

Spontaneity and Entropy DCI

Name _____

Section _____

1. Entropy (S) is a second driving force for chemical reactions. Define the word entropy. How is the sign of ΔS for a chemical reaction interpreted?

Entropy is a measure of the randomness of a chemical system. Randomness is measure in terms of the number of possible positions matter has in a chemical system, and the number of energy states the matter has. The greater the number of possible states in position and energy (number of microstates) the higher/greater the entropy. In a chemical or physical change a positive ΔS means the products are more random, have a greater number of microstates compared to the reactants. If ΔS is negative than the products are less random, have fewer number of microstates compared to the reactants.

2. Predict which of the following thermodynamically favored reactions have an increase in entropy of the system.



The products have a greater number of positional microstates possible because gases are mostly empty space and the gas particles can occupy any of the available positions. In the liquid phase, while the molecules are mobile, the phase is condensed so there is considerably less empty space so there are many fewer positional microstates.



The products phase is solid and the reactants are a solid and a gas. So the reactants are less ordered compared to the products. Gases have high entropies because the particles are well separated in space, so there are many more microstates possible. Also there are fewer numbers of product particles compared to the reactants. When there are fewer moles of products there are fewer arrangements/microstates possible. So both the phase change and the number of particles point to a more ordered products compared to reactants.

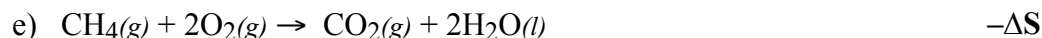


The product phases are aqueous solution, a gas and a liquid and the reactants are both solids. The reactants are more ordered compared to the products. Gases have high entropies because the particles are well separated in space, so there are many more microstates possible. In general a substance dissolved in water with have more disorder compared to a solid phase. In solution ions are hydrated, and are able to distribute throughout the solution. There are 13 moles of product compared to 3 moles of reactants, so there are many more substances that the atoms can be distributed between. When there are more moles of products there are larger arrangements/microstates possible. So

both the phase change and the number of particles point to a more disordered products compared to reactants.



The products phase is a liquid and a gas and the reactants are a both gases. So the reactants are more disordered compared to the products. Gases have high entropies because the particles are well separated in space, so there are many more microstates possible. Liquids are much more ordered as a condensed phase. There are fewer positions particles can occupy in the liquid phase compared to the gaseous phase. There are equal numbers of product particles and reactants. So the phase change points to a more ordered products compared to reactants.



The products phase is a liquid and a gas and the reactants are a both gases. So the reactants are more disordered compared to the products. Gases have high entropies because the particles are well separated in space, so there are many more microstates possible. Liquids are much more ordered as a condensed phase. There are fewer positions particles can occupy in the liquid phase compared to the gaseous phase. There are equal numbers of product particles and reactants. So the phase change points to a more ordered products compared to reactants.



The products phase is solid and the reactants are a solid and a liquid. So the reactants are less ordered compared to the products. Liquids are more disordered compared to solids as a condensed phase. In the liquid phase particles are able to move very close to each other, and occupy more positions compared to solids where the particles are static and cannot move. Also there is a wider range of energies for liquids compared to solids. Also there are fewer numbers of product particles compared to the reactants. When there are fewer moles of products there are fewer arrangements/microstates possible. So both the phase change and the number of particles point to a more ordered products compared to reactants.

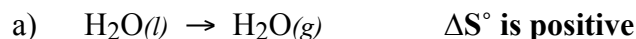
3. A table of absolute entropies (S°) for selected substances is at the end of this DCI. Identify differences between ΔS° and ΔH°_f as thermodynamic values.

The entropy values are positive, while the enthalpy of formation values are positive and negative. The entropy values for the solids are the lowest and the entropy values for gases are the highest. For enthalpy of formations the same substance in different phases the trend is to become more positive from solid, to liquid to gas.

4. Write the mathematical equation that relates the standard entropy change in a chemical reaction to the absolute entropy of the reactants and products.

$$\Delta S^\circ_{\text{rxn}} = \Sigma(mS^\circ(\text{products})) - \Sigma(nS^\circ(\text{reactants}))$$

5. Calculate the change in entropy ($\Delta S^\circ_{\text{rxn}}$) for the chemical reactions in question 2.



$$\Delta S^\circ_{\text{rxn}} = \Sigma(mS^\circ(\text{products})) - \Sigma(nS^\circ(\text{reactants}))$$

$$\Delta S^\circ_{\text{rxn}} = S^\circ(\text{H}_2\text{O}(g)) - S^\circ(\text{H}_2\text{O}(l))$$

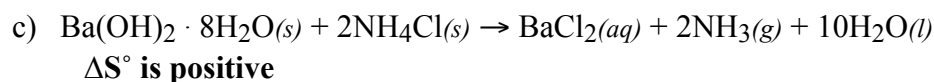
$$\Delta S^\circ_{\text{rxn}} = 189 \text{ J mol}^{-1} \text{ K}^{-1} - 70 \text{ J mol}^{-1} \text{ K}^{-1} = +119 \text{ J mol}^{-1} \text{ K}^{-1}$$



$$\Delta S^\circ_{\text{rxn}} = \Sigma(mS^\circ(\text{products})) - \Sigma(nS^\circ(\text{reactants}))$$

$$\Delta S^\circ_{\text{rxn}} = 2S^\circ(\text{MgO}(s)) - [2S^\circ(\text{Mg}(s)) + S^\circ(\text{O}_2(g))]$$

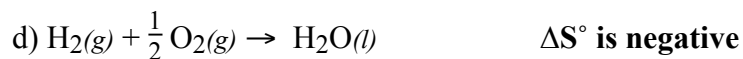
$$\Delta S^\circ_{\text{rxn}} = 2 \cdot 26.9 \text{ J mol}^{-1} \text{ K}^{-1} - [2 \cdot 33 \text{ J mol}^{-1} \text{ K}^{-1} + 205 \text{ J mol}^{-1} \text{ K}^{-1}] = -217 \text{ J mol}^{-1} \text{ K}^{-1}$$



$$\Delta S^\circ_{\text{rxn}} = \Sigma(mS^\circ(\text{products})) - \Sigma(nS^\circ(\text{reactants}))$$

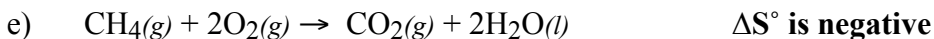
$$\Delta S^\circ_{\text{rxn}} = [S^\circ(\text{BaCl}_2(aq)) + 2S^\circ(\text{NH}_3(g)) + 10S^\circ(\text{H}_2\text{O}(l))] - [S^\circ(\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}(s)) + 2S^\circ(\text{NH}_4\text{Cl}(s))]$$

$$\Delta S^\circ_{\text{rxn}} = 123 \text{ J mol}^{-1} \text{ K}^{-1} + 2 \cdot 193 \text{ J mol}^{-1} \text{ K}^{-1} + 10 \cdot 70 \text{ J mol}^{-1} \text{ K}^{-1} - [427 \text{ J mol}^{-1} \text{ K}^{-1} + 2 \cdot 95 \text{ J mol}^{-1} \text{ K}^{-1}] = +592 \text{ J mol}^{-1} \text{ K}^{-1}$$



$$\Delta S^\circ_{\text{rxn}} = \Sigma(mS^\circ(\text{products})) - \Sigma(nS^\circ(\text{reactants}))$$

$$\Delta S^\circ_{\text{rxn}} = -164 \text{ J mol}^{-1} \text{ K}^{-1}$$



$$\Delta S^\circ_{\text{rxn}} = \Sigma(mS^\circ(\text{products})) - \Sigma(nS^\circ(\text{reactants}))$$

$$\Delta S^\circ_{\text{rxn}} = -242 \text{ J mol}^{-1} \text{ K}^{-1}$$



$$\Delta S^\circ_{\text{rxn}} = \Sigma(mS^\circ(\text{products})) - \Sigma(nS^\circ(\text{reactants}))$$

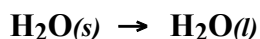
$$\Delta S^\circ_{\text{rxn}} = -72.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

6. The natural tendency for spontaneous chemical reactions is to increase entropy. Is the entropy an absolute predictor of spontaneity? Defend your answer.

The entropy of a chemical reaction is not an absolute predictor of the spontaneity of a chemical reaction. In Q5 note that all reactions are spontaneous, however there are some reactions with a negative ΔS and some reactions with a positive ΔS .

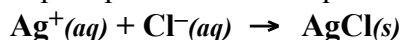
7. Predict whether the entropy of the system increases, remains constant or decreases when the following processes occur. Explain your reasoning.

- a. Ice melts at 0 °C.



Liquids are more disordered compared to solids as a condensed phase. In the liquid phase particles are able to move very close to each other, and occupy more positions compared to solids where the particles are static and cannot move. Also there are a wider range of energies for liquids compared to solids. ΔS is positive.

- b. A precipitate forms in aqueous solution.



Ions dissolved in water are mobile, therefore they can occupy many more positions compared to the ions in the solid phase. In the solid phase ions are static, so there is effectively one positional microstate. The products are less random compared to the reactants and ΔS is negative.

- c. A solid dissolves in water.

$\text{C}_6\text{H}_{12}\text{O}_6(s) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(aq)$ A covalent solid like glucose dissolves in water the molecules are more mobile and can move around in the solution. In the solid phase the molecules of glucose are static, there is only one positional microstate compared to the many positional microstates available to a hydrated glucose molecule. ΔS is positive.

- d. A gas condenses to a liquid.

$\text{N}_2(g) \rightarrow \text{N}_2(l)$ gases are mostly empty space and the gas particles can occupy any of the available positions. In the liquid phase, while the molecules are mobile, the phase is condensed so there is considerably less empty space so there are many fewer positional microstates. ΔS is negative.

Substance and State	ΔH_f° (kJ/mol)	Substance and State	ΔH_f° (kJ/mol)
C(s) (graphite)	0	HCl(g)	-92.3
C(s) (diamond)	2	HBr(g)	-36.4
CO(g)	-110.5	HI(g)	26.5
CO ₂ (g)	-393.5	I ₂ (g)	62.25
CH ₄ (g)	-75	O ₂ (g)	0
CH ₃ OH(g)	-201	O(g)	249
CH ₃ OH(l)	-239	O ₃ (g)	143
H ₂ CO(g)	-116		
CCl ₄ (l)	-135.4	N ₂ (g)	0
HCOOH(g)	-363	NH ₃ (g)	-46
HCN(g)	135.1	NH ₃ (aq)	-80
CS ₂ (g)	117.4	NH ₄ ⁺ (aq)	-132
CS ₂ (l)	89.7	NH ₄ Cl(s)	-314.4
C ₂ H ₂ (g)	227	N ₂ H ₄ (l)	50.6
C ₂ H ₄ (g)	52	NO(g)	90.25
CH ₃ CHO(g)	-166	NO ₂ (g)	33.18
C ₂ H ₅ OH(l)	-278	N ₂ O(g)	82.0
C ₂ H ₅ O ₂ N(g)	-533	N ₂ O ₄ (g)	9.16
C ₂ H ₆ (g)	-84.7	N ₂ O ₄ (l)	20
C ₃ H ₆ (g)	20.9	HNO ₃ (aq)	-207.36
C ₃ H ₈ (g)	-104	HNO ₃ (l)	-174.10
C ₄ H ₁₀ (g)	-126	NH ₄ ClO ₄ (s)	-295
C ₈ H ₁₈ (l)	-208		
CH ₂ = CHCN(l)	152		
CH ₃ COOH(l)	-484	S ₂ Cl ₂ (g)	-18
C ₆ H ₁₂ O ₆ (s)	-1275	SO ₂ (g)	-296.83
		H ₂ S(g)	-20.6
Cl ₂ (g)	0	SOCl ₂ (g)	-213
Cl ₂ (aq)	-23		
Cl ⁻ (aq)	-167.5	SiCl ₄ (g)	-657
		SiO ₂ (s)	-910.94
H ₂ (g)	0	SiF ₄ (g)	-1614.9
H(g)	217		
H ⁺ (aq)	0	Ba(OH) ₂ ·8H ₂ O(s)	-3342
OH ⁻ (aq)	-230	BaCl ₂ (aq)	-872
H ₂ O(l)	-286	AlBr ₃ (s)	-526
H ₂ O(g)	-242	ZnS(s)	-206

Thermodynamic Values (25°C)

Substance and State	ΔH_f^0 ($\frac{\text{kJ}}{\text{mol}}$)	ΔG_f^0 ($\frac{\text{kJ}}{\text{mol}}$)	S^0 ($\frac{\text{J}}{\text{K}\cdot\text{mol}}$)	Substance and State	ΔH_f^0 ($\frac{\text{kJ}}{\text{mol}}$)	ΔG_f^0 ($\frac{\text{kJ}}{\text{mol}}$)	S^0 ($\frac{\text{J}}{\text{K}\cdot\text{mol}}$)
Aluminum				Iodine			
AlBr ₃ (g)	-526.3	-505	184	I ₂ (s)	0	0	116.7
Al(s)	0	0	28.32	I ₂ (g)	62.25	19.37	260.57
				HI(g)	25.94	1.30	206.3
Barium				Magnesium			
BaCl ₂ (aq)	-872	-823	123	Mg(s)	0	0	33
Ba(OH) ₂ ·8H ₂ O(s)	-3342	-2793	427	Mg ²⁺ (aq)	-492	-456	-118
				MgO(s)	-601	-569	26.9
Bromine				Oxygen			
Br ₂ (l)	0	0	152.231	O ₂ (g)	0	0	205
BrCl(g)	14.64	-0.96	239.99	O(g)	249	232	161
				O ₃ (g)	143	163	239
Carbon				Nitrogen			
C(s) (graphite)	0	0	6	N ₂ (g)	0	0	192
C(s) (diamond)	2	3	2	NCl ₃ (g)	230	271	-137
CO(g)	-110.5	-137	198	NF ₃ (g)	-125	-83.6	-139
CO ₂ (g)	-393.5	-394	214	NH ₃ (g)	-46	-17	193
CH ₄ (g)	-75	-51	186	NH ₃ (aq)	-80	-27	111
CH ₃ OH(g)	-201	-163	240	NH ₂ CONH ₂ (aq)	?	?	174
CH ₃ OH(l)	-239	-166	127	NO(g)	90	87	211
H ₂ CO(g)	-116	-110	219	NO ₂ (g)	34	52	240
HCOOH(g)	-363	-351	249	N ₂ O(g)	82	104	220
HCN(g)	135.1	125	202	N ₂ O ₄ (g)	10	98	304
C ₂ H ₂ (g)	227	209	201	N ₂ O ₅ (g)	-42	134	178
C ₂ H ₄ (g)	52	68	219	N ₂ H ₃ CH ₃ (l)	54	180	166
CH ₃ CHO(g)	-166	-129	250	HNO ₃ (aq)	-207	-111	146
C ₂ H ₅ OH(l)	-278	-175	161	HNO ₃ (l)	-174	-81	156
C ₂ H ₆ (g)	-84.7	-32.9	229.5	NH ₄ Cl(s)	-314	-201	95
C ₃ H ₆ (g)	20.9	62.7	266.9	NH ₄ ClO ₄ (s)	-295	-89	186
C ₃ H ₈ (g)	-104	-24	270				
Chlorine				Silver			
Cl ₂ (g)	0	0	222.957	Ag(s)	0	0	42.6
Cl ₂ (aq)	-23	7	121	Ag ⁺ (aq)	105.6	77.1	72.7
Cl ⁻ (aq)	-167	-131	57	AgBr(s)	-100.4	-96.9	107.1
HCl(g)	-92	-95	187	AgCl ₃ (s)	-127.1	-109.8	96.2
Fluorine				Sulfur			
F ₂ (g)	0	0	203	S(rhombic)	0	0	31.8
F ⁻ (aq)	-333	-279	-14	S(monocl)	0.3	0.1	32.6
HF(g)	-271	-273	174	SO ₂ (g)	-296.8	-300.2	248.8
				SO ₃ (g)	-395.7	-371.1	256.3
Hydrogen				Titanium			
H ₂ (g)	0	0	131	H ₂ S(g)	-20.17	-33.0	205.6
H(g)	217	203	115				
H ⁺ (aq)	0	0	0				
OH ⁻ (aq)	-230	-157	-11	TiCl ₄ (g)	-763	-727	355
H ₂ O(l)	-286	-237	70	TiO ₂ (s)	-945	-890	50
H ₂ O(g)	-242	-229	189				