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Exam 4 - F22 - McCord - ch301

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232.04	231.04	238.03	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(266)

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

	$\Delta H_{\rm f}^{\circ}$	S°
Substance	kJ/mol	J/mol K
$H_2O(\ell)$	-286	70
$H_2O(g)$	-242	189
$CHCl_3$ (g)	-103	296
$CHCl_3(l)$	-134	202
CO_2 (g)	-393.5	214
CH_4 (g)	-75	186
C_3H_8 (g)	-104	270
$C_6H_{12}O_2~(\ell)$	-555	

Multiple Bond Energies (kJ/mol)					
C=C 614	C=N 615	C=O 799			
$C\equiv C 839$	C=S 577	$C\equiv O 1072$			
N=N 418	O=O 495	N \equiv N 941			

Single Bond Energies

SII	igic .	DOIR	I L/II	ergie	6		
	Η	С	Ν	0	Cl		
Η	432						
С	413	347					
	391						
	467						
Cl	427	339	200	203	239		
	(all values are kJ/mol)						
co	nstar	nts a	nd n	ore.	••		
<i>R</i> =	= 0.03	8206	L atı	n/mo	ol K		
<i>R</i> =	$R=8.314~{\rm J/mol~K}$						
$N_{\rm A}=6.022\times 10^{23}~/{\rm mol}$							
$k=1.38\times 10^{-23}~{\rm J\cdot s}$							
1 cal = 4.184 J							
$1 \text{ m}^3 = 1000 \text{ L}$							
1 L·atm = 101.325 J							
1 lb = 453.6 g							
$1 \ \mathrm{atm} = 101325 \ \mathrm{Pa}$							
1 atm = 760 Torr							

water data

 $C_{\rm s,ice} = 2.09 \ {\rm J/g} \ ^{\circ}{\rm C}$ $C_{\rm s,water} = 4.184 \text{ J/g} \circ \text{C}$ $C_{\rm s,steam} = 2.03~\rm J/g~^\circ C$ $\rho_{\rm water} = 1.00~{\rm g/mL}$ $\rho_{\rm ice} = 0.9167~{\rm g/mL}$ $\rho_{\rm seawater} = 1.024~{\rm g/mL}$ $\Delta H_{\rm fus} = 334~{\rm J/g}$ $\Delta H_{\rm vap} = 2260~{\rm J/g}$ $K_{\rm w} = 1.0 \times 10^{-14}$

metal heat capacities

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

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. 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. 10.6 L

- b. $4.4~\mathrm{L}$
- c. 15.2 L $\,$
- d. $0.0106 \ {\rm L}$
- e. 0.0044 L
- f. 0.0152 L
- g. infinite volume

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 $w = -P_{\text{ext}}\Delta V$. Putting all of this together while keeping our signs straight, we find that $q = P_{\text{ext}}\Delta V$. Rearranging, pluging in numbers, and doing the proper unit conversions we find $\Delta V = q/P_{\text{ext}} = (1074 \text{ J} / 101325 \text{ Pa})^*(1000 \text{ L/m}^3) = 10.6 \text{ L}.$

2. 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. -38.0 J/mol·K
- b. 11.8 J/mol·K
- c. -11.8 J/mol·K
- d. 38.0 J/mol·K
- e. 27.5 $J/mol \cdot K$
- •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 - $(3/2(131) + 41.0) = -27.5J/mol \cdot K$ 3. 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 ΔU 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. +42.9 kJ/g
- c. -59.3 kJ/g
- d. +48.4 kJ/g
- e. $-25.7~\mathrm{kJ/g}$
- f. +28.1 kJ/g

Explanation: bomb calorimetry: $\Delta U = -q_{cal}$ $q_{cal} = mC\Delta T + C\Delta T$

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

4. Which of the following processes has a positive ΔH value?

- •a. sublimation
 - b. freezing
 - c. deposition
 - d. condensation

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 ΔH for the process. The other three are all exothermic.

5. The balanced chemical equation for the fluorination of benzene is given below. Given the formation reactions, what is the ΔH°_{rxn} for the fluorination of benzene?

$C_6H_6(\ell) + 6F_2(g) \rightarrow C_6F_6(\ell)$	$+ 6 \mathrm{HF}(\mathrm{g})$	(overall)
$\overline{\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \rightarrow HF(g)}$	$\Delta H_{\rm f}^{\rm o} = x$	
$6C(s)+3H_2(g)\to C_6H_6(\ell)$	$\Delta H_{\rm f}^{\rm o} = y$	
$6C(s)+3F_2(g)\to C_6F_6(\ell)$	$\Delta H_{\rm f}^{\rm o} = z$	
a. $-6x + y - z$		
b. $6x + y + z$		
c. $6xz/y$		
d. $3x - y + z$		
e. $x + 6y - z$		

• f. 6x - y + 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.

6. 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. $C(s) + 4H(g) \rightarrow CH_4(g)$
- •c. $1/2H_2(g) + 1/2F_2(g) \to HF(g)$
- d. $H_2(g) + O_2(g) \rightarrow H_2O(\ell)$
- 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 $1/2H_2(g) + 1/2F_2(g) \rightarrow HF(g)$

7. 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. $\Delta G>0,~\Delta S>0,~\Delta H<0$
- b. The sign of ΔG is temperature dependent, $\Delta S < 0, \Delta H > 0$
- c. The sign of ΔG 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 moles of gas. $\Delta H < 0$ because this reaction is exothermic (combustion). Thus, overall $\Delta G < 0$.

8. For a certain reaction, $\Delta H = -2400 \text{ kJ/mol}$ and $\Delta S = -8 \text{ kJ/mol}\cdot\text{K}$. At what temperature does the reaction switch from being spontaneous to nonspontaneous?

•a. 300 K

- b. 400 $^{\circ}\mathrm{C}$
- c. $-300~{\rm K}$
- d. -400 K
- e. $40~{\rm K}$
- f. 400 K
- g. 300 °C
- h. 3.3 mK
- 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 = $(-2400 \text{ kJ/mol})/(-8 \text{ kJ/mol}\cdot\text{K}) = 300\text{K}.$ **9.** 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. 184 kJ
- b. 95.6 kJ
- ●c. 110 kJ
- d. 222 kJ
- e. 920 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

10. Consider the evaporation of ethanol at room temperature. Which of the following statements are true?

- $$\begin{split} & \text{I. } \Delta S_{\text{univ}} < 0 \\ & \text{II. } \Delta S_{\text{sys}} < 0 \\ & \text{III. } |\Delta S_{\text{sys}}| > |\Delta S_{\text{surr}}| \\ & \text{IV. } \Delta H_{\text{vap}} > 0 \end{split}$$
- a. I only
- b. none of the above
- c. all of the above
- d. I & II only
- e. II, III, & IV only
- f. IV only
- g. III only
- •h. III & IV only

Explanation: I. $\Delta S_{\text{univ}} < 0$ can never occur, the entropy of the universe must always increase for any process. II. $\Delta S_{\text{sys}} < 0$ 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 $\Delta S_{\text{sys}} > 0$. III. We are adding heat to the system from the surroundings, thus the surroundings ends up with fewer microstates and $\Delta S_{\text{surr}} < 0$. In order for the overall entropy of the universe to increase, $|\Delta S_{\text{sys}}| > |\Delta S_{\text{surr}}|$. IV. Evaporation is always an endothermic process, thus $\Delta H_{\text{vap}} > 0$.

11. The following reaction is the oxidation from methanol to formaldehyde. Using bond energies, calculate the approximate ΔH for one mole of this reaction.

$$CH_3OH \rightarrow CH_2O + H_2$$

a. $+448~\mathrm{kJ}$

b. $-448~\mathrm{kJ}$

c. $-7~\mathrm{kJ}$

•d. +7 kJ

e. $+90~\mathrm{kJ}$

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.

12.	Consider	the following	heat	capacities	(all in J/g
$^{\circ}C)$:	for various	s substances:			

$C_{\rm s,chromium} = 0.449$	$C_{\rm s,titanium} = 0.523$
$C_{\rm s,water} = 4.184$	$C_{\rm s,air} = 1.012$

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. air

b. titanium

c. water

•d. chromium

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

13. (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 ΔH for this process?

a. +50 kJ
b. −176 kJ
c. −50 kJ
d. +0.176 kJ
e. +176 kJ
f. −0.176 kJ

Explanation: $C_{\rm s}$ for iron is 0.449 J/g °C. $\Delta H = 2234(0.449)(175) = 176$ kJ

14. (Part 2 of 2) Referring to the previous question, what is the value of ΔS for the process described?

- a. +2310 J/K
 b. -664 J/K
- c. +664 J/K
- •d. +463 J/K
- e. -2310 J/K
- f. -463 J/K

Explanation: $C_{\rm s}$ 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.)

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

15. 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_{cal} is positive
- •a. I and IV
 - b. I, II, III, and IV
 - c. II, III, and IV
 - d. I, III, and IV
- e. II and IV

Explanation: For this process, the q_{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.

16. For which reactions will $\Delta S > 0$ as the process proceeds from left to right?

I. $CO_2(s) \rightarrow CO_2(g)$ II. $Li^+(aq) + Cl^-(aq) \rightarrow LiCl(s)$ III. $2H_2O(g) \rightarrow O_2(g) + 2H_2(g)$ a. I, II b. II, III c. II

- d. I
- ●e. I, III
- f. III
- g. I, II, III

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.

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

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 $\Delta G = 0$.

18. 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 ΔH for this neutralization process?

- a. +539 kJ
- b. $-269\ {\rm J}$
- c. -392 J
- ●d. -539 J
- e. $-711~{\rm J}$
- f. +1.11 kJ

Explanation: Solve for q_{cal} and then flip the sign for q_{sys} .

 $q = (80 \text{ g})(4.184 \text{ J/g}^{\circ}\text{C})(1.61 ^{\circ}\text{C})$

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 ΔH 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. 19. 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?

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

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

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

20. The enthalpy of vaporization of Al(s) at its normal boiling point is 307.6 kJ/mol. Given that the normal boiling point of Al(s) is 2470°C, calculate the entropy for this process.

- a. $+124.5 \text{J/mol} \cdot \text{K}$
- b. $-112.1 \text{J/mol} \cdot \text{K}$
- c. $-124.5 \text{J/mol} \cdot \text{K}$
- •d. $+112.1 \text{J/mol} \cdot \text{K}$
- e. $-54.3 \text{J/mol} \cdot \text{K}$
- f. $+52.7 \text{J/mol} \cdot \text{K}$

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 ΔS . This yields $\Delta S = \Delta H/T = (307.6 \text{ kJ/mol})/(2470+273 \text{ K}) = +112.1 \text{J/mol} \cdot \text{K}$

21. An increase in the number of microstates leads to...

- a. increased enthalpy
- b. decreased enthalpy
- •c. increased entropy
 - d. a more ordered universe
 - e. decreased entropy
 - f. increased free energy

Explanation: Increased number of microstates leads to increased entropy.

22. The main driving force for heat flow between two objects is a/an _____ difference.

- a. work
- b. enthalpy
- c. entropy
- •d. temperature
- 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.

23. 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.

24. Which of the following choices is composed only of state functions?

- a. heat, work
- b. free energy, enthalpy, entropy, work
- •c. internal energy, enthalpy, entropy, free energy
- d. internal energy, heat, work
- e. enthalpy, heat, entropy, temperature

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

25. Which of the following choices is the correct thermodynamic assessment of "the universe"?

•a. it is an isolated system

- b. it is a closed system
- c. it is an open 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.

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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