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ANSWER KEY

CHEMISTRY F14O3 THIRD EXAM PROFESSOR J. MORROW				12/8/99		
PRINT	NAME, LAST	T				
FIRST:						
	MAXIMU	JM POINT V	ALUE IS IN PA	RENTHESES		
1	(10)	7	(10)	13	(20)	
2	(20)	8	(10)	14	(10)	
3	(15)	9	(10)	15	(15)	
4	(15)	10	(10)	16	(20)	
5	(20)	11	(10)	17	(20)	
6	(20)	12	(10)	18	(20)	
CC	DLUMN TOTA	LS (MAXIN	ИUМ):			
(100)			(60)		(105)	
EXA	M TOTAL (20	05 pts)		OUT OF 100		

1) Given the following table of thermodynamic data for the indicated species. All of the following species are in the gaseous state at 298 K.

SPECIES S	$\int_{0}^{\infty} \left(\frac{J}{\text{mol} \cdot K}\right) = \Delta H^{0}$	$f(\frac{kJ}{mol})$
CO ₂ 213.7	9 -393.5	51
NO ⁻	214.86	?
CO ₂	218.70 -441.4	4O
NO	210.76	90.29

For the following reaction, $K_p = 2.189 \text{ x } 10^{-7}$

$$CO_2^- + NO \longrightarrow CO_2 + NO^-$$

Calculate ΔG^{o}_{rxn} (in kJ) at 298 K for this reaction. (10 pts)

$$\Delta G^{0} = - RT \ln K_{p} = -(8.314 \times 10^{-3})(298) \ln(2.189 \times 10^{-7}) = 38.00 \text{ kJ}$$

$$\Delta G^{o}_{rxn} = \underline{\hspace{1cm}}$$

2) Calculate ΔH^{o}_{f} (in kJ) for NO at 298 K for the reaction using the data from problem 1. (20 pts) SHOW WORK

$$CO_2^- + NO \longrightarrow CO_2 + NO^-$$

 $T\Delta S_{rxn} = (298)(214.86 + 213.79 - 218.70 - 210.76)(10^{-3}) = -0.241 \text{ kJ}$ (FROM TABLE)

$$\Delta H_{rxn} = (\Delta H^{o}_{f} + (-393.51) - (-441.40) - (90.29)) = \Delta H^{o}_{f} - 42.40 \text{ kJ} \qquad (FROM TABLE)$$

$$\Delta G_{\rm rxn} = \Delta H_{\rm rxn} - T\Delta S_{\rm rxn}$$
 : $38.00 = \Delta H^{\rm o}_{\rm f} - 42.40 \text{ kJ} - (-0.241)$
 $\Delta H^{\rm o}_{\rm f} = 80.2 \text{ kJ}$

$$\Delta H^{0}_{f} = \underline{\hspace{1cm}}$$

3) Using the ion-electron method, balance the following reaction under the conditions given. Show the balanced oxidation and reduction half reactions where indicated. Write your answers in the space provided.

$$C_3H_4O_4 + S_2O_6^{2-} \longrightarrow CH_3OH + 2CO_{2(g)} + SO_{2(g)}$$
 (acidic)

oxidation half reaction: (5 pts)

$$C_3H_4O_4 + H_2O \longrightarrow CH_3OH + 2CO_2 + 2H^+ + 2e^-$$

reduction half reaction: (5 pts)

$$2 e^{-} + 4 H^{+} + S_{2}O_{6}^{2-} \longrightarrow 2 SO_{2} + 2 H_{2}O_{2}$$

ANSWER: (5 pts) Subscripts need NOT be shown in final answer.

BAL EQ.
$$C_3H_4O_4 + S_2O_6^{2-} + 2H^+ \longrightarrow CH_3OH + 2CO_2 + 2SO_2 + H_2O$$

4)
$$MnO_{4 \text{ (aq)}}^{-} + S^{2-}_{\text{(aq)}} \longrightarrow MnS_{2(S)} + S^{0}_{\text{(S)}}$$
 (basic)

oxidation half reaction: (5 pts)

$$S^{2-}_{(aq)} \longrightarrow S^{0}_{(S)} + 2 e^{-}$$

reduction half reaction: (5 pts)

$$3 e^{-} + 8 H^{+} + MnO_{4}^{-} + 2 S^{2-} \longrightarrow MnS_{2} + 4 H_{2}O$$

ANSWER: (5 pts) Subscripts need NOT be shown in final answer.

$$16 \text{ H}^+ + 2 \text{ MnO}_4^- + 7 \text{ S}^{2^-} \longrightarrow 2 \text{ MnS}_2 + 3 \text{ S}^0 + 8 \text{ H}_2\text{O} \text{ (ACIDIC)}$$

 $8 \text{ H}_2\text{O} + 2 \text{ MnO}_4^- + 7 \text{ S}^{2^-} \longrightarrow 2 \text{ MnS}_2 + 3 \text{ S}^0 + 16 \text{ OH}^-\text{(BASIC SOL'N)}$

5) The vapor pressure of water at 298 K is O.O3132 atm. The standard free energy of formation of $H_2O_{(\ell)}$, $\Delta G^o{}_f$, is -237.2 kJ/mol also at 298 K. Using this information, calculate the standard free energy of formation, $\Delta G^o{}_f$ (in kJ), of $H_2O_{(g)}$. BE CAREFUL USING THE DEFINITION OF EACH TERM! (20 pts) SHOW WORK

GIVEN: For the reaction,
$$H_2O_{(\ell)} \longrightarrow H_2O_{(g)}$$
, $\Delta G_{rxn} = - RT \ln P_{(atm)}$
a) - 224.3 b) - 232.9 c) - 245.8 d) - 228.6 $H_2O_{(\ell)} \longrightarrow H_2O_{(g)}$ $\Delta G_{rxn} = \Delta G^o_{f(g)} - \Delta G^o_{f(\ell)} = -RT \ln P = -(8.314)(298)\ln(0.03132)$ $\Delta G_{rxn} = \Delta G^o_{f(g)} - (-237.2 \text{ kJ/mol}) = 8581 \text{ J/mol} = 8.581 \text{ kJ/mol}$ $\Delta G^o_{f(g)} = 8.581 - 237.2 = -228.6 \text{ kJ/mol}$

ANSWER IS: d

6) The equilibrium constant for the reaction

$$I_2$$
 + C_5H_8 \longrightarrow HI + C_5H_7I cyclopentene iodocyclopentene

was measured spectrophotometrically in the gas phase between

175°C and 415°C. The following equation was obeyed:

$$\log_{10} K_{p_{(atm)}} = -\frac{2611.4}{T} + 7.55$$

Calculate ΔH^{o} and ΔS^{o} for this reaction (20 pts)

SHOW WORK

a)
$$\Delta H^{0} = 25.0 \text{ kJ}$$
 b) $\Delta H^{0} = 50.0 \text{ kJ}$ c) $\Delta H^{0} = 21.7 \text{ kJ}$ d) $\Delta H^{0} = 25.0 \text{ kJ}$ e) $\Delta H^{0} = 50.0 \text{ kJ}$
 $\Delta S^{0} = 78 \text{ J}$ $\Delta S^{0} = 145 \text{ J}$ $\Delta S^{0} = 63.0 \text{ J}$ $\Delta S^{0} = 145.0 \text{ J}$ $\Delta S^{0} = 63.0 \text{ J}$

c)
$$\Delta H^0 = 21.7 \text{ kJ}$$

1)
$$\Delta H^0 = 25.0 \text{ kJ}$$

e)
$$\Delta H^0 = 50.0 \text{ k}$$
.

$$\begin{split} & \ln \, \text{K} = \, - \, \frac{\Delta G^o}{RT} \quad \log_{10} \, \text{K} = \, - \, \frac{\Delta G^o}{2.303 RT} \quad = \, - \frac{\Delta H^o}{2.303 RT} \, + \, \frac{\Delta S^o}{2.303 R} \\ & - \frac{\Delta H^o}{2.303 RT} \quad = \, - \, \frac{2611.4}{T} \qquad \qquad \text{AND} \qquad \qquad \frac{\Delta S^o}{2.303 R} \, = \, 7.55 \end{split}$$

$$\Delta H^{0} = 50.0 \text{ kJ} \text{ AND}$$
 $\Delta S^{0} = 145 \text{ J}$

(15 pts) ANSWER IS: b

7) If equal pressures (1 atm each) of I₂ and cyclopentene (see question 6) are mixed at 300°C, what will be the equilibrium partial pressure of HI (in atm)? (10 pts) SHOW WORK

a) 0.21 b) 0.044 c) 0.46 d) 0.12 e) 0.34
$$\log_{10}K_{p(atm)} = -\frac{2611.4}{300} + 7.55 \therefore K_{p} = 0.0700 = \frac{x^{2}}{(1-x)^{2}}$$
$$x = 0.209 \text{ atm} = P_{HI} (= 0.21 \text{ atm})$$

(15 pts) ANSWER IS: 0.21

8) If an ideal gas is expanded at constant temperature, then;

a)
$$\Delta E > 0$$
 and $\Delta S > 0$

a)
$$\Delta E > 0$$
 and $\Delta S > 0$ b) $\Delta E = 0$ and $\Delta S = 0$ c) $\Delta E = 0$ and $\Delta S < 0$

$$\Delta E = 0$$
 and $\Delta S < 0$

d)
$$\Delta E < 0$$
 and $\Delta S > 0$ e) $\Delta E = 0$ and $\Delta S > 0$

e)
$$\Delta E = 0$$
 and $\Delta S > 0$

ANSWER IS: e

9) If $\Delta G^{o}_{f}(HI_{(g)}) = 1.70 \text{ kJ}$ what is the equilibrium constant at 25°C for the reaction, 2 $HI_{(g)}$ $H_{2(g)} + I_{2(s)}$? (10 pts)

- a) 3.9
- b) 2.0
- c) 0.69
- d) 0.50
- e) 0.25

ANSWER IS: a

10) For the reaction, $H_2O_{(\ell)} \longrightarrow H_2O_{(g)}$ at 100° C and 1 atm pressure, which of the following is (10 pts) true :

- a) $\Delta H = 0$ b) $\Delta S = 0$ c) $\Delta H = \Delta E$ d) $\Delta H = T\Delta S$ e) $\Delta H = \Delta G$

ANSWER IS: d

- 11) For the gas phase decomposition, $PCl_{5(g)} = PCl_{3(g)} + Cl_{2(g)}$ (10 pts)
- c) $\Delta H > 0$ and $\Delta S < 0$ a) $\Delta H < 0$ and $\Delta S < 0$ b) $\Delta H > 0$ and $\Delta S > 0$ d) $\Delta H < 0$ and $\Delta S > 0$ e) $\Delta H = 0$ and $\Delta S > 0$

ANSWER IS: b

12) You are given four reactions along with their equilibrium constants and heats of reaction: (10 pts)

REACTION	<u>K</u>		ΔH_{rxn}	
1.		K ₁		ΔH_1
2.		K_2		ΔH_2
3.		K_3		ΔH_3
4.		K_{4}		ΔH_{4}

You want to combine these four reactions to obtain a fifth reaction.

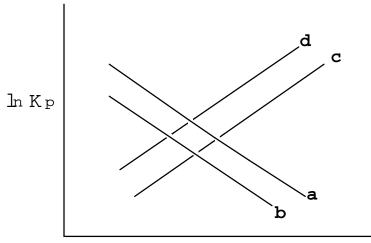
If for the fifth reaction, $K_5 = \frac{K_2 K_{4}^3}{K_1 K_2^2}$, then $\Delta H_5 =$

- a) $\Delta H_2 + 2\Delta H_4 \Delta H_1 3\Delta H_3$ b) $\Delta H_2 + 3\Delta H_4 \Delta H_1 2\Delta H_3$ c) $\Delta H_1 + 2\Delta H_3 \Delta H_2 3\Delta H_4$ d) $3\Delta H_2 + \Delta H_4 \Delta H_1 2\Delta H_3$

ANSWER IS: b

13) Correlate each of the curves in the figure with the appropriate reaction. 20 pts - 5 pts each answer

HINT:
$$\ln K_p = -\frac{\Delta H}{RT} + \text{constant } (y = mx + b), \text{ and, } \Delta G^o = -RT \ln K_p$$



	T/T			
	$\Delta G^{o}(kJ)$	ΔH^{o} (kJ)		ANSWERS
- 16.4	- 41		<u>b</u>	
- 9.8	+ 2O		<u>c</u>	
- 14.8	+ 20		<u>d</u>	
- 24.6	- 41		<u>a</u>	
	- 9.8 - 14.8	$ \begin{array}{ccc} & \Delta G^{o} \text{ (kJ)} \\ -16.4 & -41 \\ -9.8 & +20 \\ -14.8 & +20 \end{array} $		$ \frac{\Delta G^{o} (kJ)}{-16.4} \frac{\Delta H^{o} (kJ)}{-41} \frac{b}{c} $ $ -9.8 + 2O \frac{c}{d} $ $ -14.8 + 20 \frac{d}{d} $

GIVEN THE FOLLOWING PISTON FOR USE IN QUESTIONS 14 and 15.

$$P_{\rm ex} = 0.86 \text{ atm}$$

14) A 1.25 L sample of a gas is heated and expands against a constant pressure of 0.86 atm to a final volume of 3.75 L. Calculate the work done by this gas during the expansion in joules. THIS IS QUESTION 54 FROM YOUR TEXTBOOK.

(10 pts)

$$W = -P_{ex}\Delta V = -(0.86)(3.75 - 1.25)(101.3)$$
$$W = -217.8 \text{ J}$$

ANSWER IS:

15) The above piston contains 0.50 mol of an inert gas at an initial temperature of 300 K. An adiabatic expansion now occurs with the volume changing from 1.25 L to 3.75 L at a constant external pressure of 0.86 atm.

Calculate the final temperature, T_f (in Kelvin), in the piston at the end of this expansion. Given: $C_{v,m} = 12.47 \frac{J}{\text{deg:mol}}$. (15 pts)

$$\Delta E = nC_{v,m}\Delta T = W$$
 $\therefore \Delta T = \frac{W}{nC_{v,m}} = \frac{-217.8}{(0.5)(12.47)} = -34.9^{\circ}(=-35^{\circ})$
 $\therefore T_f = 265 \text{ K}$

ANSWER IS: 265 K

16) 5O.O g of ice at O°C are mixed with 4O.O g of liquid (water) at O°C and an unknown mass of liquid (water) at 75°C. At equilibrium the final temperature of the entire system is 1O°C. Calculate the starting mass of liquid at 75°C. (20 pts) SHOW WORK

GIVEN: specific heat of liquid = $4.18 \text{ J/g} \cdot \text{deg}$; heat of fusion = 333 J/g.

a) 15.0 g b) 75.1 g c) 25.5 g d) 50.1 g e) 30.2 g
$$q_1 \qquad q_2$$

$$H_2O_{(S)} \longrightarrow H_2O_{(\ell)} \longrightarrow H_2O_{(\ell)}$$
 50g, 0°C 50g, 10°C
$$q_3 \qquad q_4$$

$$H_2O_{(\ell)} \longrightarrow H_2O_{(\ell)} \longrightarrow H_2O_{(\ell)}$$
 40g, 0°C 40g, 10°C
$$m, 75^{\circ}C \qquad m, 10^{\circ}C$$

$$q_1 + q_2 + q_3 + q_4 = O$$

(5O)(333) + (5O)(4.18)(1O) + (4O)(4.18)(1O) + (m)(4.18)(-65) = O
 $m = 75.1 \text{ g}$

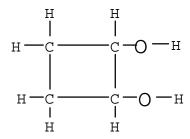
ANSWER IS: b

17) BOND ENTHALPIES (kJ/mole)

Using the above table of bond enthalpies, calculate the heat of reaction, ΔH_{rxn} , for the gaseous reaction, (20 pts) SHOW WORK

$$H_2O_2$$
 + C_4H_6 \longrightarrow $C_4H_6(OH)_2$
2-butyne cyclobutadiol

where C₄H₆ is CH₃CCCH₃ (one triple bond) and cyclobutadiol (all single bonds) is,



HINT: FIRST WRITE THE LEWIS STRUCTURE FOR EACH MOLECULE.

ANSWER IS: -431 kJ

18) Use the following data,

1.
$$\operatorname{Fe_2O_{3(S)}} + 3 \operatorname{CO_{(g)}} \longrightarrow 2 \operatorname{Fe_{(S)}} + 3 \operatorname{CO_{2(g)}}$$
 $-3 \operatorname{O.O}$

2.
$$3 \operatorname{Fe_2O_{3(S)}} + \operatorname{CO_{(g)}} \longrightarrow 2 \operatorname{Fe_3O_{4(S)}} + \operatorname{CO_{2(g)}}$$
 -57.0

3.
$$\operatorname{Fe_3O_{4(S)}} + \operatorname{CO}_{(g)} \longrightarrow \operatorname{3FeO}_{(S)} + \operatorname{CO}_{2(g)} + \operatorname{42.0}$$

to determine the heat of reaction, $\Delta H^o_{\ rxn}$, for the reduction of ferrous oxide by carbon monoxide (20 pts) SHOW WORK according to;

$$FeO_{(S)} + CO_{(g)} \longrightarrow Fe_{(S)} + CO_{2(g)}$$

f)
$$+19.5 \text{ kJ}$$
 g) $+3.0 \text{ k}$

$$\begin{array}{lll} (\frac{1}{3})(-3) & \operatorname{FeO}_{(S)} + \frac{1}{3} \operatorname{CO}_{2(g)} \longrightarrow & \frac{1}{3} \operatorname{Fe_3O_{4(S)}} + \frac{1}{3} \operatorname{CO}_{(g)} & (\frac{1}{3})(-42.0) \\ (\frac{1}{2})(1) & \frac{1}{2} \operatorname{Fe_2O_{3(S)}} + \frac{3}{2} \operatorname{CO}_{(g)} \longrightarrow & \operatorname{Fe}_{(S)} + \frac{3}{2} \operatorname{CO}_{2(g)} & (\frac{1}{2})(-30.0) \\ (\frac{1}{6})(-2) & \frac{1}{3} \operatorname{Fe_3O_{4(S)}} + \frac{1}{6} \operatorname{CO}_{2(g)} \longrightarrow & \frac{1}{2} \operatorname{Fe_2O_{3(S)}} + \frac{1}{6} \operatorname{CO}_{(g)} & (\frac{1}{6})(+57.0) \end{array}$$

$$FeO_{(S)} + CO_{(g)} \longrightarrow Fe_{(S)} + CO_{2(g)}$$
 $\Delta H^{o}_{rxn} = -19.5 \text{ kJ}$

ANSWER IS: e