This print-out should have 21 questions. Multiple-choice questions may continue on the next column or page – find all choices before answering.

## 001 10.0 points

Which law of thermodynamics governs the spontaneity of reactions?

- 1. The  $2^{nd}$  Law correct
- 2. There is no thermodynamic law associated with reaction spontaneity.
  - **3.** The  $1^{st}$  Law
  - **4.** The  $0^{th}$  Law
  - **5.** The  $3^{rd}$  Law

## **Explanation:**

The second law of thermodynamics states that the entropy of the universe is always increasing. Consequently, only processes which increases the overall entropy of the universe satisfy the second law and happen spontaneously.

# 002 10.0 points

Consider the formation reactions below and pick the most stable species from the answer choices.

$$2C_{graphite}(s) + 3H_2(g) \rightarrow C_2H_6(g)$$
  
 $\Delta G_f^{\circ} = -7.86 \text{ kcal} \cdot \text{mol}^{-1}$ 

$$3C_{graphite}(s) + 4H_2(g) \rightarrow C_3H_8(g)$$
  
 $\Delta G_f^{\circ} = -5.614 \text{ kcal} \cdot \text{mol}^{-1}$ 

$$8C_{graphite}(s) + 9H_2(g) \rightarrow C_8H_{18}(g)$$
  
$$\Delta G_f^{\circ} = 4.14 \text{ kcal} \cdot \text{mol}^{-1}$$

$$10C_{graphite}(s) + 11H_2(g) \rightarrow C_{10}H_{22}(g)$$
 
$$\Delta G_f^{\circ} = 8.23 \text{ kcal} \cdot \text{mol}^{-1}$$

- 1.  $C_2H_6(g)$  correct
- **2.**  $C_3H_8(g)$
- **3.**  $C_8H_{18}(g)$
- **4.**  $C_{10}H_{22}(g)$

#### **Explanation:**

The formation of ethane is the most exergonic of the formation reactions and thus ethane is the most stable of the species formed.

### 003 10.0 points

For which of the following reactions at room temperature (25 °C) would there be 5.0 kJ of work done on the system?

1. 
$$CH_2O(g) + N_2(g) + 2H_2(g) \rightarrow N_2H_2(g) + CH_3OH(g)$$
 correct

**2.** 
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

3. 
$$N_2H_2(g) + CH_3OH(g) \rightarrow CH_2O(g) + N_2(g) + 2H_2(g)$$

4. 
$$2H_2O(l) + O_2(g) \rightarrow 2H_2O_2(l)$$

**5.** 
$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

6. 
$$CO_2(g) + 2H_2O(g) \rightarrow CH_4(g) + 2O_2(g)$$

## Explanation:

At room temperature (298 K), the product of the gas constant (R = 8.314 J · mol<sup>-1</sup> · K<sup>-1</sup>) and T is very close to 2.5 kJ · mol<sup>-1</sup>. Based on the equation 5.0 kJ =  $-\Delta n_{gas}$  · 2.5 kJ · mol<sup>-1</sup>, the reaction for which  $\Delta n_{gas}$  is -2 will be the correct answer.

#### 004 10.0 points

The formation of ammonia from hydrogen and nitrogen gases becomes less and less spontaneous as temperature is increased, eventually becoming non-spontaenous at sufficiently high temperatures. Which of the following statements must be true?

- 1. The change in entropy is large.
- 2. The change in entropy is small.
- **3.** The reaction is endothermic.
- 4. The reaction is exothermic. correct

# **Explanation:**

Since the reaction becomes more and more spontaneous as the temperature is lowered, it must be spontaneous at T=0 K. Since  $\Delta G = \Delta H$  at T=0 K,  $\Delta H$  must be negative and the reaction is exothermic.

#### 005 10.0 points

Which of the following state functions are extensive?

- I) Pressure (P)
- II) Temperature (T)
- III) Enthalpy (H)
  - 1. II only
  - **2.** II, III
  - **3.** I, III
  - **4.** I, II, III
  - **5.** I only
  - 6. III only correct
  - **7.** I, II
  - 8. None are true

# **Explanation:**

Examples of extensive state functions include: mass, volume, enthalpy, entropy, internal energy, free energy etc.

#### 006 10.0 points

Consider the following specific heats: copper, 0.384 J/g·°C; lead, 0.159 J/g·°C; water, 4.18 J/g·°C; glass, 0.502 J/g·°C. Which substance, once warmed, would be more likely to maintain its heat and keep you warm through a

long football game on a cold night?

- 1. glass
- **2.** lead
- 3. copper
- 4. water correct

## Explanation:

Water has the highest specific heat of the substances listed, so it has the capacity to emit the largest quantity of heat with minimal temperature loss; the emitted heat keeps you warm. The substance continues to warm you until its temperature is at or below your body temperature.

## 007 10.0 points

Calculate the standard reaction enthalpy for the reaction of calcite with hydrochloric acid

$$CaCO_3(s) + 2 HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(\ell) + CO_2(g)$$

The standard enthalpies of formation are:

for  $CaCl_2(aq) : -877.1 \text{ kJ/mol};$ for  $H_2O(\ell) : -285.83 \text{ kJ/mol};$ for  $CO_2(g) : -393.51 \text{ kJ/mol};$ for  $CaCO_3(s) : -1206.9 \text{ kJ/mol};$ and for HCl(aq) : -167.16 kJ/mol.

- 1. -72.7 kJ/mol
- **2.** -38.2 kJ/mol
- 3. -215 kJ/mol
- **4.** -116 kJ/mol
- **5.** -165 kJ/mol
- 6. -15.2 kJ/mol correct
- 7. -98.8 kJ/mol

# **Explanation:**

We use Hess' Law:

$$\Delta H^{\circ} = \sum n \, \Delta H_{\rm j,prod}^{\circ} - \sum n \, \Delta H_{\rm j,reac}^{\circ}$$

$$\begin{split} &= \Delta H_{\rm f, \, CaCl_2(aq)}^{\circ} + \Delta H_{\rm f, \, H_2O(\ell)}^{\circ} \\ &+ \Delta H_{\rm f, \, CO_2(g)}^{\circ} - \left[\Delta H_{\rm f, \, CaCO_3(s)}^{\circ} \right. \\ &\left. + 2 \, \left(\Delta H_{\rm f, \, HCl(aq)}^{\circ}\right)\right] \\ &= -877.1 \, \, \text{kJ/mol} + \left(-285.83 \, \, \text{kJ/mol}\right) \\ &+ \left(-393.51 \, \, \text{kJ/mol}\right) \\ &- \left[-1206.9 \, \, \text{kJ/mol}\right] \\ &- \left[-1206.9 \, \, \text{kJ/mol}\right] \\ &= -15.22 \, \, \text{kJ/mol} \,. \end{split}$$

#### 008 10.0 points

Estimate the heat released when ethene  $(CH_2 = CH_2)$  reacts with HBr to give  $CH_3CH_2Br$ . Bond enthalpies are C = H: 412 kJ/mol; C = C: 348 kJ/mol; C = C: 612 kJ/mol; C = Br: 276 kJ/mol; Br = Br: 193 kJ/mol; H = Br: 366 kJ/mol.

- 1. 200 kJ/mol
- **2.** 424 kJ/mol
- 3. 58 kJ/mol correct
- **4.** 1036 kJ/mol
- **5.** 470 kJ/mol

#### **Explanation:**

$$H \longrightarrow C = C \longrightarrow H + H \longrightarrow Br \longrightarrow H \longrightarrow C \longrightarrow C \longrightarrow Br$$

$$H \longrightarrow H \longrightarrow H \longrightarrow H \longrightarrow H$$

$$\begin{split} \Delta H &= \sum E_{\rm break} - \sum E_{\rm make} \\ &= \left[ ({\rm C} - {\rm C}) + ({\rm H} - {\rm Br}) \right] \\ &- \left[ ({\rm C} - {\rm H}) + ({\rm C} - {\rm Br}) + ({\rm C} - {\rm C}) \right] \\ &= (612 \; {\rm kJ/mol} + 366 \; {\rm kJ/mol}) \\ &- \left[ 412 \; {\rm kJ/mol} + 276 \; {\rm kJ/mol} \right] \\ &+ 348 \; {\rm kJ/mol} \right] \\ &= -58 \; {\rm kJ/mol} \; , \end{split}$$

so 58 kJ/mol of heat was released.

## 009 10.0 points

Which of the following is NOT a feature of the bomb calorimetry apparatus used to measure the internal energy of a reaction?

- 1. The heat capacity of the calorimeter should be known to accurately correct for any heat lost to it.
- 2. The thermometer is inserted directly into the reaction vessel to measure  $\Delta T$  of the reaction. **correct**
- **3.** The large heat capacity of water is beneficial in measuring heat released by combustion reactions.
- **4.** The volume of the reaction vessel is held constant to eliminate energy released as work.
- **5.** Large quantities of water surrounding the reaction vessel absorb the majority of the heat loss.

#### Explanation:

The thermometer is placed in the water that surrounds the reaction vessel.

## 010 10.0 points

Which of the following reactions has the largest value of  $\Delta S^{\circ}$ ?

- 1.  $K(s) + O_2(g) \rightarrow KO_2(s)$
- 2.  $BaCl_2 \cdot 2H_2O(s) \rightarrow BaCl_2(s) + 2H_2O(g)$ correct
- 3.  $N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$
- 4.  $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
- 5.  $2 H_2(\ell) + O_2(\ell) \rightarrow 2 H_2O(g)$

### Explanation:

We can predict the sign and magnitude of  $\Delta S$  by noting the relative order of entropy:

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solids (lowest) < liquids < solutions < gases (highest) and the number of moles of each type. For the reactions given we have

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

2 mol gas 
$$\rightarrow$$
 1 mol solid;  $\Delta S < 0$ 

$$2 H_2(\ell) + O_2(\ell) \rightarrow 2 H_2O(g)$$

3 mol liquid 
$$\rightarrow$$
 2 mol gas;  $\Delta S > 0$ 

$$N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$$

4 mol gas 
$$\rightarrow$$
 2 mol gas;  $\Delta S < 0$ 

$$K(s) + O_2(g) \rightarrow KO_2(s)$$

1 mol solid + 1 mol gas 
$$\rightarrow$$
 1 mol solid;

$$\Delta S < 0$$

$$BaCl_2 \cdot 2 H_2O(s) \rightarrow BaCl_2(s) + 2 H_2O(g)$$
  
1 mol solid  $\rightarrow$  1 mol solid + 1 mol gas;

$$\Delta S > 0$$

The greatest increase in S would be for the reaction

$$BaCl_2 \cdot 2 H_2O(s) \rightarrow BaCl_2(s) + 2 H_2O(g)$$

## 011 10.0 points

For which of the following processes does the entropy of the universe decrease?

- 1. None of these is correct. **correct**
- **2.** melting one mole of ice to water at  $0^{\circ}$ C
- **3.** freezing one mole of water to ice at  $0^{\circ}$ C
- 4. freezing one mole of water to ice at  $0^{\circ}$ C and then cooling it to  $-10^{\circ}$ C
- 5. freezing one mole of water to ice at  $-10^{\circ}$ C

#### **Explanation:**

For spontaneous changes, the entropy of the universe increases.

#### 012 10.0 points

Consider the equation

$$NH_4Br(s) \rightarrow NH_3(g) + HBr(g)$$

carefully, and think about the sign of  $\Delta S$  for the reaction it describes.  $\Delta H = +188.3$  kJ. Which response describes the thermodynamic spontaneity of the reaction?

- 1. The reaction is spontaneous only at relatively low temperatures.
  - **2.** All responses are correct.
- **3.** The reaction is spontaneous at all temperatures.
- **4.** The reaction is not spontaneous at any temperatures.
- **5.** The reaction is spontaneous only at relatively high temperatures. **correct**

#### **Explanation:**

Entropy (S) is high for systems with high degrees of freedom, disorder or randomness and low for systems with low degrees of freedom, disorder or randomness.

$$S(g) > S(\ell) > S(s)$$
.

A reaction is spontaneous only when  $\Delta G$  is negative.  $\Delta H$  is positive for this reaction and  $\Delta S$  is positive.

$$\Delta G = \Delta H - T \Delta S$$
$$= (+) - T (+)$$
$$= (+) - T$$

 $\Delta G$  will be negative (spontaneous reactions) only at high values of T.

# 013 10.0 points

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

- I) The internal energy of the universe is always increasing.
- II) Internal energy lost by a system is always gained by the surroundings.
- III) The universe is an isolated system.
  - **1.** I only
  - **2.** I and II only
  - 3. II and III only correct
  - 4. III only
  - **5.** I and III only

## **6.** II only

#### 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 and III are true; internal energy in the universe is conserved, and thus energy lost by the system is always gained by the surroundings. The universe is the most obvious example of an isolated system in that energy and matter are conserved in the universe.

#### 014 10.0 points

You observe that carbon dioxide sublimes. Which of the following statements about the signs of this process is/are true?

- I) Work (w) is positive.
- II) Heat (q) is negative.
- III) Change in Gibbs free energy  $(\Delta G)$  is positive.
- IV) Change in entropy  $(\Delta S)$  is positive.
  - 1. II and III
  - **2.** I only
  - 3. I and II
  - 4. I, II and III
  - 5. IV only correct
  - **6.** III and IV

#### **Explanation:**

Sublimation results in a significant increase in the volume of the system, allowing it to do work on its surroundings, i.e. the pressure-volume work function is negative. Sublimation is also an endothermic process, making heat positive. Since the process described "happens" as a given in the problem, the change in free energy must be negative. Change in entropy must be positive since a solid is becoming a gas.

#### 015 10.0 points

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

1. 
$$CH_4(g) + 2O_2(g) \longleftrightarrow CO_2(g) + 2H_2O$$

2.  $2Fe(s) + 3/2O_2(g) \longleftrightarrow Fe_2O_3(s)$  correct

3. 
$$C_{diamond}(s) + 2H_2(g) \longleftrightarrow CH_4(g)$$

4. 
$$Hg(s) + 1/2O_2(g) \longleftrightarrow HgO(s)$$

### Explanation:

Formation reactions describe production of exactly one mole of one product from stoichiometric quantities of elements in their standard states.

# 016 10.0 points

If we set up a bomb calorimetry experiment to determine the molar enthalpy of combustion of ethene ( $C_2H_4$ ) using 1 L of water as our heat sink, 2.805 g of ethene, and measure an initial and final temperature of 25.20 °C and 58.92 °C, respectively, what will be the experimentally determined molar enthalpy of combustion of ethene? Assume the density of water is 1.00 g · mL<sup>-1</sup>. Assume the calorimeter itself absorbs no heat. The specific heat capacity of water is 4.184 J · g<sup>-1</sup> · K<sup>-1</sup>.

1. 
$$-141.1 \text{ kJ} \cdot \text{mol}^{-1}$$

2. 
$$-1,411 \text{ kJ} \cdot \text{mol}^{-1} \text{ correct}$$

3. 
$$-14$$
,  $110 \text{ kJ} \cdot \text{mol}^{-1}$ 

**4.** 
$$-14.11 \text{ kJ} \cdot \text{mol}^{-1}$$

**5.** 
$$-141$$
,  $100 \text{ kJ} \cdot \text{mol}^{-1}$ 

#### **Explanation:**

$$\Delta T = T_f - T_i = 58.92 \,^{\circ}\text{C} - 25.20 \,^{\circ}\text{C} = 33.72 \,^{\circ}\text{C} = 33.72 \,^{\circ}\text{K}$$

$$m = 1 \text{ L} \cdot \frac{1000 \text{ mL}}{\text{L}} \cdot \frac{1.00 \text{ g}}{\text{mL}} = 1000 \text{ g}$$

$$n=2.805~\mathrm{g}$$
 ethene  $\cdot \frac{28.05~\mathrm{g}}{\mathrm{mol}}=0.1~\mathrm{mol}$ 

$$\Delta H_{rxn} = -\Delta H_{cal} = -mc\Delta T$$

$$\frac{-mc\Delta T}{n} = -\frac{1000 \text{ g} \cdot \frac{4.184 \text{ J}}{\text{g·K}} \cdot 33.72 \text{ K}}{0.1 \text{ mol}}$$
$$= -1,411 \text{ kJ} \cdot \text{mol}^{-1}$$

# 017 10.0 points

If an MP3 player does 200 kJ of work and releases 100 kJ of heat, what is the change in internal energy for the MP3 player?

- 1. -300 kJ correct
- **2.** 300 kJ
- **3.** 100 kJ
- **4.** -100 kJ

#### **Explanation:**

$$\Delta U = q + w$$

$$= -100 \text{ kJ} + -200 \text{ kJ} = -300 \text{ kJ}$$

#### 018 10.0 points

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

- I) When the change in entropy of the system is equal in magnitude and opposite in sign to the change in entropy of the surroundings, the change in entropy of the universe is zero.
- II) The change in entropy of the universe can be rewritten as  $-\Delta G_{sutem}/T$ .
- III) In a perfect, pure crystal at absolute zero the entropy of the system is zero.
  - 1. III only
  - **2.** II, III
  - 3. I only
  - 4. I, III

- **5.** II only
- 6. I, II, III correct
- 7. I, II

#### **Explanation:**

Statement I is true; the second law equation states that the change in entropy of the universe is the sum of the change in entropy of the system and the surroundings. Statement II is true; this is a mathematical identity derived from the second law equation. Statement III is true; the third law states that as the temperature of a system approaches absolute zero, the entropy of the system approaches its minimum, which in the case of a perfect crystalline solid, is zero.

## 019 10.0 points

For a given reaction, if  $\Delta H_{rxn}^{\circ}$  is (negative/positive/either) and  $\Delta S_{rxn}^{\circ}$  is (negative/positive/either), then the value of  $\Delta G_{rxn}^{\circ}$  will always decrease as you raise the temperature.

- 1. either, positive correct
- 2. positive, either
- **3.** either, negative
- 4. negative, either
- **5.** positive, negative
- 6. negative, positive

#### Explanation:

Only the sign of  $\Delta S_{rxn}^{\circ}$  determines how  $\Delta G_{rxn}^{\circ}$  will be effected by changes in temperature. When  $\Delta S_{rxn}^{\circ}$  is positive,  $\Delta G_{rxn}^{\circ}$  will always decrease in value as you raise the temperature. This can be intuited from the Maxwell equation,  $\Delta G = \Delta H - T\Delta S$ . Note that only  $\Delta S$  is multiplied by T, not  $\Delta H$ .

In the formula  $\Delta U = q + w$ , work done by the system during expansion is (negative/positive), and heat (gained/lost) by the system is positive.

- 1. negative, gained correct
- 2. negative, lost
- 3. positive, gained
- 4. positive, lost

#### **Explanation:**

The sign conventions for process functions (like work and heat) are such that a positive sign is attributed to the system if it gains energy (in the form of heat or work).

## 021 10.0 points

Which of the following statements about the first and second laws of themodynamics is/are true?

- I) The energy of the universe is always conserved.
- II) The energy of a system is always conserved.
- III) The energy of the system always increases.
- IV) The entropy of the universe always increases.
- V) The entropy of the universe always conserved.
- VI) The entropy of the system is always conserved.
  - 1. III and IV
  - 2. I and IV correct
  - 3. II and V
  - 4. II and VI
  - **5.** I and V
  - **6.** III and VI

#### **Explanation:**