CODS

Chemistry Olympiads

- Welcome -

2021 USNCO Locals Detailed Solutions

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Note: If you'd like me to explain any other question, please fizzest#000). Or join our server.

6. The concentration of an aqueous solution of a nonvolatile, monoprotic acid is measured first by freezing point depression and then by boiling point elevation. The solution is found to be 0.93 *m* by freezing point depression and to be 0.82 *m* by boiling point elevation. Which is the best explanation for this discrepancy?

(A) Ionization of the acid is markedly exothermic.

(B) The solute associates partially into dimers at lower temperatures.

(C) The volume of the solution is greater at higher temperatures.

(D) The boiling point elevation constant for water is smaller than its freezing point depression constant.

Topic: Colligative Properties | **Difficulty:** Moderate | **Answer:** A

This experiment determines the molality of monoprotic acid with two colligative properties; **freezing-point depression** and **boiling point elevation**.

$$\Delta T_b = i \cdot K_b \cdot m$$

"found to be" refers to observed molality. This means the molality determined is actually the van't Hoff factor (*i*) multiplied by the formal molality, or the molality of the acid before any dissociation occurs. You cannot calculate the van't Hoff factor without knowing the formal molality.

Let's first take a look at **(A)**. Ionization of the acid is markedly exothermic. Write the hypothetical equation:

$$HA\ (aq) + H_2O\ (l) \rightleftharpoons A^-\ (aq) + H_3O^+\ (aq) + \textbf{heat}$$

At higher temperatures, this reaction will be shifted more towards the **left** (K will decrease), and therefore **less acid** will be dissociated in water. This will lead to a **smaller van't Hoff factor (*i*)**, as more formation of products would lead to a larger van't Hoff factor. This larger van't Hoff factor at lower temperatures will in return illustrate a **higher observed molality** in comparison to higher temperatures.

Let's look at other answers as well.

(B) is incorrect for many reasons, but if a solute associates partially into dimers (benzoic acid tends to do that) at low temperatures, we'd expect the **van't Hoff factor (*i*)** calculated from the freezing point to be **lower**, not higher.

(C) is incorrect because colligative properties use **molality** instead of molarity for this exact reason. It is not a plausible explanation.

(D) is just simply not true. The reason why chemists use freezing point depression instead of boiling point elevation is because freezing point depression tends to have a much significant temperature change in comparison to boiling point elevation. This is because the molar entropy change from solid to liquid is much smaller in comparison to liquid to gas (while the molar enthalpy change from solid to liquid or liquid to gas is fairly similar).

16. The melting point of water decreases with increasing pressure. Which is the best explanation for this observation?

(A) Liquid water is denser than solid water at 0 °C.

(B) Melting of ice is endothermic at 0 °C.

(C) The vapor pressure of liquid water is lower than the vapor pressure of solid water at 0 °C.

(D) Solid and liquid water cannot coexist at equilibrium at 0 °C at pressures different from 1 atm.

Topic: Phase Changes | **Difficulty:** Easy | **Answer:** A

I just want to briefly mention this question because some people have gotten it wrong. **A** is correct because liquid water is indeed dense than solid water at 273 K. The **Clapeyron equation** illustrates this in great detail:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$$

This is the equation that is used to calculate the **solid-liquid** phase boundaries. As liquid water is denser than solid water, we expect the **entropy change to be negative**, and therefore, the slope of the solid-liquid phase boundary to be negative as well (which is characteristic of water's phase diagram).

(B) is incorrect as it alludes to a **positive slope** from the Clapeyron equation.

(C) is incorrect as it is simply not true in the first place.

(D) is **factually correct**, but it **does not** explain why the melting point of water decreases with increasing pressure.

17. A cylinder containing a mixture of CO and CO_2 has a pressure of 2.00 atm at 93 °C (366 K). The cylinder is then cooled to –90 °C (183 K), where CO is still a gas but CO_2 is a solid with a vapor pressure of 0.25 atm. The pressure in the cylinder at this temperature is 0.90 atm. What is the mole fraction of CO_2 in the cylinder?

(A) 0.10

(B) 0.28

(C) 0.35

(D) It cannot be determined from the information given.

Topic: Vapor Pressure | **Difficulty:** Moderate | **Answer:** C

The question presents two different gases, CO_2 and CO. They decrease the temperature of the system by half, so we expect the pressure of the system to halve as well (to 1.00 atm). **Assuming the cylinder has constant volume**, we can use partial pressures as if they were moles of gas, and stoichiometry can be applied. Because 0.25 atm of CO_2 exists as vapor, and the pressure of the cylinder at 183 K is 0.90 atm, we expect 0.65 atm to exist as CO. This means that the partial pressure of CO at 366 K was **1.3 atm**, and therefore, the partial pressure of CO_2 at 366 K was 0.7 atm. The mole fraction can be calculated by dividing the partial pressure of CO_2 at 366 K by the total pressure (2.0 atm), which gives **(C)**.

20. Two metal samples, labeled A and B, absorb the same amount of heat. Sample A has a mass of 10.0 g, and its temperature increases by 38 °C. Sample B has a mass of 20.0 g, and its temperature increases by 23 °C. Which sample has the greater specific heat capacity?

(A) Sample A

(B) Sample B

(C) Both samples have the same specific heat capacity.

(D) It is impossible to determine from the information given.

Topic: Heat capacity | **Difficulty:** Easy | **Answer:** A

If both samples absorb the same amount of heat, then we can set the two equations of q = mCdT to be equal to each other.

$$(10.0\ \text{g})C_A(38\ ^\circ\text{C}) = (20.0\ \text{g})C_B(23\ ^\circ\text{C})$$

Do the math, and we should get:

$$C_A = 1.21C_B$$

Illustrating that $C_A > C_B$.

22. What is the boiling point of water in a pressure cooker with a pressure of 2.00 atm? (The enthalpy of vaporization of water is 40.7 kJ mol^{-1}.)

(A) 101 °C **(B)** 121 °C **(C)** 141 °C **(D)** 200 °C

Topic: Thermodynamics | **Difficulty:** Easy | **Answer:** B

They gave you the enthalpy of vaporization of water, and asked for the boiling point of water at 2.00 atm. You should know that water boils at 373 K, and the atmospheric pressure is 1.00 atm. Plug all of these values into the **Clausius-Clapeyron equation**, and you should get your answer.

24. Titanium has a normal melting point of 1668 °C and a molar enthalpy of fusion of 14.15 kJ mol^{-1}. The standard molar entropy of liquid titanium is 97.53 J mol^{-1} K^{-1} at 1668 °C. What is the standard molar entropy of solid titanium at this temperature?

(A) 89.05 J mol^{-1} K^{-1} **(B)** 90.24 J mol^{-1} K^{-1}

(C) 97.52 J mol^{-1} K^{-1} **(D)** 104.82 J mol^{-1} K^{-1}

Topic: Thermodynamics | **Difficulty:** Moderate | **Answer:** B

When a phase change occurs, the temperature of the system remains constant. We can exploit this fact to calculate the molar entropy of solid.

$$dG = dH - TdS$$

Because the temperature remains constant, and when a phase change occurs, both phases are in equilibrium ($dG = 0$),

$$dS_{fus} = dH_{fus}/T$$

Knowing this, the question becomes extremely simple. dS_{fus} = 14150 J / (1668 + 273 K) = 7.29 J mol^{-1} K^{-1}, and because the molar entropy of liquid titanium is 97.53 J mol^{-1} K^{-1}, we should know that the entropy of the solid should be B.

Note: if you remembered the equation but forgot if there was a negative sign or not, always remember that in most cases, the molar entropy of solid will be smaller than the molar entropy of liquid.

26. When the rate of the reversible reaction A + B $\leftrightarrows$ C is studied under a certain set of conditions, it is found that the rate of the forward reaction is k_f[A]. What can be concluded about the rate law for the reverse reaction under these conditions?

(A) Rate = k_r[C]

(B) Rate = $k_r\frac{[C]}{[B]}$

(C) The rate law of the reverse reaction cannot be determined from the information given.

(D) An error must have been made, since if the reaction is reversible, the forward rate law must be Rate = k_f[A][B].

Topic: Elementary Rate Law | **Difficulty:** Hard | **Answer:** B

This question is tricky in many ways. First, you must realize that the reaction given is **not an elementary rate law**. If you chose (A)/(D) as your answer, you've fallen into the first trap. The second trap is not taking into consideration that **there are only a few plausible mechanisms**. If you chose (C), you fell into the second trap and didn't consider the fact that all of the reasonable mechanisms lead to one forward and reverse rate law.

So what is an example of a plausible mechanism? See below.

$$A \rightleftharpoons I \text{ (slow)}$$
$$I + B \rightleftharpoons C \text{ (fast)}$$

The first step is the rate-determining step, so we know that it is in agreement with the fact that the rate law of the reaction is k_f[A]. The reverse rate of this reaction would then be k_r[I] (remember that the above are **elementary rate laws**). To make things *look* easier, let's consider what the reverse reaction would look like:

$$C \rightleftharpoons I + B \text{ (fast)}$$
$$I \rightleftharpoons A \text{ (slow)}$$

This **meets the requirements to apply pre-equilibrium**. K = ([I][B])/[C], and solving this for [I], we get

$$[I] = K[C]/[B]$$

Plugging this into our reverse rate gives the answer as **(B)**.

Note: A participant brought a question whether the validity of this question would still hold if B was solid. Even if B was a solid (or a liquid), equilibrium will still be applied and this question would still be valid. In reality, **pure substances such as solids and liquids are contained in equilibrium**, but they are **omitted** as in most cases they are considered to stay relatively constant throughout the reaction. It is very similar to

pseudo reactions in kinetics, where one reactant's concentration is magnitudes higher than the other, that it can be considered to be constant throughout the reaction and its change is negligible.

If B was not considered because "it isn't present in the equilibrium expression", it would logically not make sense. If B isn't actually present in the equilibrium expression, then consider the situation where there is no B. Would the reaction still occur?

30. The oxidation of sulfite ion by triiodide ion is proposed to take place by the following mechanism:

$I_3^- \leftrightarrows I_2 + I^-$	*fast, unfavorable*
$SO_3^{2-} + I_2 \rightarrow ISO_3^- + I^-$	*slow*
$ISO_3^- + H_2O \rightarrow HSO_4^- + I^- + H^+$	*fast*

What rate law is predicted by this mechanism?

(A) Rate = $k[I_3^-]$

(B) Rate = $k[I_3^-][SO_3^{2-}]$

(C) Rate = $\frac{k[I_3^-][SO_3^{2-}]}{[I^-]}$

(D) Rate = $\frac{k[I_3^-][SO_3^{2-}]}{[H^+]}$

Topic: Pre-equilibrium | **Difficulty:** Moderate | **Answer:** C

The first step is unfavorable and fast. The second step is the rate-determining step. We can approximate that all of the species in the first step are at equilibrium throughout the reaction, because the first step is significantly faster than the second step. This is pre-equilibrium. Because the reaction rate is:

$$v = k[I_2][SO_3^{2-}]$$

We can use the equilibrium expression of the first step to substitute for $[I_2]$.

$$K = [I_2]/([I_3^-][I^-])$$

The answer is **(C)**.

34. A pure sample of a monoprotic acid is dissolved in water. The sample is titrated with sodium hydroxide solution. At the point where 20.0 mL of the NaOH solution has been added, the pH is 4.15. The phenolphthalein endpoint of the titration is observed when 50.0 mL of NaOH have been added. What is the pK_a of the acid?

(A) 4.15 **(B)** 4.33 **(C)** 4.55 **(D)** 5.19

Topic: HH equation | **Difficulty:** Moderate | **Answer:** B

We utilize the **Henderson-Hasselbalch equation** for this question. pH is given. You can calculate the ratio of $[A^-]/[HA]$ using the volume of NaOH used. Because 50.0 mL of NaOH is required to reach the endpoint, and 20.0 mL of NaOH is required to reach a pH of 4.15, if we assume that the molarity of the NaOH solution is k, we'd expect $20k$ mmol to exist as A^- and $30k$ mmol to exist as HA (because there is $50k$ mmol of acid in total, as proven by the endpoint). The ratio of $[A^-]/[HA]$ is therefore ⅔. The rest is plugging in numbers. You should get **(B)**.

35. Consider the reaction:

$$H_2(g) + I_2(g) \leftrightarrows 2\ HI(g) \qquad K_{eq} = ???$$

Into a 1.00 L vessel, 1.00 mol $H_2(g)$ and 1.00 mol $I_2(g)$ are placed at a high temperature. When the reaction mixture stops changing, it is found that 79.0% of the $H_2(g)$ has reacted. What is the equilibrium constant for this reaction at this temperature?

(A) 14.2 **(B)** 17.9 **(C)** 35.8 **(D)** 56.6

Topic: Equilibrium | **Difficulty:** Moderate | **Answer:** D

The difficulty of this question does not come from the question itself, but how many sillies are made on this type of question, despite the fact that it comes up almost every year.

If 79.0% of H_2 has reacted, then we expect 0.21 mol of H_2 **and** I_2 to be present at equilibrium. Because one mole of H_2 forms two moles of HI, we therefore expect 0.79 × 2 moles of HI to be present at equilibrium. We use the equilibrium expression to calculate the equilibrium constant, which is **(D)**.

39. Chromium is electroplated industrially by the electrolysis of solutions of $K_2Cr_2O_7$. How much time would be required to deposit 1.00 kg of Cr using a current of 200.0 A?

(A) 2.58 h **(B)** 7.74 h **(C)** 15.5 h **(D)** 31.0 h

Topic: Electrolysis | **Difficulty:** Moderate | **Answer:** C

Dichromate ($Cr_2O_7^{2-}$) is in a +6 oxidation state. Therefore, in order for one chromium atom in a +6 oxidation state to be reduced into its 0 oxidation state, it would require six electrons.

$$n_e = 6 \times m(\mathrm{Cr})/M_r(\mathrm{Cr}) = \mathrm{I}t/\mathrm{F}$$

The answer is **(C)**.

// Full solutions are being worked on.