION  $\Delta G = \Delta H - T\Delta S$  AT LOW TEMPERATURES,  $\Delta G$  IS NEGATIVE BECAUSE  $\Delta S$  IS NEGATIVE CAUSING " $-T\Delta S$ " TO HAVE A POSITIVE VALUE. IF THE TEMPERATURE IS LOW ENOUGH, THE  $\Delta H$  WILL CAUSE  $\Delta G$  TO HAVE A NEGATIVE VALUE. HOWEVER, AT HIGHER TEMPERATURES, THE  $\Delta H$  ~~W~~ VALUE IS NOT "NEGATIVE ENOUGH" TO ALLOW  $\Delta G$  TO HAVE A NEGATIVE VALUE.
- d) ALTHOUGH THE VALUE OF  $\Delta G$  IS NEGATIVE, A LOW TEMPERATURE MAY CAUSE THE REACTION TO REACT AT A VERY SLOW RATE. RATE AND  $\Delta G$  DO NOT REPRESENT IDENTICAL IDEAS TOWARD A REACTION. ALSO, CONSIDER AT LOW TEMPERATURES GAS PARTICLES ARE NOT MOVING AS FAST (OR COLLIDING AS OFTEN) AT AS THEY WOULD AT HIGHER TEMPERATURES.

2004B



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

- 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.
- Does the entropy change of the reaction favor the reactants or the product? Justify your answer.
- For the reaction under the conditions specified, which is favored, the reactants or the product? Justify your answer.
- Explain how to determine the value of the equilibrium constant,  $K_{eq}$ , for the reaction. (Do not do any calculations.)
- Predict whether the value of  $K_{eq}$  for the reaction is greater than 1, equal to 1, or less than 1. Justify your prediction.

a) BOND ENERGY =  $\sum_{\text{REACTANTS}} - \sum_{\text{PRODUCTS}}$   
 SINCE  $\Delta H$  IS HAS A POSITIVE VALUE, THE REACTANTS  
 HAVE HIGHER BOND ENERGIES THAN THE PRODUCTS.

b) ENTROPY,  $\Delta S$ , IS NEGATIVE (FAVORS THE REACTANTS).  
 THE REACTANTS HAVE THREE PARTICLES VS. ONE  
 PRODUCT PARTICLE.

c) REACTANTS.  $\Delta G$  HAS A POSITIVE VALUE. BASED  
 ON THE GIVEN  $\Delta H$  AND  $\Delta S$  VALUES (ABOVE)

$$\Delta G = \left( +95.4 \frac{\text{kJ}}{\text{mol}} \right) - (298\text{K}) \left( \frac{-176 \text{ J}}{\text{K} \cdot \text{mol}} \left| \frac{1 \text{ kJ}}{1000 \text{ J}} \right. \right) =$$

$$\Delta G = +147.8 \frac{\text{kJ}}{\text{mol}}$$

d) USE THE EQUATION:  $\Delta G = -RT \ln K_{eq}$ .

$$\ln K_{eq} = \frac{\Delta G}{-RT} \quad \text{PLUG IN THE } \Delta G \text{ VALUE (FROM}$$

PART c)),  $R = 8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}}$ ;  $T = 298\text{K}$ . THEN SOLVE

FOR  $K_{eq}$ .

(DAY III, EXAMPLES PART II)

e)  $K_{eq}$  WILL BE LESS THAN ONE.  $\Delta G > 0$  THEN  $K < 1$ .

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 Standard Free Energies of Formation at 298 K
 

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Substance	$\Delta G^\circ_{f, 298 \text{ K}}, \text{kJ mol}^{-1}$
$\text{C}_2\text{H}_4\text{Cl}_2(\text{g})$	-80.3
$\text{C}_2\text{H}_5\text{Cl}(\text{g})$	-60.5
$\text{HCl}(\text{g})$	-95.3
$\text{Cl}_2(\text{g})$	0

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 Average Bond Dissociation Energies at 298 K
 

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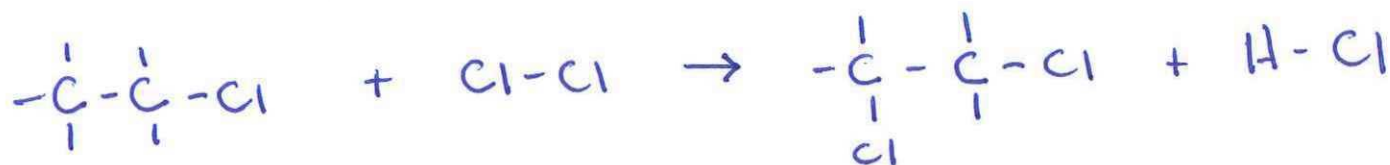
Bond	Energy, $\text{kJ mol}^{-1}$
C-H	414
C-C	347
C-Cl	377
Cl-Cl	243
H-Cl	431

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



- (a) Calculate the  $\Delta H^\circ$  for the reaction above, using the table of average bond dissociation energies.  
 (b) Calculate the  $\Delta S^\circ$  for the reaction at 298 K, using data from either table as needed.  
 (c) Calculate the value of  $K_{eq}$  for the reaction at 298 K.  
 (d) What is the effect of an increase in temperature on the value of the equilibrium constant? Explain your answer.

$$\text{a) } \Delta H_{\text{B.E.}} = \sum_{\text{REACTANTS}} - \sum_{\text{PRODUCTS}}$$



$$\begin{array}{l} 1 \text{ C-C} : 347 \\ 5 \text{ C-H} : 5(414) \\ 1 \text{ C-Cl} : 377 \\ 1 \text{ Cl-Cl} : 243 \\ \hline 3037 \frac{\text{kJ}}{\text{mol}} \end{array}$$

$$\begin{array}{l} 1 \text{ C-C} : 347 \\ 4 \text{ C-H} : 4(414) \\ 2 \text{ C-Cl} : 2(377) \\ 1 \text{ H-Cl} : 431 \\ \hline 3188 \frac{\text{kJ}}{\text{mol}} \end{array}$$

$$\Delta H_{\text{B.E.}} = 3037 \frac{\text{kJ}}{\text{mol}} - 3188 \frac{\text{kJ}}{\text{mol}} = -151 \frac{\text{kJ}}{\text{mol}} = \Delta H$$



b)  $\Delta S = ?$

$$\Delta H = -151 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta G = \sum \text{PRODUCTS} - \sum \text{REACTANTS}$$



$$\Delta G = \left[ -80.3 \frac{\text{kJ}}{\text{mol}} + -95.3 \frac{\text{kJ}}{\text{mol}} \right] - \left[ -60.5 \frac{\text{kJ}}{\text{mol}} + 0 \frac{\text{kJ}}{\text{mol}} \right]$$

$\text{C}_2\text{H}_4\text{Cl}_2$                        $\text{HCl}$                        $\text{C}_2\text{H}_5\text{Cl}$                        $\text{Cl}_2$

$$\Delta G = -175.6 \frac{\text{kJ}}{\text{mol}} - (-60.5 \frac{\text{kJ}}{\text{mol}}) = \boxed{-115.1 \frac{\text{kJ}}{\text{mol}} = \Delta G}$$

$$\Delta G = \frac{-\Delta H}{T} - \Delta S ;$$

$$\Delta G - \Delta H = -T\Delta S ; \quad \frac{\Delta G - \Delta H}{-T} = \Delta S$$

$$\Delta S = \frac{(-115.1 \frac{\text{kJ}}{\text{mol}}) - (-151 \frac{\text{kJ}}{\text{mol}})}{-298 \text{ K}} = -0.120 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}$$

$$\Delta S = \frac{-0.120 \text{ kJ} \left| \frac{1000 \text{ J}}{1 \text{ kJ}} \right.}{\text{mol} \cdot \text{K}} = \boxed{\frac{-120 \text{ J}}{\text{mol} \cdot \text{K}} = \Delta S}$$

c)  $\Delta G = -RT \ln K ; \quad \ln K = \frac{\Delta G}{-RT} \quad R = \frac{8.31 \text{ J}}{\text{mol} \cdot \text{K}} \left| \frac{1 \text{ kJ}}{1000 \text{ J}} \right.$

$$\ln K = \frac{-115.1 \frac{\text{kJ}}{\text{mol}}}{-(0.00831 \frac{\text{kJ}}{\text{mol} \cdot \text{K}})(298 \text{ K})} = 46.479$$

$$K = e^{46.479} = 1.53 \times 10^{20}$$

d) INCREASING THE ~~TEMPERATURE~~ TEMPERATURE WILL CAUSE THE VALUE OF  $K_{eq}$  TO DECREASE.

$$\ln K = \frac{\Delta G}{-RT}$$

↑ TEMPERATURE

OR

• LE CHATLIER EXPLANATION: REACTION IS EXOTHERMIC,

$\Delta H = -151 \frac{\text{kJ}}{\text{mol}}$ , THEREFORE INCREASING THE TEMPERATURE (ADDING ENERGY TO THE PRODUCT) WILL CAUSE THE REACTION TO SHIFT LEFT (SHIFT TO FORM MORE REACTANTS).