

ACS Physical Chemistry: Thermochemistry Practice Test (Sample)

Study Guide



Everything you need from our exam experts!

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SAMPLE

Questions

1. What formula represents the vapour pressure in the presence of applied pressure?
 - A. $p = p^*e^{(V_m\Delta P/RT)}$
 - B. $p = p^*e^{(\Delta_{\text{trs}}S/\Delta_{\text{trs}}V)}$
 - C. $p = \Delta_{\text{vap}}H/RT^2$
 - D. $p = \sum n_J d\mu_J$
2. What is the result of a binary mixture at temperatures above the lower critical solution temperature?
 - A. Complete miscibility
 - B. Partial miscibility
 - C. Phase separation occurs
 - D. Azeotropic behavior is observed
3. What is the symbol for internal energy?
 - A. H
 - B. S
 - C. U
 - D. E
4. What is the standard free energy of formation for an element in its standard state (ΔG_f)?
 - A. 1
 - B. -1
 - C. 0
 - D. Infinity
5. For a monoatomic ideal gas, what is the equation for C_v ?
 - A. $C_v = (1/2)R$
 - B. $C_v = (3/2)R$
 - C. $C_v = 2R$
 - D. $C_v = R$

6. What is the work done in an expansion against constant external pressure according to the work equation?
- A. $W = P_{\text{ext}} (V_f + V_i)$
 - B. $W = -P_{\text{ext}} (V_f - V_i)$
 - C. $W = -P_{\text{ext}} (V_i - V_f)$
 - D. $W = P_{\text{ext}} (V_i - V_f)$
7. Which quantity does the term " γ_A " represent in terms of activity?
- A. Activity coefficient
 - B. Vapor pressure
 - C. Mole fraction
 - D. Concentration
8. What does a large value for W indicate about a system?
- A. There are fewer microstates
 - B. There is a higher energy level
 - C. There are more microstates
 - D. There is less disorder
9. What happens to absorbance (A) as transmittance (T) decreases?
- A. Absorbance increases
 - B. Absorbance stays the same
 - C. Absorbance decreases
 - D. Absorbance varies randomly
10. How can standard reaction entropy be determined from standard emf temperature dependence?
- A. $\Delta_r S^\circ = \nu F dE^\circ / dT$
 - B. $\Delta_r S^\circ = dE^\circ / \nu F$
 - C. $\Delta_r S^\circ = \nu F (dE/dT)$
 - D. $\Delta_r S^\circ = dE/dT$

Answers

SAMPLE

1. A
2. C
3. C
4. C
5. B
6. B
7. A
8. C
9. A
10. A

SAMPLE

Explanations

SAMPLE

1. What formula represents the vapour pressure in the presence of applied pressure?

A. $p = p^*e^{(V_m\Delta P/RT)}$

B. $p = p^*e^{(\Delta_{\text{trs}}S/\Delta_{\text{trs}}V)}$

C. $p = \Delta_{\text{vap}}H/RT^2$

D. $p = \sum n_J d\mu_J$

The correct answer is based on the relationship between vapor pressure and the applied pressure, which is described by the formula for the effect of pressure on the vapor phase equilibrium of a substance. The formula $p = p^*e^{(V_m\Delta P/RT)}$ incorporates several important thermodynamic concepts. In this equation, ' p^* ' represents the equilibrium vapor pressure of the substance, ' V_m ' is the molar volume of the substance in the gas phase, ' ΔP ' is the change in pressure (which could be an increase due to applied external pressure), ' R ' is the universal gas constant, and ' T ' is the absolute temperature. This expression arises from the application of the ideal gas law along with the considerations of how external pressure modifies the equilibrium state of the vapor-liquid system. When pressure is applied to a system, the term ' ΔP ' describes this change, and since the vapor phase is affected, we see how the vapor pressure adjusts in response. The exponential factor indicates that there is a significant sensitivity of vapor pressure to changes in volume and temperature, leading to a non-linear relationship between applied pressure and vapor pressure. This formula is particularly useful in chemical engineering and physical chemistry for understanding how vapor pressures behave under varying conditions

2. What is the result of a binary mixture at temperatures above the lower critical solution temperature?

A. Complete miscibility

B. Partial miscibility

C. Phase separation occurs

D. Azeotropic behavior is observed

In a binary mixture at temperatures above the lower critical solution temperature (LCST), the components exhibit complete miscibility. The LCST is the temperature below which a solution of two components becomes immiscible. When the temperature is increased above this point, the energy interactions between the molecules of the two components become favorable enough that they can mix completely in all proportions. At this elevated temperature, the favorable interactions lead to a single homogeneous phase rather than separating into distinct layers. Therefore, the result of a binary mixture at temperatures above the LCST is complete miscibility rather than phase separation. Complete miscibility indicates that the two substances can dissolve in one another fully, leading to a single-phase solution. This is a crucial concept in understanding how temperature affects the solubility and behavior of mixtures in thermodynamics.

3. What is the symbol for internal energy?

- A. H
- B. S
- C. U**
- D. E

The symbol for internal energy is denoted by U. Internal energy represents the total energy contained within a system, which includes kinetic and potential energy at the molecular level. This concept is fundamental in thermodynamics and is crucial for understanding processes such as heat transfer, work, and changes in state. While H represents enthalpy, S signifies entropy, and E typically refers to energy in a more general sense, it is U that specifically corresponds to internal energy in thermodynamic equations and discussions. Understanding the correct symbol is important for accurately interpreting formulas and performing calculations in physical chemistry.

4. What is the standard free energy of formation for an element in its standard state (ΔG_f)?

- A. 1
- B. -1
- C. 0**
- D. Infinity

The standard free energy of formation, ΔG_f , for an element in its standard state is defined as zero. This is based on the convention used in thermodynamics where the formation of an element from itself is essentially a reference point. In practical terms, when we talk about the formation of an element in its standard state, we are referring to a process that does not require any energy change; it is essentially a definition rather than a reaction. Therefore, the standard free energy of formation for elements like oxygen, hydrogen, carbon, and others in their most stable forms (e.g., $O_2(g)$, $H_2(g)$, C(s, graphite)) is set to zero. This allows us to calculate the standard free energies of formation for compounds relative to these elements. This convention provides a consistent basis for determining the thermodynamic stability of substances, where positive or negative values of ΔG_f for compounds indicate their stability compared to the elemental forms. Elements in their standard state serve as a baseline reference for all other compounds.

5. For a monoatomic ideal gas, what is the equation for C_v ?

A. $C_v = (1/2)R$

B. $C_v = (3/2)R$

C. $C_v = 2R$

D. $C_v = R$

For a monoatomic ideal gas, the heat capacity at constant volume, known as C_v , is determined by the degrees of freedom of the gas molecules. In the case of monoatomic gases, such as helium, neon, or argon, each atom has only three translational degrees of freedom (movement in the x, y, and z directions). The equipartition theorem states that each degree of freedom contributes $(1/2)kT$ to the internal energy, where k is the Boltzmann constant, and T is the temperature. In terms of the ideal gas constant, R , for a monoatomic ideal gas, the total contribution to the internal energy comes from these three translational degrees of freedom. Thus, the expression for C_v becomes: $C_v = (3/2)R$. This value reflects the amount of energy required to raise the temperature of one mole of a monoatomic ideal gas by one degree Kelvin when the volume is held constant. The other choices do not correspond to the properties of a monoatomic ideal gas.

6. What is the work done in an expansion against constant external pressure according to the work equation?

A. $W = P_{\text{ext}} (V_f + V_i)$

B. $W = -P_{\text{ext}} (V_f - V_i)$

C. $W = -P_{\text{ext}} (V_i - V_f)$

D. $W = P_{\text{ext}} (V_i - V_f)$

The work done during an expansion against constant external pressure can be articulated through the relationship defined in thermodynamics. In this case, the formula $W = -P_{\text{ext}} (V_f - V_i)$ is used, where: $-W$ represents the work done, $-P_{\text{ext}}$ is the external pressure, $-V_f$ is the final volume, and $-V_i$ is the initial volume. When a system expands, the final volume (V_f) is greater than the initial volume (V_i), leading to a positive change in volume ($V_f - V_i$). The negative sign in the work equation indicates that work is being done by the system on the surroundings. Thus, for a typical expansion process where the volume increases, the work done by the system is considered negative because the system is losing energy in the form of work. This understanding leads to the conclusion that option B accurately reflects the proper relationship for work done in a constant external pressure scenario. The formula shows that as the system expands (with the final volume greater than the initial), the work done is indeed a negative value, consistent with the energy loss from the system.

7. Which quantity does the term " γ_A " represent in terms of activity?

A. Activity coefficient

B. Vapor pressure

C. Mole fraction

D. Concentration

The term " γ_A " represents the activity coefficient, which plays a crucial role in thermodynamics, particularly in the context of solution chemistry. The activity coefficient is a factor used to account for the deviation of a solution's behavior from an ideal solution. In an ideal solution, the interactions between different species are the same as those between similar species. However, in real solutions, interactions can vary significantly, and the activity coefficient quantifies this difference. Specifically, the activity of a species in a solution is defined as the product of its activity coefficient and its concentration or mole fraction, expressed as a unitless number. Therefore, understanding the activity coefficient is essential for predicting how species behave in non-ideal solutions, allowing for accurate calculations of chemical potential, vapor-liquid equilibria, and other thermodynamic properties. The other choices do not appropriately define " γ_A ": vapor pressure pertains to the pressure exerted by a vapor in equilibrium with its liquid or solid form, mole fraction is a ratio of a component to the total composition, and concentration refers to the amount of substance per unit volume. None of these terms capture the concept of the activity coefficient, making it the correct interpretation of " γ_A ."

8. What does a large value for W indicate about a system?

A. There are fewer microstates

B. There is a higher energy level

C. There are more microstates

D. There is less disorder

A large value for W signifies that there are more microstates available in the system. In statistical mechanics, W represents the number of ways in which a system can be arranged at the microscopic level while still exhibiting the same macroscopic properties. When W is high, it means that the system can exist in many different configurations or arrangements, reflecting a greater degree of disorder or randomness. This concept is intimately connected to entropy, as entropy is a measure of the number of microstates corresponding to a given macrostate. According to the Boltzmann formulation of entropy, $S = k \ln(W)$, where S is the entropy, k is the Boltzmann constant, and W is the number of microstates. A larger W would thus correlate with a higher entropy, indicating that the system is in a more disordered state. In summary, a large value for W demonstrates that the system has a greater potential for microstates, indicating increased disorder and a more complex underlying structure.

9. What happens to absorbance (A) as transmittance (T) decreases?

- A. Absorbance increases
- B. Absorbance stays the same
- C. Absorbance decreases
- D. Absorbance varies randomly

To understand the relationship between absorbance (A) and transmittance (T), it's important to recall the definitions and their mathematical relationship. Absorbance is a measure of the amount of light absorbed by a sample, while transmittance refers to the fraction of light that passes through the sample. The relationship between absorbance and transmittance is given by the equation: $A = -\log(T)$. This equation indicates that as transmittance decreases, which means that less light is passing through the sample, the value of the logarithm becomes larger in magnitude, resulting in an increase in absorbance. In simpler terms, if more light is absorbed (as fewer photons transmit through), the absorbance value will increase. Thus, when transmittance decreases, absorbance consequently increases because less light is transmitted through the sample due to more absorption. This direct relationship is a cornerstone in spectrophotometry and is fundamental when analyzing how substances interact with light.

10. How can standard reaction entropy be determined from standard emf temperature dependence?

- A. $\Delta_r S^\circ = \nu F dE^\circ / dT$
- B. $\Delta_r S^\circ = dE^\circ / \nu F$
- C. $\Delta_r S^\circ = \nu F (dE/dT)$
- D. $\Delta_r S^\circ = dE/dT$

The determination of standard reaction entropy from the temperature dependence of standard emf is grounded in thermodynamic principles that connect electrochemical properties with thermodynamic quantities. The expression for standard reaction entropy, $\Delta_r S^\circ$, is derived from the relationship between the cell potential (emf) and temperature. The correct formulation states that the change in standard reaction entropy can be determined using the relationship: $\Delta_r S^\circ = \nu F (dE/dT)$. Here, ν represents the number of moles of electrons transferred in the reaction, F is Faraday's constant, and dE/dT is the change in the standard electromotive force with respect to temperature. This relationship arises from the fundamental equation of thermodynamics that links Gibbs free energy (G) to emf (E), showing that the change in Gibbs energy of a system is related to its entropy. Using this equation provides a clear connection between the electrochemical behavior of a reaction and its thermodynamic properties, illustrating how shifts in temperature influence system entropy. This approach is particularly useful because measuring emf is often easier than directly calculating the entropy changes through other methods. Thus, the first option embodies this connection accurately, reflecting both the dependency of emf on temperature and the amount of charge represented by νF for ionic or electron