1. Theory: First Law of Thermodynamic

Which of the following statements is/are true concerning the first law of thermodynamics?

I. The internal energy of the universe may increase, decrease, or stay the same for a given process, depending on the changes in enthalpy and entropy.

II. Chemists often consider the universe to be made up of two things: the system and the surroundings (aka everything in existence other than the system)

III. If the energy of a system increases, then the energy of the surroundings must also increase to compensate.

- 1. I only
- 2. II only correct
- 3. III only
- 4. I and II
- 5. I and III
- 6. II and III
- 7. I, II and III

Explanation: Statement I is false; the first law states that the energy of the universe is conserved, in other words a constant value. Statement II is true, at least for the study of thermodynamics. Statement 3 is false because it violates the first law. Internal energy in the universe is conserved, and thus energy gained by the system is LOST by the surroundings. The way this statement is phrased, it would imply an INCREASE in the energy of the universe, which is basically the opposite of the first law.

## 2. Definition: Enthalpy

Which of the following is **not** a correct description of enthalpy or change in enthalpy?

1. In the absence of gas,  $\Delta H \sim \Delta E$ .

- 2.  $\Delta H = q$  in a closed system.
- 3. Enthalpy is an indirect measure of the change in entropy of the surroundings.

4. In an open system,  $\Delta H = q$  so the change in enthalpy is a path function, not a state function. correct

Explanation: It is NOT true that the change in enthalpy is a path function, in any scenario, it is always a state function – besides,  $\Delta H = q$  only in a open system, not a closed system. The rest are all true and come almost exclusively from the last page of lecture 23 which describes enthalpy. It is highly recommended you read and understand this page.

3. Signs for thermodynamic quantities

Ice melts at 50 °C, changing from ice (s) to water (l). Which of the following statements about the signs of the process are true?

- I. Work w is positive (but small).
- II. Heat q is positive.
- III. The change in free energy is positive.
- IV. The change in entropy is positive.
  - 1. I only
  - 2. III only
  - 3. IV only
  - 4. I and II

5. III and IV

6. I, II and IV correct

Explanation: Statement I is a bit tricky because unlike most materials, ice is actually less dense as a solid than a liquid. Therefore, it will condense rather than expand when it melts. A block of ice takes up less volume once it is melted! Because the system was compressed, the sign of w is positive, albeit small because no gases were involved and therefore the change in volume was small. Statement II is true – in order to melt the ice, energy was added to the system to break the hydrogen bonds holding all the molecules in place. Statement III is false because it is a spontaneous process at 50 C. Statement IV is true because liquids have more entropy than solids.

4. Definition: state functions

Which of the following quantities is **not** a path function? Choose the BEST answer.

- 1. Both enthalpy (H) and pressure (P). correct
- 2. work (w)
- 3. enthalpy (H)
- 4. pressure (P)
- 5. Both heat (q) and work (w).
- 6. heat (q)
- 7. Both enthalpy (H) and heat (q).

Explanation: Work (w) and heat (q) are both path functions, the only ones we have learned. All other functions, S, H, G, E, P, V, T, and so on are state functions. You can't say "the work at the final state of the system is \_\_\_\_\_" or "the heat at the initial state of the system is \_\_\_\_\_" or "the heat at the initial state of the system is \_\_\_\_\_" or the state of the system is \_\_\_\_\_" because they describe the **process (aka path taken)** of energy changes not the state of the system at a given point in time. The opposite is true for all the other functions mentioned.

5. Definition: Heats of formation

Which of the following reactions is an enthalpy of formation reaction?

- 1.  $2K(s) + F_2(g) = 2KF(s)$
- 2.  $K(g) + 1/2F_2(g)$  KF(s)
- 3.  $K(s) + 1/2F_2(g)$  KF(s) correct
- 4. KF(s) K(s) +  $1/2F_2(g)$

Explanation: A formation reaction is the formation of ONE mole of product (and no other products) from its component elements in their standard states. I have made it really obvious what errors to avoid here so that you know what to look for. When you do this problem, check to make sure their reactants are in their standard state – here, you have to know that the standard state of potassium K is solid not gas. Potassium is a metal so you would guess it's a solid at 298K and 1 bar (which is roughly 1 atm) ...should be pretty easy. Then, you have to make sure you are only making sure you make only one product. You should be able to look for these errors even if the answer choices are different reactions rather than variations of the same, as given here.

6. Definition: Heat capacity

It will take \_\_\_\_\_ (more/less) energy to raise the temperature of 10 g of water than 1 g of nickel because \_\_\_\_\_?

1. more; it has a higher specific heat capacity and more mass correct

2. more; it has a higher specific heat capacity

- 3. less; it has a lower specific heat capacity and more mass
- 4. less; it has more mass

Explanation: Heat capacity is an extensive property, meaning the amount of matter involved does matter; specific heat capacity is an intensive property. It would take more energy to raise the temperature of 10 g of water by a degree K than it would for only 1 g. Furthermore, heat capacity is a measure of how much energy is required to raise a material's temp so it also matters. High heat capacity implies more energy is required for the same temperature change. Water has a higher heat capacity than metal.

## 7. Calculation: Bomb calorimeter

You set up a bomb calorimetry experiment using 2 liter of water as your heat sink and combust a 12.2122 g sample of benzoic acid ( $C_6H_5COOH$ ). If the initial and final temperature are 10.00 °C and 48.57 °C respectively, what is the molar enthalpy of combustion of benzoic acid? (Assume the calorimeter itself absorbs no heat [aka the heat capacity of the calorimeter is zero] and assume the density of water is 1 g·mL). Remember that the specific heat capacity of water is 4.184 J g<sup>-1</sup> K<sup>-1</sup>.

- 1. -3,228 J⋅mol<sup>-1</sup>
- 2. -322.8 kJ·mol<sup>-1</sup>
- 3. -322.8 J⋅mol<sup>-1</sup>
- 4. -3,228 kJ·mol<sup>-1</sup> correct
- 5. -32.28 kJ mol<sup>-1</sup>

Explanation: Since this is a calorimetry problem, we want to use our  $q = mC\Delta T$  formula. To find m we do this:

$$m = 2 L * (1000 mL \cdot L^{-1})* (1.00 g \cdot mL^{-1}) = 2000 g$$

To find  $\Delta T$  we do this:

$$\Delta T = T_f - T_i = 48.57$$
 °C - 10.00 °C = 38.57 °C = 38.57 K

And we already know C = 4.184 J  $g^{-1}$  K<sup>-1</sup> so we can calculate q:

 $q = mC\Delta T = (2000g)(4.184 J g^{-1} K^{-1})(38.57 K) = 322753 J or roughly 322.8 kJ$ 

Which is the heat absorbed by the water in the calorimeter setup. Note that this is a closed system so  $\Delta H_{cal} = q$ . Knowing that, we can say that  $-\Delta H_{rxn} = \Delta H_{cal}$ . Therefore,  $\Delta H_{rxn} = -322.8$  kJ. However, we want the MOLAR enthalpy of this reaction so we must divide by the moles of benzoic acid (12.2122g/122.122g mol<sup>-1</sup> = 0.1 mol). Therefore, our final answer is -3228 kJ. If you had trouble with the sign mathematically, remember, it's a combustion reaction so you expect it to release heat which is an exothermic reaction which has a negative enthalpy change.

8. Calculation: Hess' Law and heats of formation

Which of the following correctly mathematically describe how to calculate  $\Delta H_{rxn}$  for the following generalized reaction?

1.  $\Delta H_{rxn} = [\Delta H_f(C) + \Delta H_f(D)] - [\Delta H_f(A) + \Delta H_f(B)]$ 

2. 
$$\Delta H_{rxn} = [1*\Delta H_f(C) + 2*\Delta H_f(D)] - [3*\Delta H_f(A) + 1*\Delta H_f(B)]$$

3.  $\Delta H_{rxn} = [3*\Delta H_f(A) + 1*\Delta H_f(B)] - [1*\Delta H_f(C) + 2*\Delta H_f(D)]$ 

4.  $\Delta H_{rxn} = [1*\Delta H_f(A) + 2*\Delta H_f(B)] - [3*\Delta H_f(C) + 1*\Delta H_f(D)]$ 

5. 
$$\Delta H_{rxn} = [3*\Delta H_f(C) + 1*\Delta H_f(D)] - [1*\Delta H_f(A) + 2*\Delta H_f(B)]$$
 correct

Explanation:  $\Delta H_{rxn} = \Sigma H_{f,products} - \Sigma H_{f,reactants}$ 

Make sure you remember to do PRODUCTS minus REACTANTS not the other way around. Also remember that you will need to use the coefficients – obviously you should match up the coefficients for A with the enthalpy of formation value of A and so forth. Be

prepared to use actual numbers on the exam and do a calculation, this problem is given in a more conceptual format for instructional purposes. Also, don't forget that if, for example, A was in its standard state, that would mean that  $\Delta H_f(A) = 0$ .

9. Calculation: Hess's Law and combined reaction enthalpies

Given the following data:

 $\begin{array}{ll} CH_2CO(g) + 2O_2(g) & 2CO_2(g) + H_2O(g)\Delta H = -981.1 \text{ kJ} \cdot \text{mol}^{-1} \\ CH_4(g) + 2 O_2(g) & CO_2(g) + 2H_2O(g) \Delta H = -802.3 \text{ kJ} \cdot \text{mol}^{-1} \end{array}$ 

calculate  $\Delta H$  for the reaction

 $2CH_4(g) + 2O_2(g) CH_2CO(g) + 3H_2O(g)$ 

1. -623.5 kJ·mol<sup>-1</sup> correct

- 2. 623.5 kJ·mol<sup>-1</sup>
- 3. -1783.4 kJ·mol<sup>-1</sup>
- 4. 1783.4 kJ·mol<sup>-1</sup>
- 5. 178.8 kJ∙mol<sup>-1</sup>

Explanation:

 $\begin{array}{ll} CH_2CO(g) + 2O_2(g) & 2CO_2(g) + H_2O(g) & \Delta H = -981.1 \text{ kJ} \cdot \text{mol}^{-1} \\ \underline{CH_4(g) + 2 O_2(g)} & \underline{CO_2(g) + 2H_2O(g)} & \Delta H = -802.3 \text{ kJ} \cdot \text{mol}^{-1} \\ 2CH_4(g) + 2O_2(g) & CH_2CO(g) + 3H_2O(g) & \Delta H = ? \end{array}$ 

To solve for the missing  $\Delta H$  value, we need to manipulate the other two equations so that they add up to the final equation. In short, we need to flip the first equation and double the second:

$2CO_2(g) + H_2O(g)$	$CH_2CO(g) + 2O_2(g)$	ΔH = (-981.1 kJ·mol <sup>-1</sup> ) * -1
$2CH_4(g) + 4O_2(g)$	$2CO_2(g) + 4H_2O(g)$	$\Delta H = (-802.3 \text{ kJ} \cdot \text{mol}^{-1}) * 2$
$2CH_4(g) + 2O_2(g)$	$CH_2CO(g) + 3H_2O(g)$	$\Delta H = -623.5 \text{ kJ} \cdot \text{mol}^{-1}$

Note that the two carbon dioxide molecules in the reactants of the first and products of the second will cancel and so on, so that the first two now add up conveniently to the third. Since we reversed the first reaction we change the sign of the enthalpy by multiplying it by a negative and the second reaction got doubled we multiply it by two. If we had hypothetically had to reverse one and triple it, we would multiply it's enthalpy by -3 and so on. Anyway, then we add up the enthalpies of our reactions to get the enthalpy of the summed reaction. Be prepared to do this with more than 2 input reactions...

10. Calculation: Statistical mechanics determination of internal energy

How much energy would be associated with the motion of 2.5 moles of methane (CH<sub>4</sub>)?

- 1.3.75RT
- 2. 3.75kT
- 3. 18.75RT correct
- 4. 18.75kT
- 5. 7.5kT

Explanation: The energy associated with any motional mode is 0.5kT. We then multiply this by the total number of motional modes (aka degrees of freedom, types of motion, whatever) which is given by 3N where N is the number of atoms in the molecule. Finally, we have this much energy for EVERY molecule so we need to multiply by 2.5 moles. In other words,

E = 0.5kT \* 3N \* 2.5NA where NA is avogadro's number. Because  $k*N_A$  = R and N = 5 for methane, we conclude that E = 18.75RT.

Be prepared to do this same type of problem for just the rotational, translational, or vibrational modes.

11. Calculation: Bond energies Using bond enthalpy data, calculate the change in enthalpy for the following reaction.  $C_{3}H_{8}(g) + 5O_{2}(g) = 3CO_{2}(g) + 4H_{2}O(g)$ You will need the following data C-C 348 kJ mol<sup>-1</sup> C-H 413 kJ mol<sup>-1</sup> 0=0 498 kJ mol<sup>-1</sup> C=0 728 kJ mol<sup>-1</sup>  $O-H 463 k1 mol^{-1}$ 1. -1322 kJ mol<sup>-1</sup> 2. 1322 kJ·mol<sup>-1</sup> 3. -496 kJ⋅mol<sup>-1</sup> 4. 496 kJ·mol<sup>-1</sup> 5. 1582 kJ·mol<sup>-1</sup> 6. -1582 kJ·mol<sup>-1</sup> correct Explanation:  $\Delta H_{rxn} = \Sigma B E_{reactants} - \Sigma B E products$ = (2\*C-C + 8\*C-H + 5\*O=O) - (6\*C=O + 8\*O-H)=  $(2^{3}48 \text{ kJ} \cdot \text{mol}^{-1} + 8^{4}413 \text{ kJ} \cdot \text{mol}^{-1} + 5^{4}498 \text{ kJ} \cdot \text{mol}^{-1}) - (6^{7}728 \text{ kJ} \cdot \text{mol}^{-1} + 8^{4}463 \text{ kJ} \cdot \text{mol}^{-1})$ kJ·mol<sup>-1</sup>)  $= -1582 \text{ kJ} \cdot \text{mol}^{-1}$ 

12. Calculation: Work calculation

Consider the hypothetical reaction below and approximate the value of the work function at room temperature.

18A(l) + 5B(g) 6C(g) + 14D(l) 1. 2.5 kJ 2. 5 kJ 3. -2.5 kJ correct 4. -5 kJ 5. 0 kJ

Explanation: At room temperature (~300K), the product of the RT term in w =  $-\Delta n_{gas}RT$  is approximately 2.5 kJ. Since  $\Delta n_{gas}$  is +1 for this reaction, the work function is approximately -2.5 kJ. Remember that the number of moles of non-gaseous reactants or products (here A and D) do not affect our answer. Be prepared to do this with a real, honest-to-goodness reaction.

13. Definition: Internal Energy

Which of the following is **not** a definition of internal energy or change in internal energy?

1. An intensive path function. correct

2.  $\Delta U = q_V$ 

3. The difference between the final and initial internal energy of a system.

 $4. \Delta U = q + w$ 

Explanation: Internal energy is not an intensive property. Two moles of a substance will have more internal energy than one mole of the same substance. This should be intuitive to you having done problem number ten. The other statements are true. Again, this question will draw almost exclusively from the last page of Lecture 23 so....READ IT LEARN IT DO IT. Make sure you understand all the answer choices whether they are written mathematically or described in words...

## 14. Theory: Calorimetry

Which of the following statements concerning calorimetry is/are true?

- I. One calorie is the same thing as one Calorie.
- II. Calorimetry is done at constant volume.
- III. In real life, we must compensate for heat lost to the calorimeter.
  - 1. I only
  - 2. II only
  - 3. III only
  - 4. I and II
  - 5. I and III
  - 6. II and III only correct
  - 7. I, II and III

Explanation: Statement I is false; a Calorie (capital C) is a kilocalorie – these are used to describe the energy content of food. A calorie (lowercase c) is 1000x smaller. As a chemist (or a student taking a chemistry class at least), you should know this. Statement II is true; we keep the system at constant volume by using a tightly closed, rigid steel cylinder (the bomb!). Statement III is true; we have already done this mathematically in problems you have worked.

The test question will be similar to this but with some other concepts and if you don't understand the concepts of bomb calorimetry it will be one of the tougher problems.

15. Calculation: Internal Energy calculation (q and w)

If the car from the Jetsons does 11000 kJ of work and absorbs 10 kJ of heat (it's the FUTURE, anything could happen...), what is the change in internal energy for the car?

- 1. -10990 kJ correct
- 2. +11010 kJ
- 3. 10990 kJ
- 4. -11010 kJ

Explanation:  $\Delta U = q + w = -11000 \text{ kJ} + 10 \text{ kJ} = -10990 \text{ kJ}$ ; make sure you understand the signs here!

16. Ranking: Predicting entropy change in a chemical reaction

Rank the following reactions from least to greatest in terms of change in entropy  $(\Delta S_{rxn})$ :

- a.  $2H_{2(g)} + O_{2(g)} 2H_2O_{(s)}$
- b.  $2Na_{(s)} + O_{2(g)} = 2NaO_{(s)}$
- c.  $C_6H_{12}O_{6(s)} + 6O_{2(g)} 6H_2O_{(g)} + 6CO_{2(g)}$
- d.  $MgCO_{3(s)}$   $MgO_{(s)} + CO_{2(g)}$

- 1. a<c<b<d
- 2. a<b<d<c correct
- 3. c<d<b<a
- 4. d<b<c<a

Explanation: Reaction a has a decrease in the number of moles of gas, and a change of state from gaseous to solid. Thus (a) has a large negative  $\Delta S_{rxn}$ . Reaction b has a smaller decrease in the number of moles of gas, also a change in state from solid/gas to just solid. Thus (b) has a smaller negative  $\Delta S_{rxn}$ . Reaction d has an increase in the number of moles of gas, and a change of state from solid to solid/gas. Thus reaction (d) has a positive  $\Delta S_{rxn}$ . Finally, reaction c has a large increase in the number of moles of gas and a change of state from solid/gas. Thus reaction (d) has a positive  $\Delta S_{rxn}$ . Finally, reaction c has a large increase in the number of moles of gas and a change of state from solid/gas to gas. Thus reaction c has the greatest  $\Delta S_{rxn}$ .

17. Calculation: Entropy change at a phase transition

An unknown compound X was discovered on mars. The standard molar entropy is 300  $J \cdot mol^{-1} \cdot K^{-1}$  for X(g), 100  $J \cdot mol^{-1} \cdot K^{-1}$  for X(I), and 30  $J \cdot mol^{-1} \cdot K^{-1}$  for X(s),. What is the change in entropy for the melting of X?

- 1. 70 J·mol<sup>-1</sup>·K<sup>-1</sup> Correct
- 2.  $-100 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
- 3. -80 J⋅mol<sup>-1</sup>⋅K<sup>-1</sup>
- 4. -500 J·mol<sup>-1</sup>·K<sup>-1</sup>

Explanation: The change in entropy for melting X can be described by the equation  $X(s) \rightarrow X(l)$   $\Delta S_{melting} = \Sigma S_{m,liquid} - \Sigma S_{m,solid}$ = 100 J·mol<sup>-1</sup>·K<sup>-1</sup> - 30 J·mol<sup>-1</sup>·K<sup>-1</sup> = 70 J·mol<sup>-1</sup>·K<sup>-1</sup>

18. Theory: Second and Third Laws of Thermodynamic

Which of the following statements concerning the second and third laws of thermodynamics is/are true?

- I. Entropy can be zero at a certain temperature
- II.  $\Delta G_{sytem} = -T\Delta S_{universe}$
- III. The universe is getting less ordered because  $\Delta S_{universe}$  is always negative.
  - 1. I
  - 2. II only
  - 3. III only
  - 4. I and II only correct
  - 5. I and III only
  - 6. II and III only
  - 7. I, II and III

Explanation: Statement I is true; at 0 K, the entropy is zero, according to the third law. Statement II is a variation of the second law (see, pg 185 in study guide for derivation). Statement III is false because the universe is getting less ordered because  $\Delta S_{universe}$  is always positive, not negative.

19. Theory: Statistical thermodynamics and entropy

When calculating the positional entropy of a system using the Boltzmann formula (S =kln(W), which of the following statements is/are true?

Presence of intermolecular force decreases the complexity (W) of the system. I.

II. The absolute entropy can be negative.

III. Two water molecules would have twice the positional entropy as a single water molecule.

- 1.
- Ι II only 2.
- 3. III only
- 4. I and II only
- 5. I and III only correct
- 6. II and III only
- 7. I, II and III

Explanation: Statement I is true. As IMF increases, it biases positions toward an arrangement that maximizes electrostatic interactions and thus "orders" the system decreasing its "complexity" and therefore descreases W. Statement II is false; W can never be less than one, and this positional entropy can never be less than zero. Statement III is true. The exponent of the W term (2 in this case) can be factored out and moved to the front of the expression, serving as a coefficient.

20. Calculation: Statistical thermodynamics and entropy

What is the positional entropy of 5 moles of CH<sub>3</sub>F at absolute zero?

- 1. 57.6 J⋅K<sup>-1</sup> correct
- 2. 10.1 J·K<sup>-1</sup>
- 3. 9.56x10<sup>-23</sup> J·K<sup>-1</sup>
- 4. 3.03x10<sup>-23</sup> J·K<sup>-1</sup>

Explanation: CH<sub>3</sub>F has 4 possible orientations, i.e. the f can be in any of four locations around the central carbon. We use R instead of K because we are working with moles, not molecules. S =  $5R \cdot \ln 4 = 57.6 \text{ J} \cdot \text{K}^{-1}$ 

21. Ranking: Statistical thermodynamics, ranking molar entropy in a compound Rank the following compounds in terms of decreasing molar entropy:  $CO_2(q)$ ,  $CO_2(l)$ ,  $CO_2(s), CO(I).$ 

- $CO_2(g) > CO_2(I) > CO(I) > CO_2(s)$  Correct 1.
- 2.  $CO_2(I) > CO_2(q) > CO(I) > CO_2(s)$
- 3.  $CO_2(s) > CO(l) > CO_2(l) > CO_2(g)$
- $CO_2(q) > CO(l) > CO_2(l) > CO_2(s)$ 4.

Explanation: The three phases of  $CO_2$  can be easily ranked, since phase changes have very predictable effects on molar entropy, typically increasing significantly going from solid to liquid and again from liquid to gas. Comparing CO(I) to  $CO_2(I)$ , simply require comparing number of bonds, with  $CO_2(I)$  having greater molar entropy because it has more bonds.

22. Problem: Non-ideality and absolute entropy

Assuming you have one mole of each of the following, rank them in terms of decreasing value of the term W in the Boltzmann equation: HCl, HF, CN.

- 1. CN > HCl > HF correct
- $2. \qquad HCl > CN > HF$
- $3. \qquad HF > HCI > CN$
- 4. HF > HCI > CN

Explanation: Since the strength of the IMF determines the extent of the perturbation of W from its ideal value, this problem essentially requires ranking by increasing IMF. The greater the IMF, the closer the value of W will be to unity.

23. Calculation of  $\Delta S$  from heat transfer

If a system at 1000 °C absorbs 1000 J of heat, what is its change in entropy?

1.  $-0.79 \text{ J} \cdot \text{K}^{-1}$ 2.  $-1 \text{ J} \cdot \text{K}^{-1}$ 3.  $0.79 \text{ J} \cdot \text{K}^{-1}$  correct 4.  $1 \text{ J} \cdot \text{K}^{-1}$ 

Explanation: Heat released by a system will increase its entropy by an amount equal to q/T, in this case 1000 J/(1000+273) K = 0.79 J·K-1.

24. Calculation involving the second law equation

An unknown compound Y was found on Mars. The S<sup>o</sup>m for Y(s) and Y(g) are 300 J·mol<sup>-1</sup>·K<sup>-1</sup> and 100 J·mol<sup>-1</sup>·K<sup>-1</sup>, respectively. Y naturally sublimes at 100K. But what is  $\Delta S_{universe}$  for the sublimation of Y at 50K?

- 1.  $-200 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
- 2. 200 J·mol<sup>-1</sup>·K<sup>-1</sup> correct
- 3. 150 J⋅mol<sup>-1</sup>⋅K<sup>-1</sup>
- 4. 175 J·mol<sup>-1</sup>·K<sup>-1</sup>

Explanation: Sublimation means the transition from solid to gas, Y(s) = Y(q)

 $\Delta S_{system} = \Sigma S_{m,products} - \Sigma S_{m,reactants}$ = 100 J·mol<sup>-1</sup>·K<sup>-1</sup> - 300 J·mol<sup>-1</sup>·K<sup>-1</sup> = -200 J·mol<sup>-1</sup>·K<sup>-1</sup>  $\Delta H_{system} = T\Delta S_{system} = 100 \text{ K} * (-200 \text{ J·mol}^{-1} \cdot \text{K}^{-1}) = -20,000 \text{ J·mol}^{-1}$ 

Since the only process during a phase change is heat exchange,  $\Delta S_{surroundings} = -\Delta H_{system} / T_{surroundings}$ 

= 20,000 J·mol<sup>-1</sup>/50 K = 400 J·mol<sup>-1</sup>·K<sup>-1</sup>

 $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$ = -200 J·mol<sup>-1</sup>·K<sup>-1</sup> + 400 J·mol<sup>-1</sup>·K<sup>-1</sup> = 200 J·mol<sup>-1</sup>·K<sup>-1</sup>

25. Calculation involving the second law equation

If a given process increases the entropy of the universe by 5,000  $J \cdot K^{-1}$  while the entropy

of the system decreases by 3,000  $J \cdot K^{-1}$ , what must the change in entropy of the surroundings?

 $\begin{array}{ll} 1. \ 10,000 \ J \cdot K^{-1} \\ 2. \ 8,000 \ J \cdot K^{-1} \\ 3. \ -10,000 \ J \cdot K^{-1} \\ 4. \ -8,000 \ J \cdot K^{-1} \\ \end{array}$ Explanation:  $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \\ 5,000 \ J \cdot K^{-1} = -3,000 \ J \cdot K^{-1} + \Delta S_{surroundings} \\ \Delta S_{surroundings} = 8,000 \ J \cdot K^{-1} \end{array}$ 

26. Calculation of phase transition temperature using the Gibbs equation at equilibrium Compound Z has  $\Delta H^{\circ}_{fusion} = 10 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta S^{\circ}_{fusion} = 80 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ . What is the normal melting point of Z expressed in centigrade?

1. 125 °C

2. -125 °C

3. 148 °C

4. -148 °C correct

Explanation: Because melting is an equilibrium process,  $\Delta G^{o}_{fusion} = 0 = \Delta H^{o}_{fusion} - T\Delta S^{o}_{fusion}$ .

And so  $T\Delta S^{\circ}_{fusion} = \Delta H^{\circ}_{fusion}$ and  $T = \Delta H^{\circ}_{fusion} / \Delta S^{\circ}_{fusion}$ = 10,000 J·mol<sup>-1</sup>/80 J·mol<sup>-1</sup>·K<sup>-1</sup> = 125 K = -148°C.

27. Theory: The temperature dependence of  $\Delta$ Gro

For a given reaction, if  $\Delta H^{\circ}_{rxn}$  is positive and  $\Delta S^{\circ}_{rxn}$  is negative, then the value of  $\Delta G^{\circ}_{rxn}$  will always \_\_\_\_\_ as you decrease the temperature.

1. Decrease correct

- 2. Increase
- 3. Both of the above
- 4. Undetermined

Explanation:  $\Delta G = \Delta H - T\Delta S$ . If  $\Delta S$  is negative, any decrease in temperature decreases  $\Delta G$ . Plug in some numbers if this does not conceptually make sense to you.

28. Problem: temperature dependence of reaction spontaneity for a chemical reaction Which of the following reactions ONLY occurs at low temperature?

I.  $H_2O(I)$   $H_2O(s)$ II.  $CO_2(s)$   $CO_2(g)$ III.  $C_3H_8(g) + 5O_2(g)$   $3CO_2(g) + 4H_2O(g)$ 1. I only correct 2. II only 3. III only 4. I, II, and III.

Explanation: Reaction I has a negative  $\Delta H$  and a negative  $\Delta S$ , and thus would occur (have a negative  $\Delta G$ ) only then temperature is low. Reaction II has a positive  $\Delta H$  and a positive  $\Delta S$ , thus would occur only when temperature is high. Reaction II has a negative

 $\Delta H$  (it is a combustion reaction, highly exothermic) and a positive  $\Delta S$  (due to the change in the moles of gas), thus it is spontaneous only at any temperature.

29. Problem: predicting compound stability from  $\Delta$ Gro Consider the reaction below:

 $\Delta G^{\circ}_{rxn} = -100 \text{ kJ} \cdot \text{mol}^{-1}$  at room temperature. X(s) + Y(g)Z(s) How would you characterize the stability of Z at room temperature?

- 1. Stable correct
- 2. Not Stable
- 3. Not enough information

Explanation: The reaction written above describes the formation of Z and has a negative change in Gibbs free energy, i.e. is spontaneous, meaning octane must be thermodynamically stable at room temperature.

30. Calculation:  $\Delta$ Gro from table values of  $\Delta$ Hfo and Sfo

Exam

Consider the reaction below:

A + B C + D

Using the provided table values, calculate  $\Delta G^{\circ}_{rxn}$  if it is performed under standard conditions.

	∆H° <sub>f</sub> (kJ∙mol⁻¹)	$\Delta S^{\circ}_{m}$ (J·mol <sup>-1</sup> ·K <sup>1</sup> )
A	-100	200
В	-400	150
С	100	200
D	200	250

- 200 250
  - 1. 773 kJ·mol<sup>-1</sup> correct
  - 2. 750 kJ·mol<sup>-1</sup>
  - 3. 800 kJ⋅mol<sup>-1</sup>
  - 4. -1000 kJ⋅mol<sup>-1</sup>

Explanation:

 $\Delta H_{rxn} = \Sigma H_{f,products} - \Sigma H_{f,reactants}$ =  $(100 \text{ kJ} \cdot \text{mol}^{-1} + 200 \text{ kJ} \cdot \text{mol}^{-1}) - (-100 \text{ kJ} \cdot \text{mol}^{-1} + -400 \text{ kJ} \cdot \text{mol}^{-1})$  $= 800 \text{ kJ} \cdot \text{mol}^{-1}$  $\Delta S_{rxn} = \Sigma S_{m,products} - \Sigma S_{m,reactants}$ = (200 J·mol<sup>-1</sup>·K<sup>-1</sup> + 250 J·mol<sup>-1</sup>·K<sup>-1</sup>) - (200 J·mol<sup>-1</sup>·K<sup>-1</sup> + 150 J·mol<sup>-1</sup>·K<sup>-1</sup>) =  $100 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 0.1 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  $\Delta G^{\circ}_{rxn} = \Delta H^{\circ}_{rxn} - T\Delta S^{\circ} rxn$ = 800 kJ·mol<sup>-1</sup> - 273 K\*0.1 J·mol<sup>-1</sup>·K<sup>-1</sup>  $= 773 \text{ kJ} \cdot \text{mol}^{-1}$