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[1] For each system below, indicate whether ΔS and ΔH is a positive or negative value. Then indicate if the reaction is entropy driven, enthalpy driven, or neither. Will the reaction be spontaneous at high temperatures, low temperatures, always or never? Qualitative, explain to your table group.

A) NaCl (s) $+$	$H_2O(l)$ +	heat \rightarrow	NaCl (aq)
$\Delta S =$	ΔH =	_driven?	
B) $O_2(g) + H$	$I_2O(l) \rightarrow O$	$h_2(aq) + hea$	t
$\Delta S = $	ΔH =	_driven?	
C) $CO_2(s) +$	heat \rightarrow	$CO_{2}(g)$	
$\Delta S =$	ΔH =	driven?	

[2] Calculate the ΔH_{rxn} , ΔS_{rxn} , $\Delta S_{universe}$, ΔG_{rxn} . For each system below, indicate whether ΔS and ΔH is a positive or negative value. Then indicate of the reaction is entropy driven, enthalpy driven, or neither. Quantitative

Substance	$\Delta H^{\circ}_{formation}$ (KJ/mole)	$\Delta S^{\circ}_{\text{formation}} (J/\text{mole}^{\circ}K)$	$\Delta G^{\circ}_{\text{formation}}$ (KJ/mole)
$C_{3}H_{8}(l)$	-103.8	269.9	-23.5
$O_2(g)$	0	205.1	0
$CO_2(g)$	-393.5	213.7	-394.4
$H_2O(g)$	-241.8	188.8	-228.6
$TiO_2(s)$	-939.7	49.9	-884.5
$TiCl_4(l)$	-804.2	252.3	-737.2
C (s)	0	5.7	0
$\operatorname{Cl}_{2}(g)$	0	223.1	0

A) $C_{3}H_{8}(l) + 5O_{2}(g) \rightarrow 3CO_{2}(g) + 4H_{2}O(g)$

B) $TiO_2(s) + C(s) + 2Cl_2(g) \rightarrow TiCl_4(l) + CO_2(g)$

[iii] Calculate G° in kJ for the following reactions, using the appropriate data tables.

Use $G^{\circ} = G_{\text{products}} - G_{\text{reactants}}$		<u>∆H°_f(KJ/mol)</u>	<u>∆G°_f(KJ/mol)</u>	∆S° _f
(a) $SO_3(g) + H_2O(I) \rightarrow H_2SO_4(I)$	CaCl ₂ :	-795	-750.2	114
(b) 2 NH ₄ Cl(s) + CaO(s) \rightarrow CaCl ₂ (s) + H ₂ O(l) + 2 NH ₃ (g)	CH₃CI:	-83.7	-60.2	234
(c) $CaSO_4(s) + 2 HCl(g) \rightarrow CaCl_2(s) + H_2SO_4(l)$	KCI:	-436.69	-408.8	82.55
(d) $C_2H_4(g) + H_2O(I) \rightarrow C_2H_5OH(I)$	K ₂ SO ₄ :	-1437.8	-1321.4	175.6
(e) Ca(s) + 2 H ₂ SO ₄ (l) \rightarrow CaSO ₄ (s) + SO ₂ (g) + 2 H ₂ O(l)				

[iv] Calculate the G° in kJ for the following reactions at 100°C using the appropriate data tables.

(a) $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

(b) 5 SO₃(g) + 2 NH₃(g)
$$\rightarrow$$
 2 NO(g) + 5 SO₂(g) + 3 H₂O(g)
(c) N₂O(g) + NO₂(g) \rightarrow 2 NO(g)

1. When solid potassium iodide is dissolved in water, a cooling of the mixture occurs because the solution process is endothermic for these substances. Explain, in terms of what happens to the molecules and ions, why this mixing occurs spontaneously?

2. Predict the algebraic sign of the entropy change for the following reactions?

 $\begin{array}{l} (a) \ \mathsf{PCI}_{3(g)} + \mathsf{CI}_{2(g)} \to \mathsf{PCI}_{5(g)} \\ (b) \ \mathsf{SO}_{2(g)} + \mathsf{CaO}_{(s)} \to \mathsf{CaSO}_{3(s)} \\ (c) \ \mathsf{CO}_{2(g)} + \mathsf{H}_2\mathsf{O}_{(l)} \to \mathsf{H}_2\mathsf{CO}_{3(aq)} \\ (d) \ \mathsf{Ni}_{(s)} + 2 \ \mathsf{HCI}_{(aq)} \to \mathsf{H}_{2(g)} + \mathsf{NiCI}_{(aq)} \\ (e) \ \mathsf{I}_{2(s)} \to \mathsf{I}_{2(g)} \\ (f) \ \mathsf{CI}_{2(g)} + \mathsf{Br}_{2(g)} \to 2 \ \mathsf{BrCI}_{(g)} \\ (g) \ \mathsf{NH}_{3(g)} + \mathsf{HCI}_{(g)} \to \mathsf{NH}_4\mathsf{CI}_{(s)} \\ (h) \ \mathsf{CaO}_{(s)} + \mathsf{H}_2\mathsf{O}_{(l)} \to \mathsf{Ca}(\mathsf{OH})_{2(s)} \end{array}$

- 3. Show that ΔS for the melting of ice is positive.
- 4 Calculate the entropy change in J/mol K for each of the following reactions.

 $\begin{array}{l} (a) \ CaO_{(s)} \ + 2 \ HCI_{(g)} \rightarrow CaCI_{2(s)} \ + H_2O_{(l)} \\ (b) \ C_2H_{4(g)} \ + H_{2(g)} \ \rightarrow C_2H_{6(g)} \end{array}$

5. What would be the algebraic signs of ΔS for the following reaction?

 $CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}$

6. Calculate ΔS° (in J/mol K) for the following reaction.

 $\begin{array}{l} (a) \ H_2O_{(l)} + SO_{3(g)} \rightarrow H_2SO_{4(l)} \\ (b) \ 2 \ KCI_{(s)} \ + H_2SO_{4(l)} \rightarrow K_2SO_{4(s)} \ + 2 \ HCI_{(g)} \\ (c) \ C_2H_4 + H_2O_{(g)} \rightarrow C_2H_5OH_{(l)} \end{array}$

7. Predict the probability of the following reactions by approximating the sign of Δ G. Classify each reaction as exothermic or endothermic.

a) $H_2O_{(1)} \rightarrow H_{2(q)} + \frac{1}{2}O_{2(q)}$	∆H= +285 kJ
	T∆S = -245 kJ
b) $C_6H_{14(q)} \rightarrow 6 C(s) + 7 H_{2(q)}$	∆H = +167 kJ
	T∆S = +168 kJ

c) 2 Fe _(s) + $\frac{1}{2}$ N _{2(g)} \rightarrow Fe ₂ N _(s)	∆H = -3.8 kJ T∆S = -14.6 kJ
d) $HCI_{(g)} + H_2O_{(I)} \rightarrow H_3O^+_{(aq)} + CI^{(aq)}$	ΔH = -75.3 kJ ΤΔS = -39.3 kJ

- 8. Phosgene, $COCI_2$, was used as a war gas during World War I. It reacts with the moisture in the lungs to produce HCI, which causes the lungs to fill with fluid, leading to death of the victim. $COCI_2$ has a standard entropy, $\Delta S^\circ = +284$ J/mol K and $\Delta H_f^\circ = -223$ kJ/mol. Use this information and appropriate tables to calculate ΔG_f° for $COCI_{2(q)}$ in kJ/mol.
- Aluminum oxidizes rather easily, but forms a thin protective coating of Al₂O₃ that prevents further oxidation of the aluminum beneath. Use the data for ΔH^o_f and ΔS^o to calculate ΔG^o_f for Al₂O_{3(s)} in kJ/mol.
- 10. Calcualte ΔG° in kJ/mole for the following reactions, using the appropriate data tables. (a) $SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(l)}$
 - (b) 2 NH₄Cl_(s) + CaO_(s) \rightarrow CaCl_{2(s)} + H₂O_(l) + 2 NH_{3(g)}
 - (c) $CaSO_{4(s)} + 2 HCI_{(g)} \rightarrow CaCI_{(s)} + H_2SO_{4(l)}$
 - (d) $C_2H_{4(g)}$ + $H_2O_{(I)} \rightarrow C_2H_5OH_{(I)}$
 - (e) $Ca_{(s)} + 2 H_2SO_{4(l)} \rightarrow CaSO_{4(s)} + SO_{2(g)} + 2 H_2O_{(l)}$
- Plaster of Paris, CaSO₄·½H₂O_(s), reacts with liquid water to form gypsum, CaSO₄·2H₂O_(s). Write a chemical equation for the reaction and calculate ΔG^o in kJ/mol, using the appropriate data tables.
- 12. Given the following,

 $4 \ \text{NO}_{(g)} \rightarrow 2 \ \text{N}_2\text{O}_{(g)} \ + \ \text{O}_{2(g)} \quad \Delta\text{G}^\circ = \text{-}139.56 \ \text{kJ}$

 $2 \text{ NO}_{(g)} \ + \ \text{O}_{2(g)} \ \rightarrow 2 \text{ NO}_{2(g)} \quad \Delta \text{G}^\circ = \text{-}69.70 \text{ kJ}$

calculate ΔG° for the reaction

 $2 \ N_2 O_{(g)} \ + \ 3 \ O_{2(g)} \ \rightarrow 4 \ NO_{2(g)}$

13. Calculate ΔG in kJ/mol at 55°C for the following reaction.

$$CH_{4(g)} + CI_{2(g)} \rightarrow CH_3CI_{(g)} + HCI_{(g)}$$

14. For the reaction at 98.2 K,

 $2 \text{ NO}_{2(g)} \rightarrow N_2 O_{4(g)}$

a) The values of ΔH° and ΔS° are -58.03 kJ mol⁻¹ and -176.61 J K⁻¹ mol⁻¹ respectively. What is the value of ΔG° at 298.2 K?

- b) At what temperature is $\Delta G^{\circ} = 0$?
- c) Is ΔG negative above, or below, this temperature?

Dougherty Valley HS AP Chemistry Entropy and Free Energy II			WC	WORKSHEET			
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Show your work for every calculation. Round your answer to the correct number of significant figures and record your final answer with correct units on the line provided.

[1] Which of the following processes are spontaneous?		
a. Spreading the fragrance of perfume through a room	Yes	No
b. Separating a mixture of N_2 and O_2 into pure containers of each	Yes	No
c. Bursting of a normally inflated balloon	Yes	No
d. The reaction of sodium metal with chlorine gas to form NaCl	Yes	No
e. The dissolution of NaCl(s) in water form NaCl(aq)	Yes	No
[2] Consider what happens when the explosive TNT is detonated.		
a. Is the detonation a spontaneous process?	Yes	No
b. What is the sign of q for the process?		
a Can you determine whether wie positive pagative or zero for the process? Explain		

c. Can you determine whether w is positive, negative, or zero for the process? Explain.

d. Can you determine whether the sign of ΔE for the process? Explain.

[3] The normal boiling point of methanol is 64.7°C and its molar enthalpy of vaporization is $\Delta H_{vap} = 71.8$ kJ/mol. a. When methanol boils at its normal boiling point, will its entropy increase or decrease?

b. Calculate the value of Δ S when 1.00 mol of methanol is vaporized at 64.7°C.

[4] What do you expect the sign of ΔS to be for the following situations?

- a. In a reaction, 2 moles of gaseous reactants \rightarrow 3 moles gaseous products.
- b. In a chemical reaction, two gases combine to form a solid.
- [5] In which of the following situations does entropy of the system increases?

a. Melting of ice cubes	Yes	No
b. Dissolving sugar in a cup of hot coffee	Yes	No
c. Formation of methane and oxygen gas from CO_2 and H_2O	Yes	No
d. A solid sublimes	Yes	No
e. Volume of a gas increases	Yes	No

[6] For each of the following pairs, circle the one with the higher entropy per mole at room temp.

a. Ar(l)	or	Ar(g)	b. He(g) at 3atm	or	He(g) at 1.5atm
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[7] Predict the sign of the entropy change of the system for each reaction.

- a. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ b. $Ba(OH)_2(s) \rightarrow BaO(s) + H_2O(g)$
- c. CO(g) + $2H_2(g) \rightarrow CH_3OH(I)$

Chemistry II [8] Using S° values from Appendix Four, calculate Δ S° values for each reaction.

a. $N_2H_4(g) + H_2(g) \rightarrow 2NH_3(g)$		<u>∆S°(J/mol)</u>
	$N_2H_4(g)$	238.5
	$H_2(g)$	130.7
	NH ₃ (g)	192.8

b. $2AI(s) + 3CI_2(g) \rightarrow 2AICI_3(s)$

AICl ₃ (s)	109.3
Cl ₂ (g)	223.1
Al(s)	28.3

- 9. For a certain chemical reaction, ΔH° = -35.4 kJ and ΔS° = -85.5 J/K.
 - a. Is the reaction endothermic or exothermic?
 - b. Does the reaction lead to an increase or decrease in the disorder of the system?
 - c. Calculate ΔG° for the reaction at 298 K.
 - d. Is the reaction spontaneous at 298K under standard conditions?
- [10] a. Using data in Appendix Four, calculate ΔH° , ΔS° , and ΔG° at 298K for the reaction below. H₂(g) + F₂(g) \rightarrow 2HF(g)

		$\Delta H^{\circ} = _$	
	∆S°(J/mol)	∆ (KJ/mol)ه∆	Δ G °=
H ₂ (g)	130.7	0	
F ₂ (g)	202.8	0	
HF(g)	173.8	-273.3	-275.4

b. Show that $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$

[11] a. Using data from Appendix four, calculate the change in Gibbs free energy for the following reaction.

 $2NOCI(g) \rightarrow 2NO(g) + CI_2(g)$

	∆S°(KJ/mol)	∆H°	∆G°
NOCI(g)	261.7	51.7	66.1
NO(g)	210.8	91.3	87.6
$Cl_2(g)$	2231	0	0

b. Is the reaction spontaneous under standard conditions?

Yes No

[12] A particular reaction is spontaneous at 450 K. The enthalpy change for the reaction is +34.5 kJ. What can you conclude about the sign and magnitude of Δ S for the reaction?

[1] Using enthalpies of formation (Appendix Four), calculate ΔH° for the following reaction at 25°C. Also calculate ΔS° for this reaction from standard entropies at 25°C. Use these values to calculate ΔG° for the reaction at this temperature. -1453.2 KJ, -162 KJ, -1404.9 KJ

WORKSHEET

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-55.2

 $2CH_3OH(I) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(I)$

[2] The free energy of formation of one mole of compound refers to a particular chemical equation. For each of the following, write that equation.

[a] NaCl(s)

[b] HCN(I)

 $[c] SO_2(g)$

 $[d] PH_3(g)$

[3] Calculate the standard free energy of the following reactions at 25°C, using standard free energies of formation ∆G°_f 542.96 -533.04

Ca²⁺ $[a] CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ [b] CaCO₃(s) + 2H⁺(aq) \rightarrow Ca²⁺(aq) + H₂O(l) + CO₂(g)

[4] On the basis of ΔG° for each of the following reactions, decided whether the reaction is spontaneous or non-spontaneous as written. Or, if you expect an equilibrium mixture with significant amounts of both reactants and products, say so.

 $[a] SO_2 + 2H_2S \rightarrow 3S + 2H_2O;$ $\Delta G^{\circ} = -91 \text{ KJ}$ $[b] 2H_2O_2 \rightarrow O_2 + 2H_2O;$ $\Delta G^{\circ} = -211 \text{ KJ}$ [c] HCOOH \rightarrow CO₂ + H₂; $\Delta G^{\circ} = 119 \text{ KJ}$ $[d] I_2 + Br_2 \rightarrow 2IBr$; $\Delta G^{\circ} = 7.5 \text{ KJ}$ [e] $NH_4CI \rightarrow NH_3 + HCI$; $\Delta G^{\circ} = 92 \text{ KJ}$

[5] Calculate ΔH° and ΔG° for the following reactions at 25°C, using thermodynamic data from Appendix four; *interpret* the signs of ΔH° and ΔG° .

 $[a] Al_2O_3 + 2Fe \rightarrow Fe_2O_3 + 2AI (851 KJ; 838 KJ)$

[b] $COCl_2 + H_2O \rightarrow CO_2 + 2HCl$; **COCl_2**: $\Delta H_f^{\circ} = -220KJ/mol and \Delta G_f^{\circ} = -206KJ/mol (-72 KJ; -142KJ)$

[6] Using enthalpies of formation (appendix four), calculate ΔH° for the following reactions at 25°C. Also calculate ΔS° for this reaction from standard entropies at 25°C. Use these values to calculate ΔG° for the reaction at this temperature.

 $4\text{HCN} + 5\text{O}_2 \rightarrow 2\text{H}_2\text{O} + 4\text{CO}_2 + 2\text{N}_2$

[7] The free energy of formation of one mole of compound refers to a particular chemical equation. For each of the following, write that equation.

[a] CaO(s) $[b] CH_3NH_2(g)$ $[c] CS_2(I)$ $[d] P_4O_{10}(s)$

[8] Calculate the standard free energy of the following reactions at 25°C, using standard free energies of formation from the appendix. ∆H°_f ∆G°_f ∆S°_f

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$[a] C_2H_4(g) + O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$	HCO₃ ⁻ -691.11	-587.06	95.0	
[b] Na2CO3(s) + H+(aq) → 2Na+(aq) + HCO3-(aq)				

[9] For each of the following reactions, state whether the reaction is spontaneous or non-spontaneous as written or is easily reversible (that is, is a mixture with significant amounts of reactants and products)

$\Delta G^{\circ} = -92 KJ$
∆G° = 173 KJ
∆G° = 479KJ
$\Delta G^{\circ} = -191 \text{KJ}$
$\Delta G^{\circ} = 2.6 KJ$

[10] Calculate ΔH° and ΔG° for the following reactions at 25°C, using thermodynamic data from Appendix Four; *interpret* the signs of ΔH° and ΔG° .

 $[a] \ 2PbO \ + \ N_2 \rightarrow 2Pb \ + \ 2NO$

[b] $CS_2 + 2H_2O \rightarrow CO_2 + 2H_2S$; **CS**₂: $\Delta H_f^{\circ} = 87.9$ KJ and $\Delta G_f^{\circ} = 63.6$ KJ

[11] Consider the reaction of 2 mol $H_2(g)$ at 25°C and 1 atm with 1 mol $O_2(g)$ at the same temperature and pressure to produce liquid water at these conditions. If this reaction is run in a controlled way to generate work, what is the maximum useful work that can be obtained? How much entropy is produced in this case? -474.4 KJ; 0

[12] What is the maximum work that could be obtained from 5.00 g zinc metal in the following reaction at 25° C? -16.2KJ

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

[13] Give the expression for the thermodynamic equilibrium constant for each of the following reactions: [a] $CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g)$ [b] $Mg(OH)_2(s) \leftrightarrow Mg^{2+}(aq) + 2OH^{-}(aq)$ [c] $2Li(s) + 2H_2O(I) \leftrightarrow 2Li^{+}(aq) + 2OH^{-}(aq) + H_2(g)$

[14] What is the standard free energy change ΔG° at 25°C for the following reaction? Obtain necessary information from Appendix four: (-190.6KJ, 2.5E⁻³³)

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

What is the value of the thermodynamic equilibrium constant K?

[15] Calculate the standard free energy change and the equilibrium constant K_p for the following reaction at 25°C. See appendix four for data. (-142.2KJ, 8.3E²⁴) – From another textbook

$CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g)$

[16] Obtain the equilibrium constant K_c at 25°C from the free-energy change for the reaction:

		<u>∆H°_f</u>	<u>∆G°_f</u>	<u>∆S°</u> f
$Mg(s) + Cu^{2+} \leftrightarrow Mg^{2+}(aq) + Cu(s)$	Cu ²⁺	64.39	64.98	-98.7
	Mg ²⁺	-461.96	-456.01	-118

Use appendix for data. (-520.99KJ, 1.88E⁹¹)

[17] What is the standard free-energy change ΔG° at 25°C for the following reaction? Obtain necessary information from Appendix four: **C(graphite) + O₂(g)** \rightarrow **CO₂(g)**

Calculate the value of the equilibrium constant K.

[18] Calculate the standard free energy change and the equilibrium constant K_p for the following reaction at 25°C. See appendix four for data.

$CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g)$

[19] Calculate the equilibrium constant K_c at 25°C from the free-energy change for the reaction:

		<u>∆H°_f</u>	<u>∆G°_f</u>	<u>∆S°</u> f
$Zn(s) + Cu^{2+} \leftrightarrow Zn^{2+} + Cu(s)$	Cu ²⁺	64.39	64. <u>9</u> 8	-98.7
	Zn ²⁺	-152.4	-147.21	-106.5



1. Consider the decomposition of H_2O_2 (hydrogen peroxide) at 298 K and 1 atm pressure according to:

$2 H_2O_2(liq) \leftrightarrow 2 H_2O(liq) + O_2(gas)$

Substance	∆G _f °	∆H _f °	S°
H ₂ O ₂ (liq)	-120.2 kJ/mol	-187.6 kJ/mol	109.5 J K ⁻¹ mol ⁻¹
H ₂ O(liq)	-237.0	-285.8	69.4
O ₂ (gas)			205

Please find the

a) standard enthalpy of reaction.

b) standard entropy of reaction.

2. For the reaction in the previous question, please find the

a) standard (Gibbs) free energy of reaction

b) the value of the (thermodynamic) equilibrium constant at 298 K, 1 atm

3. From the indicated standard enthalpies of formation given in kJ/mol, please calculate the standard enthalpy of reaction for:

 $NH_4CI(s) \leftrightarrow NH_3(g) + HCI(g)$

-314.4 -46.0 -92.5

4. Carbon monoxide in the atmosphere slowly converts to carbon dioxide at normal atmospheric temperatures according to:

CO(g) + ½ O₂(g) <==> CO₂(g)

The standard enthalpy of reaction is -284 kJ and the standard entropy of reaction is -87 J/K. Estimate the temperature at which the equilibrium begins to favor the decomposition of CO_2 . Assume that the enthalpy and the entropy of reaction are not affected by temperature.

5. From the indicated standard entropies given in J/K, please calculate the standard entropy of reaction for:

2 NH₃(g) ↔ N₂H₄(liq) + H₂(g) 192.5 121.2 130.6

6. Please calculate the standard (Gibbs) free energy of reaction for:

2 NO(g) + O₂(g) <==> 2 NO₂(g)

Substance	∆ G f ^o	∆H _f °	S°
NO(g)	86.69 kJ/mol	90.4 kJ/mol	210.6 J/K mol
NO ₂ (g)	51.84	34.0	240.5
O ₂ (gas)			205.0

7. Calculate the entropy of vaporization of propane given that its enthalpy of vaporization is 16.9 kJ/mol at its normal boiling point of -42.1°C.

8. Obtain the numerical value of the equilibrium constant (at 298K) for the following reaction:

Substance	∆G _f °	∆H _f °	S°
H ₂ CO ₃ (aq)	-623 kJ/mol	-700 kJ/mol	187 J/K mol
H ₂ O(liq)	-237	-286	70
CO ₂ (gas)	-394	-394	213

 $CO_2(g) + H_2O(liq) \iff H_2CO_3(aq)$

9. Please indicate if TRUE or FALSE (Explain why as well):

_____ The entropy of a gas increases with increasing temperature.

_____ The energy of a perfect crystal is zero at O K.

_____ Spontaneous processes always increase the entropy of the reacting system.

_____ All spontaneous processes release heat to the surroundings

_____ An endothermic reaction is more likely to be spontaneous at high temperatures than at low temperatures.

_____ The entropy of sugar decreases as it precipitates from an aqueous solution.

10. Ammonia gas a standard (Gibbs) free energy of formation equal to -16.367 kJ/mol
a) Find △G° for the reaction N₂(g) + 3 H₂(g) <=> 2 NH₃(g)

b) In which direction will this reaction proceed if a mixture of gases is made with: $P_{NH3} = 1.00 \text{ atm}$ $P_{H2} = 0.50 \text{ atm}$ $P_{N2} = 0.50 \text{ atm}$

c) What pressure of hydrogen gas should be added to a mixture already containing 0.20 atm NH_3 and 0.50 atm N_2 if one does not want the amounts of NH_3 and N_2 to change?

ANSWERS:

1. -196.4 kJ; 125 J/K 2. -233.6 kJ; 8.85 x 10^{40} 3. 175.9 kJ 4. 3260 K or 3300K 5. -133.2 J/K 6. -69.7 kJ 7. 73.1 J/K 8. 4.0 x 10^{-2} (using DG⁶ data); 3.1 x 1^{0-2} (using DH⁶ and S° data) 9. T F F F T T 10. -32.734 kJ; proceed to the right; 5.3x10⁻³ atm **AP Chemistry**

2007B

Free Energy & Entropy FRQs WORKSHEET #6

 $K_p = \frac{(p_{\rm UO_2Cl_2})^3(p_{\rm O_2})}{(p_{\rm Cl_2})^3}$

1. A sample of solid U_3O_8 is placed in a rigid 1.500 L flask. Chlorine gas, $Cl_2(g)$, is added, and the flask is heater to 862°C. The equation for the reaction that takes place and the equilibrium-constant expression for the reaction are given below.

$$U_3O_8(s) + 3 \operatorname{Cl}_2(g) \rightleftharpoons 3 \operatorname{UO}_2\operatorname{Cl}_2(g) + \operatorname{O}_2(g)$$

When the system is at equilibrium, the partial pressure of $Cl_2(g)$ is 1.007 atm and the partial pressure of $UO_2Cl_2(g)$ is 9.734×10^{-4} atm.

- (a) Calculate the partial pressure of $O_2(g)$ at equilibrium at 862°C.
- (b) Calculate the value of the equilibrium constant, K_p , for the system at 862°C.
- (c) Calculate the Gibbs free-energy change, ΔG° , for the reaction at 862°C.
- (d) State whether the entropy change, ΔS°, for the reaction at 862°C is positive, negative, or zero. Justify your answer.
- (e) State whether the enthalpy change, ΔH°, for the reaction at 862°C is positive, negative, or zero. Justify your answer.
- (f) After a certain period of time, 1.000 mol of $O_2(g)$ is added to the mixture in the flask. Does the mass of $U_3O_8(s)$ in the flask increase, decrease, or remain the same? Justify your answer.

2007

 $\mathrm{N_2}(g) \ + \ 3 \ \mathrm{F_2}(g) \ \rightarrow \ 2 \ \mathrm{NF_3}(g) \qquad \Delta H_{298}^{\circ} \ = \ - \ 264 \ \mathrm{kJ \ mol^{-1}}; \ \Delta S_{298}^{\circ} \ = \ - \ 278 \ \mathrm{J \ K^{-1} \ mol^{-1}}$

- 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, ΔG_{298}° , for the reaction.
 - (b) Determine the temperature at which the equilibrium constant, K_{eq} , for the reaction is equal to 1.00. (Assume that ΔH° and ΔS° are independent of temperature.)
 - (c) Calculate the standard enthalpy change, ΔH°, that occurs when a 0.256 mol sample of NF₃(g) is formed from N₂(g) and F₂(g) at 1.00 atm and 298 K.

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 NF₃ are produced according to the equation in the box above?
- (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	?

Answer the following questions about the thermodynamics of the reactions represented below.

Reaction X: $\frac{1}{2}$ I₂(s) + $\frac{1}{2}$ Cl₂(g) \rightleftharpoons ICl(g) $\Delta H_f^{\circ} = 18 \text{ kJ mol}^{-1}, \Delta S_{298}^{\circ} = 78 \text{ J K}^{-1} \text{ mol}^{-1}$ Reaction Y: $\frac{1}{2}I_2(s) + \frac{1}{2}Br_2(l) \rightleftharpoons IBr(g)$ $\Delta H_f^\circ = 41 \text{ kJ mol}^{-1}, \Delta S_{298}^\circ = 124 \text{ J K}^{-1} \text{ mol}^{-1}$

- (a) Is reaction X, represented above, spontaneous under standard conditions? Justify your answer with a calculation.
- (b) Calculate the value of the equilibrium constant, K_{eq} , for reaction X at 25°C.
- (c) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer.
- (d) Explain why the standard entropy change is greater for reaction Y than for 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.
- (f) For the vaporization of solid iodine, $I_2(s) \rightarrow I_2(g)$, the value of ΔH_{298}° is 62 kJ mol⁻¹. Using this information, calculate the value of ΔH_{298}° for the reaction represented below.

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

$\operatorname{CO}(g) + \frac{1}{2}\operatorname{O}_2(g) \rightarrow \operatorname{CO}_2(g)$ 2006

- 2. 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.

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$$
 $\Delta H_{298}^\circ = -110.5 \text{ kJ mol}^{-1}$
 $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_{298}^\circ = -393.5 \text{ kJ mol}^{-1}$

(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)
$\mathrm{CO}(g)$	197.7
$CO_2(g)$	213.7
$O_2(g)$	205.1

- (c) Determine the standard free energy change, ΔG_{rxn}° , for the reaction at 298 K. Include units with your answer.
- (d) Is the reaction spontaneous under standard conditions at 298 K? Justify your answer.
- (e) Calculate the value of the equilibrium constant, K_{eq} , for the reaction at 298 K.

2006B

- 7. 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.
 - (b) Does the entropy change of the reaction favor the reactants or the product? Justify your answer.
 - (c) For the reaction under the conditions specified, which is favored, the reactants or the product? Justify your answer.
 - (d) Explain how to determine the value of the equilibrium constant, K_{eq} , for the reaction. (Do <u>not</u> do any calculations.)
 - (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.

2004
$$2 \operatorname{Fe}(s) + \frac{3}{2} \operatorname{O}_2(g) \to \operatorname{Fe}_2 \operatorname{O}_3(s) \quad \Delta H_f^\circ = -824 \text{ kJ mol}^{-1}$$

- 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 O₂(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*)
 - (ii) $O_2(g)$
 - (b) Identify the limiting reactant when the mixture is heated to produce $Fe_2O_3(s)$. Support your answer with calculations.
 - (c) Calculate the number of moles of $Fe_2O_3(s)$ produced when the reaction proceeds to completion.
 - (d) The standard free energy of formation, ΔG_f^{\diamond} , of Fe₂O₃(s) is -740. kJ mol⁻¹ at 298 K.
 - (i) Calculate the standard entropy of formation, ΔS_f° , of Fe₂O₃(*s*) at 298 K. Include units with your answer.
 - (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.

The reaction represented below also produces iron(III) oxide. The value of ΔH^{\diamond} for the reaction is -280. kJ per mole of Fe₂O₃(*s*) formed.

$$2 \operatorname{FeO}(s) + \frac{1}{2} \operatorname{O}_2(g) \to \operatorname{Fe}_2 \operatorname{O}_3(s)$$

(e) Calculate the standard enthalpy of formation, ΔH_f° , of FeO(s).

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.

$$2 \operatorname{N}(g) \rightarrow \operatorname{N}_2(g)$$

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
$N \equiv M$	950

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

$$N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$$
 $\Delta H^\circ = -92.2 \text{ kJ}$

Predict the sign of the standard entropy change, ΔS° , for the reaction. Justify your answer.

- (c) The value of ΔG° for the reaction represented in part (b) is negative at low temperatures but positive at high temperatures. Explain.
- (d) When N₂(g) and H₂(g) are placed in a sealed container at a low temperature, no measurable amount of NH₃(g) is produced. Explain.
- 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.
 - (b) Write the expression for the equilibrium constant, K_p , for the reaction.
 - (c) Consider the following thermodynamic data.

$$\Delta G_f^{\circ} \text{ (kJ mol^{-1})} \qquad \frac{\text{NO}}{+86.55} \qquad \frac{\text{CO}}{-137.15} \qquad \frac{\text{CO}_2}{-394.36}$$

- (i) Calculate the value of ΔG° for the reaction at 298 K.
- (ii) Given that ΔH° for the reaction at 298 K is -746 kJ per mole of N₂(g) formed, calculate the value of ΔS° for the reaction at 298 K. Include units with your answer.

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

 $P_{\rm CO_2} = 3.1 \times 10^{-4}$ atm.

- (i) Calculate the value of ΔG for the reaction at 298 K when the gases are at the partial pressures given above.
- (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 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 NO₂(g).
 - (b) For the reaction at 25°C, the value of the standard free-energy change, ΔG° , is -70.4 kJ.
 - Calculate the value of the equilibrium constant, K_{eq}, for the reaction at 25°C.
 - (ii) Indicate whether the value of ΔG° would become more negative, less negative, or remain unchanged as the temperature is increased. Justify your answer.
 - (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.

	Standard Molar Entropy, S° (J K ⁻¹ mol ⁻¹)
NO(g)	210.8
$NO_2(g)$	240.1

(d) Use the data in the table below to calculate the bond energy, in kJ mol⁻¹, of the nitrogen-oxygen bond in NO2. Assume that the bonds in the NO2 molecule are equivalent (i.e., they have the same energy).

	Bond Energy (kJ mol ⁻¹)
Nitrogen-oxygen bond in NO	607
Oxygen-oxygen bond in ${\rm O}_2$	495
Nitrogen-oxygen bond in NO2	?

- **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.

$$\operatorname{CO}_2(g) + 2 \operatorname{NH}_3(g) \rightarrow \operatorname{CO}(\operatorname{NH}_2)_2(s) + \operatorname{H}_2\operatorname{O}(l) \qquad \Delta H_{298}^\circ = -134 \text{ kJ}$$

- (i) For the reaction, indicate whether the standard entropy change, ΔS_{298}° , is positive, or negative, or zero. Justify your answer.
- (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.
- (iii) For the reaction, how is the value of the standard free energy change, ΔG° , affected by an increase in temperature? Explain.
- (b) Some reactions that are predicted by their sign of ΔG° 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 ΔG° for the reaction? Explain.

WORKSHEET #7

[1] Imagine tossing two coins in the air.

- a. Predict the distribution of various combinations of heads and tails.
- b. What is the probability of the result being two heads?
- c. What is the most probable result?

Now imaging tossing three coins in the air.

- d. What is the probability of a three heads result?
- e. Which system has the highest entropy, the two-coin system or the three-coin system?

[2] Which one of the following pairs of samples has the higher entropy?

- a. $Br_2(l)$ or $Br_2(g)$
- b. $C_2H_6(g)$ or $C_3H_8(g)$
- c. MgO(s) or NaCl(s)
- d. KOH(s) or KOH(aq)

[3] Predict the entropy change for the following processes:

- a. $O_2(g) \rightarrow 2O(g)$
- b. $2O_3(g) \rightarrow 3O_2(g)$
- c. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
- d. $\operatorname{NaCl}(s) \rightarrow \operatorname{Na}^{+}(aq) + \operatorname{Cl}^{-}(aq)$
- e. $C_2H_5OH(l) \rightarrow C_2H_5OH(g)$
- f. $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

[4] Of the following reactions,

which are spontaneous at any temperature, which are never spontaneous regardless of the temperature, which are spontaneous only at a high temperature, and which are spontaneous only at low temperature?

		ΔH	ΔS
a.	$C_8H_{18}(l) + \frac{25}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(g)$	_	+
b.	$N_2(g) + 2F_2(g) \rightarrow N_2F_4(g)$	_	_
c.	$Cl_2(g) \rightarrow 2Cl(g)$	+	+
d.	$2O_3(g) \rightarrow 3O_2(g)$	_	+
e.	$2C(s) + 2H_2(g) \rightarrow C_2H_4(g)$	+	_

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- d. KOH(s) or KOH(aq)

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- a. $O_2(g) \rightarrow 2O(g)$
- b. $2O_3(g) \rightarrow 3O_2(g)$
- c. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
- d. $\operatorname{NaCl}(s) \rightarrow \operatorname{Na}^{+}(aq) + \operatorname{Cl}^{-}(aq)$
- e. $C_2H_5OH(l) \rightarrow C_2H_5OH(g)$
- f. $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

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b.	$N_2(g) + 2F_2(g) \rightarrow N_2F_4(g)$	_	_
c.	$Cl_2(g) \rightarrow 2Cl(g)$	+	+
d.	$2O_3(g) \rightarrow 3O_2(g)$	_	+
e.	$2C(s) + 2H_2(g) \rightarrow C_2H_4(g)$	+	_