

Name: \_\_\_\_\_

Period: \_\_\_\_\_

15.2 homework problems p. 247-263 (reading the section is such a good idea!!)

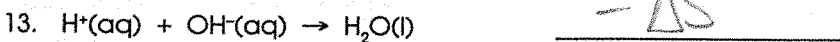
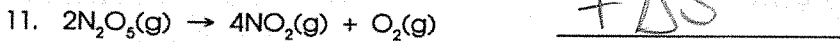
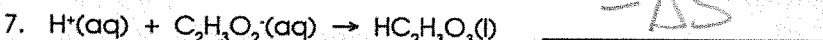
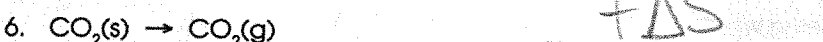
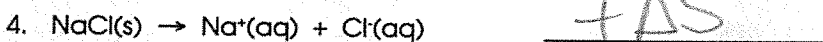
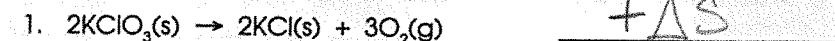
## ENTROPY

Name \_\_\_\_\_

Entropy is the degree of randomness in a substance. The symbol for change in entropy is  $\Delta S$ .

Solids are very ordered and have low entropy. Liquids and aqueous ions have more entropy because they move about more freely, and gases have an even larger amount of entropy. According to the Second Law of Thermodynamics, nature is always proceeding to a state of higher entropy.

Determine whether the following reactions show an increase or decrease in entropy.



(use # of particles / moles)

## GIBBS FREE ENERGY

Name \_\_\_\_\_

For a reaction to be spontaneous, the sign of  $\Delta G$  (Gibbs Free Energy) must be negative. The mathematical formula for this value is:

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

where  $\Delta H$  = change in enthalpy or heat of reaction  
 $T$  = temperature in Kelvin  
 $\Delta S$  = change in entropy or randomness

\* Complete the table for the sign of  $\Delta G$ ; +, - or undetermined. When conditions allow for an undetermined sign of  $\Delta G$ , temperature will decide spontaneity.

$\Delta H$	$\Delta S$	$\Delta G$
-	+	-
+	-	+
-	-	+ / -
+	+	+ / -

always never  
 +temp spontan  
 ↑temp always spontan

Answer the questions below.

- The conditions in which  $\Delta G$  is always negative is when  $\Delta H$  is negative and  $\Delta S$  is positive.
- The conditions in which  $\Delta G$  is always positive is when  $\Delta H$  is positive and  $\Delta S$  is negative.
- When the situation is indeterminate, a low temperature favors the ( enthalpy ) factor, and a high temperature favors the ( entropy / enthalpy ) factor.

Answer Problems 4-6 with always, sometimes or never.

- The reaction:  $\text{Na}(\text{OH})_s \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$  <sup>exothermic</sup> + energy will always be spontaneous.
- The reaction: energy +  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$  will never be spontaneous. <sup>endothermic</sup>
- The reaction: energy +  $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l})$  will sometimes be spontaneous. <sup>endothermic</sup>
- What is the value of  $\Delta G$  if  $\Delta H = -32.0 \text{ kJ}$ ,  $\Delta S = +25.0 \text{ kJ/K}$  and  $T = 293 \text{ K}$ ? -7357  
 $-32 - (25 \times 293) =$
- Is the reaction in Problem 7 spontaneous? yes!
- What is the value of  $\Delta G$  if  $\Delta H = +12.0 \text{ kJ}$ ,  $\Delta S = -5.00 \text{ kJ/K}$  and  $T = 290 \text{ K}$ ? 1462  
 $12 - (-5 \times 290) =$
- Is the reaction in Problem 9 spontaneous? no!

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## Exercises

54 Identify the process expected to have a value of  $\Delta S$  closest to zero?

- B **A**  $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) - \Delta S$       **C**  $CaCO_3(s) \rightarrow CaO(s) + CO_2(g) + \Delta S$   
**B**  $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$       **D**  $H_2O(l) \rightarrow H_2O(g) + \Delta S$

55 Identify the processes which have an associated increase in entropy.

- C **I**  $Br_2(g) \rightarrow Br_2(l) - \Delta S$   
**II**  $Br_2(g) \rightarrow 2Br(g) + \Delta S$   
**III**  $KBr(s) \rightarrow K^+(aq) + Br^-(aq) + \Delta S$   
**A** I and II      **B** I and III      **C** II and III      **D** I, II, and III

56 Which is the best description of the entropy and enthalpy changes accompanying the sublimation of iodine:  $I_2(s) \rightarrow I_2(g)$ ?  $+\Delta S, +\Delta H$ 

- A **A**  $\Delta S +, \Delta H +$ , reaction is endothermic  
**B**  $\Delta S +, \Delta H -$ , reaction is exothermic  
**C**  $\Delta S -, \Delta H +$ , reaction is endothermic  
**D**  $\Delta S -, \Delta H -$ , reaction is exothermic

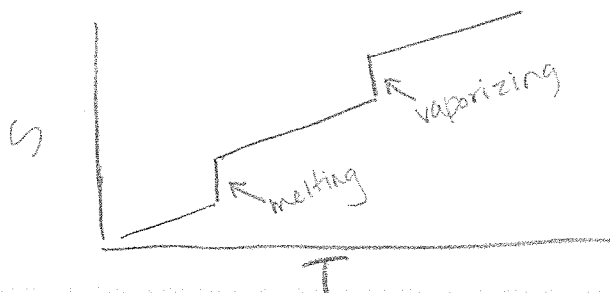
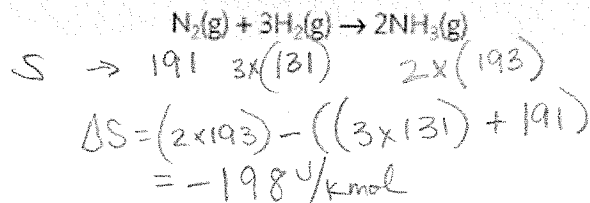
57 Identify the reaction which has the largest increase in entropy?

- D **A**  $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq) - \Delta S$   
**B**  $H_2(g) + Cl_2(g) \rightarrow 2HCl(g) 0 \approx \Delta S$   
**C**  $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) - \Delta S$   
**D**  $Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g) + \Delta S$

58 Predict the entropy change  $\Delta S$  for the following reactions.

- (a)**  $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) - \Delta S$   
**(b)**  $3Fe(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 4H_2(g) - \Delta S$   
**(c)**  $Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4SCN(s) \rightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l) + \Delta S$

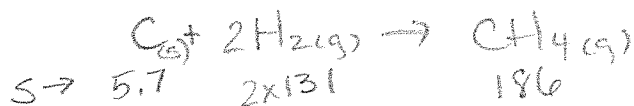
## Exercises

59 Sketch a graph to show how the entropy of a solid changes as the temperature increases.60 Calculate the entropy change  $\Delta S$  for the Haber process, shown below, using tabulated standard molar entropies at 25 °C.

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- 61 Calculate the standard entropy change associated with the formation of methane from its elements.



$$\begin{aligned} \Delta S &= (186) - (5.7 + (2 \times 131)) \\ &= -82 \text{ J/Kmol} \quad (25F) \end{aligned}$$

### Exercises

- 62 Ammonium chloride dissolves in water spontaneously in an endothermic process. Identify the best explanation for these observations.

A Endothermic processes are energetically favourable ~~NO!~~

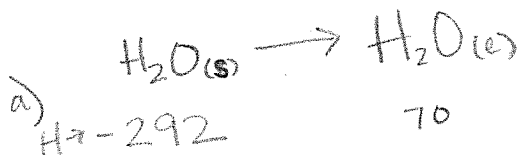
B The bonds in solid  $NH_4Cl$  are very weak. ~~ionic - NOT true~~

C The entropy change of the system drives the process.

D The entropy change of the surroundings drives the process ~~not surroundings~~

- 63 (a) Use data from section 12 of the IB data booklet and additional data ( $\Delta H_f^\circ(H_2O(s)) = -292 \text{ kJ mol}^{-1}$ ) to calculate the enthalpy change that occurs when ice melts.

- (b) The entropy change when ice melts is  $22.0 \text{ J K}^{-1} \text{ mol}^{-1}$ . Deduce a value for the melting point of ice.



$$\Delta H = 70 - (-292) = +6 \text{ kJ/mol}$$

$$b) \quad \Delta G = \Delta H - T\Delta S$$

$$T = \Delta H / \Delta S$$

$$= +6 / 0.022$$

$$= 272.7 \text{ K} \approx 0^\circ \text{C}$$

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**64** Identify the combination of  $\Delta H$  and  $\Delta S$  which results in a reaction being spontaneous at low temperatures but non-spontaneous at higher temperatures?

- A**  $\Delta S -$  and  $\Delta H -$       **B**  $\Delta S +$  and  $\Delta H -$       **C**  $\Delta S -$  and  $\Delta H +$       **D**  $\Delta S +$  and  $\Delta H +$

**65** Identify the combination of  $\Delta H$  and  $\Delta S$  which leads to a reaction that is **not** spontaneous at low temperatures but becomes spontaneous at higher temperatures?

- A**  $\Delta H -$  and  $\Delta S -$       **B**  $\Delta H -$  and  $\Delta S +$       **C**  $\Delta H +$  and  $\Delta S -$       **D**  $\Delta H +$  and  $\Delta S +$

**66** The  $\Delta H$  and  $\Delta S$  values for the combustion of hydrogen are both negative. Which is the correct description of this reaction at different temperatures?

	Low temperature	High temperature
<b>A</b>	not spontaneous	not spontaneous
<b>B</b>	spontaneous	not spontaneous
<b>C</b>	spontaneous	spontaneous
<b>D</b>	not spontaneous	spontaneous

**67** The decomposition of limestone can be represented by the equation:



- (a) Predict a sign for the enthalpy change of the reaction.  **$+\Delta H$**   
 (b) Predict a sign for the entropy change of the reaction.  **$+\Delta S$**   
 (c) Deduce how the stability of limestone changes with temperature.

high temp  
 $\Delta G = -T\Delta S$ ,  
 so is spontaneous

low temp  
 $\Delta G = \Delta H$ , so not spontaneous

### Exercises

**68** The enthalpy and entropy changes for the reaction



**$+\Delta H$**   
 **$+\Delta S$**

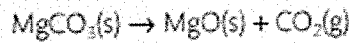
are  $\Delta H^\ominus = 100 \text{ kJ mol}^{-1}$  and  $\Delta S^\ominus = 100 \text{ J K}^{-1} \text{ mol}^{-1}$

- A** The reaction is not spontaneous at any temperature.  
**B** The reaction is spontaneous at all temperatures.  
**C** The reaction is spontaneous at all temperatures below  $1000^\circ\text{C}$ .  
**D** The reaction is spontaneous at all temperatures above  $1000 \text{ K}$ .

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- 69 Magnesium carbonate,  $\text{MgCO}_3$ , is a white solid that occurs in nature as the mineral magnesite. Magnesite decomposes to the oxide at temperatures above  $540^\circ\text{C}$ .



Identify the correct description of this reaction at  $800^\circ\text{C}$ .

	$\Delta G$	$\Delta H$	$\Delta S$
A	+	+	+
B	+	-	-
<b>C</b>	-	+	+
D	-	+	-

+  $\Delta S$  (↑ disorder)  
 +  $\Delta H$  (breaking)  
 but ↑ temp  
 $\Delta G = (+) - (\text{very negative})$   
 $\Delta G = -$

- 70 Calculate  $\Delta G_{\text{reaction}}$  for the thermal decomposition of calcium carbonate



from the following data, and comment on the significance of the value obtained.

Compound	$\Delta G_f^\circ / \text{kJ mol}^{-1}$
$\text{CaCO}_3(\text{s})$	-1129
$\text{CaO}(\text{s})$	-604
$\text{CO}_2(\text{g})$	-394

$$\begin{aligned} \Delta G &= \sum G_{\text{prod}} - \sum G_{\text{react}} \\ &= (-604 + -394) - (-1129) \\ &= \mathbf{131 \text{ kJ mol}^{-1}} \end{aligned}$$

Very positive - so calcium carbonate is very stable & doesn't decompose spontaneously

### Exercises

- 71 Calculate  $\Delta G_{\text{reaction}}$  at 2000 K for the thermal decomposition of calcium carbonate from the data given in the worked example.

Compound	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
$\text{CaCO}_3(\text{s})$	-1207	+92.9
$\text{CaO}(\text{s})$	-635	+39.7
$\text{CO}_2(\text{g})$	-394	+214



$$\Delta S = (39.7 + 214) - (92.9) = 160.8 \text{ J K}^{-1} \text{mol}^{-1}$$

$$\Delta H = (-635 + -394) - (-1207) = 178 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta G &= (178) - (2000 \times 0.1608) \\ &= \mathbf{-144 \text{ kJ mol}^{-1}} \end{aligned}$$

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72 Which property of an element has a value of zero in its standard state?

- I  $\Delta H_f^\ominus$   
 II  $S^\ominus$   
 III  $\Delta G_f^\ominus$

→ entropy is only ever 0 at absolute zero (which is theoretical)

A I and II

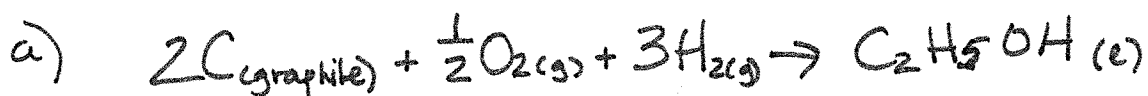
B I and III

C II and III

D I, II, and III

73 The standard enthalpy change for the formation of ethanol,  $C_2H_5OH(l)$ , and its molar entropy are given in section 12 of the IB data booklet.

- (a) Write an equation for the formation of ethanol.  
 (b) Calculate the entropy change for this process. The entropies of its constituent elements are:  
 $C(\text{graphite}) = 5.7 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $H_2(g) = 65.3 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $O_2(g) = 102.5 \text{ J K}^{-1} \text{ mol}^{-1}$   
 (c) Calculate the standard free energy change of formation of ethanol at 500 K.  
 (d) Deduce whether the reaction is spontaneous at 500 K, and give a reason.  
 (e) Predict the effect, if any, of an increase in temperature on the spontaneity of this reaction.



b)  $\Delta S = \sum \text{products} - \sum \text{reactants}$   
 $= (161) - ((2 \times 5.7) + (\frac{1}{2} \times 102.5) + (3 \times 65.3))$   
 $= -98 \text{ J K}^{-1} \text{ mol}^{-1}$

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

$= (-278) - (500 \times -0.098)$

found in data booklet →  $= -229 \text{ kJ mol}^{-1}$

d) spontaneous, because  $-\Delta G$

e) High temperature will  $\Delta G = -T\Delta S$

so  $\Delta G$  will be positive.

~~$\Delta H$  and  $T\Delta S$  only~~

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**Exercises**

74 What signs of  $\Delta H^\circ_{\text{reaction}}$  and  $\Delta S^\circ_{\text{reaction}}$  for a reaction result in a complete reaction at all temperatures?

	$\Delta H^\circ_{\text{reaction}}$	$\Delta S^\circ_{\text{reaction}}$
A	-	-
B	+	-
<b>C</b>	-	+
D	+	+

*exothermic and disordered*

75 Which conditions correspond to a system of equilibrium?

- I The entropy of the system is at a maximum.  $\checkmark +\Delta S$
- II The free energy of a system is at a minimum.  $\checkmark -\Delta G$
- III  $\Delta G^\circ_{\text{reaction}} = 0$

A I and II only      B I and III only      C II and III only      **D I, II, and III**

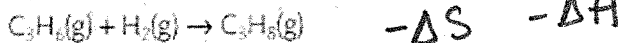
76 Which values correspond to a reaction that can be reversed by changing the temperature.

	$\Delta H^\circ_{\text{reaction}}$	$\Delta S^\circ_{\text{reaction}}$
I	-	-
II	+	-
III	+	+

*never*

A I and II only      **B I and III only**      C II and III only      D I, II, and III

77 Propene reacts with hydrogen in the presence of a nickel catalyst to form propane.



$$\Delta H^\circ_{\text{reaction}} = -123 \text{ kJ mol}^{-1}; \Delta S^\circ_{\text{reaction}} = -128 \text{ J K}^{-1} \text{ mol}^{-1}$$

Estimate the temperature range in which a mixture of all three gases will be present.

*guess & check*

78 The Haber process is an important process in which ammonia is formed from nitrogen and hydrogen:



$$\Delta S^\circ_{\text{reaction}} = -198 \text{ J K}^{-1} \text{ mol}^{-1}; \Delta H^\circ_{\text{reaction}} = -93 \text{ J K}^{-1} \text{ mol}^{-1}$$

Estimate the temperature range in which a mixture of all three gases will be present.