Exam 4 - F22 - McCord - ch301 version: 488

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1 1 H 1.008	2											13	14	15	16	17	18 2 He 4.003
3 Li 6.941	4 Be <sub>9.012</sub>											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne <sub>20.18</sub>
11 Na 22.99	12 Mg <sub>24.31</sub>	3	4	5	6	7	8	9	10	11	12	13 Al <sub>26.98</sub>	14 Si <sub>28.09</sub>	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 <b>K</b> 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni <sub>58.69</sub>	29 Cu 63.55	30 Zn 65.38	31 Ga <sub>69.72</sub>	32 Ge <sub>72.64</sub>	33 As <sub>74.92</sub>	34 Se <sub>78.96</sub>	35 Br <sub>79.90</sub>	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 <b>Mo</b> 95.94	43 Tc	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 <b>Ag</b>	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53     126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 <b>Hf</b> 178.49	73 Ta 180.95	74 W 183.84	75 <b>Re</b> 186.21	76 Os 190.23	77  r   192.22	78 Pt 195.08	79 <b>Au</b> 196.97	80 Hg <sub>200.59</sub>	81 TI 204.38	82 Pb <sub>207.20</sub>	83 Bi <sub>208.98</sub>	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 <b>Ac</b> (227)	104 <b>Rf</b> (267)	105 Db (268)	106 Sg (269)	107 Bh (270)	108 Hs (270)	109 Mt (278)	110 Ds (281)	111 Rg (282)	112 Cn (285)	113 Nh (286)	114 FI (289)	115 Mc (290)	116 Lv (293)	117 Ts (294)	118 Og (294)

<sup>58</sup> Ce	59 <b>P</b> r	60 Nd	61 Pm	62 Sm	63 Eu	<sup>64</sup> Gd	65 Th	66 Dy	67 <b>H</b> O	68 Er	69 Tm	<sup>70</sup> Yb	71   1   1
	' '		1 111				וו	, ,	110	L-1			Lu
140.12	140.91	144.24	(145)	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.04	231.04	238.03	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(266)

# Thermodynamic Data at $25^{\circ}C$

$\Delta H_{ m f}^{ m o}$ k $ m J/mol$	$S^{\circ}$ J/mol K
-286	70
-242	189
-103	296
-134	202
-393.5	214
-75	186
-104	270
-555	_
	-286 -242 -103 -134 -393.5 -75 -104

# Multiple Bond Energies (kJ/mol)

C=C 614	C=N 615	C=O799
$C \equiv C 839$	C=S 577	$C \equiv O 1072$
N=N 418	O = O495	$N\equiv N 941$

## Single Bond Energies

	Η	$\mathbf{C}$	N	Ο	Cl	
Η	432					
$\mathbf{C}$	413	347				
Ν	391	305	160			
Ο	467	358	201	146		
$\operatorname{Cl}$	427	339	200	203	239	
		11	1	1	т /	1)

# (all values are kJ/mol)

constants and more
$R=0.08206~\mathrm{L~atm/mol~K}$
$R=8.314~\mathrm{J/mol~K}$
$N_{\rm A} = 6.022 \times 10^{23} \ / {\rm mol}$
$k=1.38\times 10^{-23}\;\mathrm{J\cdot s}$
$1~\mathrm{cal} = 4.184~\mathrm{J}$
$1 \text{ m}^3 = 1000 \text{ L}$
$1~\mathrm{L}\text{-}\mathrm{atm} = 101.325~\mathrm{J}$
1  lb = 453.6  g
$1~\mathrm{atm} = 101325~\mathrm{Pa}$

1 atm = 760 Torr

## water data

 $C_{\rm s,ice} = 2.09 \text{ J/g }^{\circ}\text{C}$ 

 $C_{\rm s,water} = 4.184 \text{ J/g} \, ^{\circ}\text{C}$  $C_{\rm s,steam} = 2.03 \text{ J/g} \, ^{\circ}\text{C}$  $\rho_{\rm water} = 1.00~{\rm g/mL}$  $\rho_{\rm ice} = 0.9167~{\rm g/mL}$  $\rho_{\rm seawater} = 1.024~{\rm g/mL}$  $\Delta H_{\rm fus} = 334~{\rm J/g}$  $\Delta H_{\rm vap} = 2260~{\rm J/g}$  $K_{\rm w} = 1.0 \times 10^{-14}$ 

## metal heat capacities

$C_{\rm s,Fe} = 0.449 \text{ J/g } ^{\circ}\text{C}$
$C_{\rm s,Cu} = 0.385 \text{ J/g} ^{\circ}\text{C}$
$C_{\mathrm{s,Pb}} = 0.129 \mathrm{\ J/g\ ^{\circ}C}$
$C_{\rm s,Al} = 0.897 \text{ J/g }^{\circ}\text{C}$

This exam should have exactly 25 questions. Each question is equally weighted at 4 points each. You will enter your answer choices on the virtual bubblehseet after you have finished. Your score is based on what you submit on the virtual bubblesheet and not what is circled on the exam.

- 1. Which of the following choices is the correct thermodynamic assessment of "the universe"?
- •a. it is an isolated system
  - b. it is an open system
  - c. it is a closed system

**Explanation:** The universe keeps all energy and matter contained. And, it never losses any energy or matter. This is the definition of an isolated system.

- 2. (Part 1 of 2) You are camping and heat a 2.234 kg iron pan from 25 °C up to 200 °C over your campfire. What is the value of  $\Delta H$  for this process?
- a. -176 kJ
- b. +0.176 kJ
- c. +50 kJ
- •d. +176 kJ
  - e. -0.176 kJ
  - f. -50 kJ

**Explanation:**  $C_s$  for iron is 0.449 J/g °C.

 $\Delta H = 2234(0.449)(175) = 176 \text{ kJ}$ 

- 3. (Part 2 of 2) Referring to the previous question, what is the value of  $\Delta S$  for the process described?
- a. -664 J/K
- b. -463 J/K
- c. -2310 J/K
- d. +664 J/K
- ●e. +463 J/K
  - f. +2310 J/K

**Explanation:**  $C_s$  for iron is 0.449 J/g K (or equivalently, 0.449 J/g °C. Remember that a Kelvin is the same size a Celcius degreee, just the reference point is different.)

$$\Delta S = 2234(0.449) \ln(\frac{473}{298}) = +463 \text{ J/K}$$

- **4.** For a certain reaction,  $\Delta H = -2400 \text{ kJ/mol}$  and  $\Delta S = -8 \text{ kJ/mol·K}$ . At what temperature does the reaction switch from being spontaneous to nonspontaneous?
- a.400 K
- b. -400 K
- c. 300 °C
- •d. 300 K
- e. 40 K
- f. 3.3 mK
- g. -300 K
- h. 400 °C
- i. 30 K

**Explanation:** The temperature at which a process switches from spontaneous from non-spontaneous is known as its equilibrium temperature. Using  $\Delta G = \Delta H - T\Delta S$ , equilibrium occurs when  $\Delta G = 0$ . Rearranging the equation and plugging in values to solve for T, we find that  $T = \Delta H/\Delta S$  and thus  $T = (-2400 \text{ kJ/mol})/(-8 \text{ kJ/mol} \cdot \text{K}) = 300 \text{K}$ .

- 5. The enthalpy of vaporization of Al(s) at its normal boiling point is  $307.6~\mathrm{kJ/mol}$ . Given that the normal boiling point of Al(s) is  $2470^{\circ}\mathrm{C}$ , calculate the entropy for this process.
- a. -112.1J/mol·K
- b.  $-54.3 \text{J/mol} \cdot \text{K}$
- c. -124.5 J/mol·K
- $d. +124.5 J/mol \cdot K$
- e. +52.7J/mol·K
- •f. +112.1J/mol ⋅ K

**Explanation:** We know that vaporization is an equilibrium process. Using  $\Delta G = \Delta H - T\Delta S$  and letting  $\Delta G = 0$ , we can solve for  $\Delta S$ . This yields  $\Delta S = \Delta H/T = (307.6 \text{ kJ/mol})/(2470+273 \text{ K}) = +112.1 \text{J/mol} \cdot \text{K}$ 

- 6. The main driving force for heat flow between two objects is a/an \_\_\_\_\_ difference.
- •a. temperature
  - b. enthalpy
  - c. entropy
  - d. work
  - e. internal energy

**Explanation:** Using the microscopic view of thermal motion, heat transfer can be understood in terms of molecular collisions. At higher temperatures molecules have increased molecular motion relative to cold moleculues. Thus, heat transfer occurs when higher energy (hot) molecules collied with lower energy (cold) molecules. Therefore, the driving force for heat transfer is a temperature difference.

7. The following reaction is the oxidation from methanol to formaldehyde. Using bond energies, calculate the approximate  $\Delta H$  for one mole of this reaction.

 $CH_3OH \rightarrow CH_2O + H_2$ 

- a. -7 kJ
- b. -90 kJ
- c. -448 kJ
- d. +448 kJ
- ●e. +7 kJ
  - f. +90 kJ

**Explanation:** You BREAK 3 bonds: C-H (413), C-O (358), and O-H (467) for a total of 1238. You MAKE 2 bonds: C=O (799) and H-H (432) for a total of 1231. BREAK - MAKE = 1238 - 1231 = +7 kJ.

8. Consider the following heat capacities (all in J/g °C) for various substances:

$$C_{\text{s,chromium}} = 0.449$$

$$C_{\rm s,titanium} = 0.523$$

$$C_{\rm s, water} = 4.184$$

$$C_{\rm s,air} = 1.012$$

Which substance will have the greatest increase in temperature upon the addition of 275 joules of heat to the same mass of each substance?

- •a. chromium
  - b. titanium
  - c. air
  - d. water

**Explanation:** The greatest temperature change will be observed in the substance with the lowest specific heat capacity. This is chromium.

- 9. An increase in the number of microstates leads to...
- a. a more ordered universe
- b. decreased enthalpy
- •c. increased entropy
  - d. increased free energy
- e. increased enthalpy
- f. decreased entropy

**Explanation:** Increased number of microstates leads to increased entropy.

10. The consider the formation reaction of nitric oxide. The heat of formation  $(\Delta H_{\rm f}^{\circ})$  for nitric oxide is 90.0 kJ/mol and the entropy of formation  $(\Delta S_{\rm f}^{\circ})$  is 12.5 J/mol·K. What is the standard free energy of formation  $(\Delta G_{\rm f}^{\circ})$  for nitric oxide?

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \to NO(g)$$

- a. 145 kJ/mol
- b. 86.3 kJ/mol
- c. -145 kJ/mol
- d. 3640 kJ/mol
- e. -86.3 kJ/mol
- f. -3640 kJ/mol

**Explanation:** We know that  $\Delta G_{\rm f}^{\circ} = \Delta H_{\rm f}^{\circ}$  -  $\mathrm{T}\Delta S_{\rm f}^{\circ}$ . Thus,  $\Delta G_{\rm f}^{\circ} = 90.0~\mathrm{kJ/mol}$  -  $(298~\mathrm{K})(0.0125~\mathrm{kJ/mol\cdot K})$  =  $86.3~\mathrm{kJ/mol}$ 

- 11. When  $\Delta G = 0$ , which of the following are true?
- a.  $\Delta H = \Delta S$
- b.  $\Delta H = 0$
- c. The reaction is non-spontaneous
- •d. The reaction is at equilibrium
- e. Nothing is reacting
- f.  $\Delta S = 0$

**Explanation:** At equilibrium the system has equal forward and reverse rates and the reactants and products have equal free energies. The reaction is neither spontaneous nor non-spontaneous... is is at equilibrium and  $\Delta G=0$ .

12. Which of the following is true for the given reaction?

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$$

- a. The sign of  $\Delta G$  is temperature dependent,  $\Delta S < 0, \Delta H > 0$
- b.  $\Delta G < 0$ ,  $\Delta S < 0$ ,  $\Delta H < 0$
- c. The sign of  $\Delta G$  is temperature dependent,  $\Delta S > 0, \Delta H < 0$
- d.  $\Delta G > 0$ ,  $\Delta S < 0$ ,  $\Delta H > 0$
- e.  $\Delta G > 0$ ,  $\Delta S > 0$ ,  $\Delta H < 0$
- •f.  $\Delta G < 0$ ,  $\Delta S > 0$ ,  $\Delta H < 0$

**Explanation:**  $\Delta S > 0$  because the reaction generates 3 additional mols of gas.  $\Delta H < 0$  because this reaction is exothermic (combustion). Thus, overall  $\Delta G < 0$ .

- 13. When 0.262 g of a hydrocarbon fuel are combusted in a bomb calorimeter filled with 875 mL water, a temperature increase of 2.02 °C is measured. What is the  $\Delta U$  of the fuel in kJ/g? The heat capacity of the calorimeter hardware is equal to 1460 J/°C.
- •a. -39.5 kJ/g
  - b. -59.3 kJ/g
- c. -25.7 kJ/g
- d. +48.4 kJ/g
- e. +28.1 kJ/g
- f. +42.9 kJ/g

**Explanation:** bomb calorimetry:  $\Delta U = -q_{\rm cal}$ 

$$q_{\rm cal} = mC\Delta T + C\Delta T$$

11653 = (875)(4.184)(2.02) + (1460)(2.02)

Flip the sign to get into the system: -10344 J

Convert to kJ and divide by mass:

- -10.344 kJ/0.262 g = -39.5 kJ/g
- 14. A reaction performed in a coffee cup calorimeter makes the temperature of the water increase. Which of the following is/are true regarding this process?
- I. the reaction is exothermic
- II. the reaction is endothermic
- III. the reaction absorbs heat
- IV. the value of  $q_{\rm cal}$  is positive
- a. I, III, and IV
- b. II, III, and IV
- c. II and IV
- d. I, II, III, and IV
- •e. I and IV

**Explanation:** For this process, the  $q_{\rm cal}$  is positive (it absorbed heat which is why the temperature increased. Flip the sign to get into the perspective of the reaction system. That means that the reaction is exothermic and releases heat. Only I and IV are correct.

- 15. A neutralization reaction is performed in a coffee cup calorimeter. When 40 mL of a 0.25 M aqueous solution of HCl is added to 40 mL of a 0.25 M aqueous solution of NaOH, the temperature increases by 1.61 °C. What is the value of  $\Delta H$  for this neutralization process?
- a. +539 kJ
- b. +1.11 kJ
- •c. −539 J
  - d. -269 J
  - e. -711 J
  - f. -392 J

**Explanation:** Solve for  $q_{\rm cal}$  and then flip the sign for  $q_{\rm sys}$ .

- $q = (80 \,\mathrm{g})(4.184 \,\mathrm{J/g}\,^{\circ}\mathrm{C})(1.61\,^{\circ}\mathrm{C})$
- q = 539 J

Flip the sign to get back to the system to get -539 J.

Also note: the concentrations of 0.25 M do not matter at all from the context of this question. The value of  $\Delta H$  is what it is based on the heating of the water (80 g). The concentration terms would be important IF the answer was supposed to be in J/mol.

- 16. I want my room temperature cup of cocoa to be hot, so I put it in the microwave for a couple minutes. Then pull it out and drink it yes, it is much warmer now. I, being a smart chemistry gal, know that if the beverage is the system and it "got hot" in the microwave, then the process must be exothermic.
- •a. false
  - b. true

**Explanation:** False because heat was absorbed by the beverage which means the process is endothermic.

- 17. Which of the following processes has a positive  $\Delta H$  value?
- a. condensation
- b. sublimation
- c. freezing
- d. deposition

**Explanation:** Sublimation is an endothermic process, converting a solid directly to a gas. Such a process requires heat input which means a positive q and  $\Delta H$  for the process. The other three are all exothermic.

- 18. Which of the following is a correct standard enthalpy of formation reaction that will match up correctly with table values of  $\Delta H_{\rm f}^{\circ}$  in kJ/mol?
- a.  $2C(s) + O_2(g) \rightarrow 2CO(g)$
- b.  $H_2(g) + O_2(g) \to H_2O(\ell)$
- •c.  $1/2H_2(g) + 1/2F_2(g) \rightarrow HF(g)$ 
  - d.  $C(s) + 4H(g) \rightarrow CH_4(g)$
  - e.  $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

**Explanation:** Formation reactions involve having the elements in their standard states combine to form 1 mole of product. The only one that does this is  $1/2H_2(g) + 1/2F_2(g) \rightarrow HF(g)$ 

19. The balanced chemical equation for the fluorination of benzene is given below. Given the formation reactions, what is the  $\Delta H_{\rm rxn}^{\circ}$  for the fluorination of benzene?

$$C_6H_6(\ell) + 6F_2(g) \rightarrow C_6F_6(\ell) + 6HF(g)$$
 (overall)

$$\frac{1}{2}$$
H<sub>2</sub>(g) +  $\frac{1}{2}$ F<sub>2</sub>(g)  $\rightarrow$  HF(g)  $\Delta H_f^{\circ} = x$ 

$$6C(s) + 3H_2(g) \rightarrow C_6H_6(\ell)$$
  $\Delta H_f^{\circ} = y$ 

$$6C(s) + 3F_2(g) \rightarrow C_6F_6(\ell)$$
  $\Delta H_f^{\circ} = z$ 

- a. 6x + y + z
- •b. 6x y + z
  - c. -6x + y z
  - d. 3x y + z
  - e. 6xz/y
  - f. x + 6y z

**Explanation:** We are given the balanced formation reactions and the enthalpy of formation is assigned a variable. We see that if we start with 6x, this balances the HF for the reaction. Adding reaction z to 6x gives us the fluorobenzene, but we need to cancel out the carbon and hydrogen. This can be done by subtracting equation y, giving us 6x-y+z overall.

- 20. Calculate the amount of heat required to completely convert 350 g chloroform liquid at 23 °C to chloroform gas at its boiling point of 78 °C. The specific heat of chloroform is 0.957 J/g °C and its heat of vaporization is 263 J/g.
- a. 920 kJ
- •b. 110 kJ
- c. 222 kJ
- d. 184 kJ
- e. 95.6 kJ

**Explanation:** heat from 23 to 78, then vaporize (2 equations)

$$q1 = mC\Delta T = 350(0.957)(55) = 18422 \text{ J}$$

$$q2 = m\Delta H = 350(263) = 92050 \text{ J}$$

total = 110472 J = 110 kJ

- 21. Consider the evaporation of ethanol at room temperature. Which of the following statements are true?
- I.  $\Delta S_{\rm univ} < 0$
- II.  $\Delta S_{\rm sys} < 0$
- III.  $|\Delta S_{\rm sys}| > |\Delta S_{\rm surr}|$
- IV.  $\Delta H_{\rm vap} > 0$
- a. all of the above
- •b. III & IV only
  - c. II, III, & IV only
  - d. IV only
  - e. I only
- f. I & II only
- g. none of the above
- h. III only

Explanation: I.  $\Delta S_{\rm univ} < 0$  can never occur, the entropy of the universe must always increase for any process. II.  $\Delta S_{\rm sys} < 0$  can sometimes be true, but in this case we are taking liquid ethanol and converting it into ethanol vapor. Ethanol vapor has more entropy than liquid ethanol, thus  $\Delta S_{\rm sys} > 0$ . III. We are adding heat to the system from the surroundings, thus the surroundings ends up with fewer microstates and  $\Delta S_{\rm surr} < 0$ . In order for the overall entropy of the universe to increase,  $|\Delta S_{\rm sys}| > |\Delta S_{\rm surr}|$ . IV. Evaporation is always an endothermic process, thus  $\Delta H_{\rm vap} > 0$ .

- 22. Which of the following choices is composed only of state functions?
- a. enthalpy, heat, entropy, temperature
- b. internal energy, heat, work
- c. free energy, enthalpy, entropy, work
- d. heat, work
- •e. internal energy, enthalpy, entropy, free energy

**Explanation:** Heat and work are not state functions, they are path dependent.

- **23.** For which reactions will  $\Delta S > 0$  as the process proceeds from left to right?
- I.  $CO_2(s) \to CO_2(g)$
- II.  $Li^+(aq) + Cl^-(aq) \rightarrow LiCl(s)$
- III.  $2H_2O(g) \to O_2(g) + 2H_2(g)$
- •a. I, III
- b. I, II, III
- c. III
- d. I
- e. II, III
- f. II
- g. I, II

**Explanation:** Rxn 1 products have more entropy than the reactants because gasses have more entropy than solids therefore entropy will increase. Rxn 3 products have more entropy than the reactants because there are more mols of gas formed in the products. Rxn 2 is instead of dissolving the ions in water, reforming the crystallin LiCl salt which has less entropy than the reactants, therefore rxn 3 is the only rxn that decreases entropy from right to left.

24. The unbalanced reaction for the formation of phosphine from the elements is given below.

$$P(s) + H_2(g) \rightarrow PH_3(g)$$

The absolute entropies of P(s),  $H_2(g)$ , and  $PH_3(g)$  are 41.0, 131, and 210 J/mol·K, respectively. Calculate the standard entropy of formation for phosphine (hint: that is per mole of phosphine to be perfectly clear on this, and be sure and balance the reaction first).

- •a. -27.5 J/mol⋅K
  - b. 38.0 J/mol·K
- c. 11.8 J/mol·K
- d. -11.8 J/mol·K
- e.  $-38.0 \text{ J/mol} \cdot \text{K}$
- f. 27.5 J/mol·K

**Explanation:** We first balance the equation:  $P(s) + 3/2H_2(g) \rightarrow PH_3(g)$ . We can find the entropy change for the formation reaction by summing up the entropies of reactants and subtracting this from the entropies of the products. This gives:  $210 - (3/2(131) + 41.0) = -27.5J/mol \cdot K$ 

- 25. Dr. McCord has designed an internal combustion engine that is 100% efficient. Assuming that the change in internal energy for Dr. McCord's engine is zero, calculate the change in volume if 1074 J of heat are added as the system expands against an external pressure of 1 atmosphere.
- a. 0.0044 L
- b. 4.4 L
- c. 0.0152 L
- d. 0.0106 L
- e. infinite volume
- •f. 10.6 L
  - g. 15.2 L

**Explanation:**  $\Delta U = q + w$ . We are told that  $\Delta U = 0$ , Thus, q = -w. For an piston expanding against an external pressure, we know that  $w = -P_{\rm ext}\Delta V$ . Putting all of this together while keeping our signs straight, we find that  $q = P_{\rm ext}\Delta V$ . Rearranging, pluging in numbers, and doing the proper unit conversions we find  $\Delta V = q/P_{\rm ext} = (1074 \text{ J} / 101325 \text{ Pa})*(1000 \text{ L/m}^3) = 10.6 \text{ L}$ .

After you are finished and have all your answers circled, go to the front of the room and then use the QR code there to pull up the virtual answer page. Enter the appropriate info plus all your answers - click the SUBMIT button. Make sure you get the confirmation screen and show it to the TA or proctor. After that, turn in your exam and scratch paper. You're free to leave after that.



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