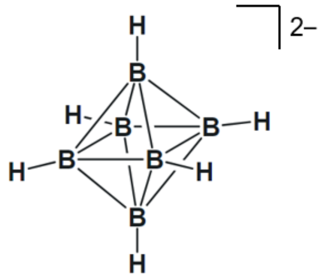
2024/25 Open Chemistry Olympiad Competition Problems
Junior group (Year 9 & 10)
21st september 2024

1. Molecular cage (10 p)

Closo-boranes (in Greek *closo* – cage-like) are polyhedral cyclic boron clusters with the general formula $[B_nH_n]^{2-}$, where n represents the number of boron and hydrogen atoms. In such a regular closed framework of boron atoms, each boron atom can be bonded to 3–6 neighboring atoms. For example, the structure of the octahedral hexahydrohexaborate anion $[B_6H_6]^{2-}$ is shown in the adjacent figure. The sodium salt of hexahydrohexaborate can be prepared by heating the toxic gas diborane (B_2H_6) with sodium borohydride ($NaBH_4$), where gaseous hydrogen is released as a by-product.



a) Write and balance the equation for the described synthesis of the sodium salt. (1)

b) Calculate how many electrons participate in forming the B–B and B–H bonds in total in the $[B_6H_6]^{2-}$ anion. (1)

In school chemistry, it is taught that a classical covalent bond is formed between atoms that share a pair of electrons. However, the $[B_6H_6]^{2-}$ anion is an electron-deficient structure, meaning that there are not exactly two outer-shell electrons available for each covalent bond between atoms.

c) Calculate the average number of electrons participating in the formation of a single covalent bond. Provide the result as a fractional number with three significant figures. (1)

d) Calculate the average charge carried by each boron atom in the $[B_6H_6]^{2-}$ anion, assuming the hydrogen atoms are neutral in charge. Give the answer with two significant figures. (1)

e) Determine by calculation the formula of a *closo*-borane that has 30 B–B bonds, where each boron atom is bonded to 5 other boron atoms. (1)

Boron-10 clusters are used in medicine for the treatment of cancer through neutron capture therapy, where boron compounds introduced into the body absorb irradiated neutrons. Upon absorbing a neutron (n), boron-10 transforms into radioactive boron-11, which decays and selectively damages cancer cells by producing particles **X** and **Y**.

$$^{10}_{5}\mathrm{B} + ^{1}_{0}\mathrm{n} \rightarrow [^{11}_{5}\mathrm{B}] \rightarrow ^{x}_{3}\mathbf{X} + ^{y}_{2}\mathbf{Y}$$

f) Determine **i)** elements **X** and **Y** and **ii)** the numerical values of the superscripts *x* and *y*. (2)

A certain boron compound (M = 219.9 g·mol^{-1}) contains 58.98% of boor-10 by mass. In the local injection solution used for therapy, the concentration of this compound is 0.05 g·cm^{-3}.

g) A patient is administered 50.00 cm^3 of the described solution. Calculate the number of boron-10 atoms in the administered solution. Avogadro's number N_A = 6.022·10^{23} mol^{-1}. (4)

2. The Charm of Doing It Yourself (10 p)

A bottle of syrup bought from the store had a label stating that the syrup contains 35% sugar, 35% plant extract, water, and citric acid. The label on the 0.5-liter bottle also provided the following instructions:

"To prepare the drink, mix the syrup with water in a volume ratio of 1 : 4."

a) Calculate how many grams of sugar are in one glass (2<u>0</u>0 ml) of syrup water, assuming the syrup's density is 1.15 g·cm^{-3}. The added sugar is sucrose. To simplify calculations, assume there is no sugar in the plant extract. (1)

b) Calculate the mass percentage of sugar in the syrup water. (1)

Mari grows red currants in her garden, from which she wants to make syrup for the winter. Mari added 500 ml of water and 800 g of sucrose for every 1.0 kg of berries. Red currants contain, per 1<u>0</u>0 g 0.61 g sucrose ($C_{12}H_{22}O_{11}$), 3.22 g glucose ($C_6H_{12}O_6$) and 3.53 g fructose ($C_6H_{12}O_6$).

c) Calculate the total sugar content (%) in Mari's syrup. To simplify, ignore any mass loss (such as the sieved mass of berry skins and seeds or evaporated water) during the syrup preparation. (1)

Mari wanted to prepare lemonade from the syrup with an approximate sugar content of 7%.

d) Calculate the ratio in which she should mix syrup and water. Give the ratio as a decimal with one significant figure. (1)

To achieve a fizzy effect, Mari added baking soda and 50 ml of lemon juice (ρ = 1.33 g·cm^{-3}), which contains 8% triprotic citric acid ($C_6H_8O_7$), to 2 liters of the drink (ρ = 1.03 g·cm^{-3}). Since acidity improves the taste, it's important that the acid is in excess.

e) Write and balance the reaction equation between citric acid and baking soda. (1)

f) Calculate the maximum amount (in grams) of baking soda Mari could add to the lemonade. Use the reaction equation to determine the amount that would react with the citric acid in the added lemon juice. (2)

g) Calculate the total sugar concentration (mol·dm^{-3}) in Mari's lemonade. (3)

3. Spectroscopy of Exoplanets (10 p)

The James Webb Space Telescope (JWST) is the largest infrared space observatory, launched into space on December 25, 2021. The infrared range allows for the study of both the earliest galaxies and the chemistry of exoplanet atmospheres using vibrational spectroscopy.

Molecules are not rigid but can vibrate. Each molecule has so-called vibrational modes, which are independent internal oscillations with specific vibrational energy and oscillation frequency.

One molecule found on exoplanets is carbon monoxide, whose only possible vibrational mode is the stretching of the C≡O bond. The oscillation frequency of a diatomic molecule can be calculated using the following formula, where k is the bond stiffness constant and μ is the reduced mass:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

The reduced mass is given as follows, where m_1 and m_2 are the masses of the atoms:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

a) Calculate the oscillation frequency of CO if the stiffness constant of the C≡O bond is 1860 kg·s^{-2}. (3)

When observing molecular movements, it is important to note that these are quantum mechanical objects. Vibrations are quantized, meaning that each vibrational mode of a molecule has multiple integer vibrational levels. The energy of a vibrational level E is expressed as follows, where h is Planck's constant (6,62·10^{-34} J·s) and n = 0, 1, 2, 3 etc., is the vibrational level number:

$$E = \left(\frac{1}{2} + n\right)h\nu$$

In spectroscopy, the interaction of molecules with light is important. Internal charges within a molecule oscillate during vibration, interacting with the electric field of light radiation. A molecule can absorb a photon of light if the energy of the photon matches the energy difference between the vibrational levels of the molecule. The energy of a photon E is given by $E = hc/\lambda$, where λ is the wavelength and c is the speed of light in a vacuum (300000 km·s^{-1}).

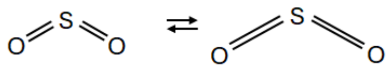
b) Calculate the maximum wavelength λ characterizing the vibration of CO in micrometers (μm). (2)

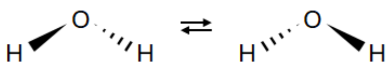
A multi-atom molecule, consisting of more than two atoms, can have several different vibrational modes. The independent movements of atoms, when combined, describe the movement of the entire molecule. The combined movement of a molecule can consist of the following types:

– Spatial movement of the molecule due to displacement of its center of mass;
– Rotation of the molecule around its axis;

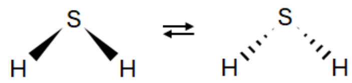
– Internal vibration of the molecule.

c) Indicate which of the following internal movements of molecules are internal vibrations that do not cause the molecule to rotate. Assume that the center of mass of the molecules does not change. (3)

i)


ii)


iii)


iv)


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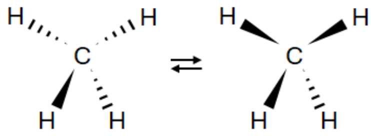

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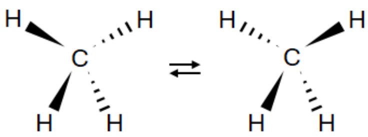
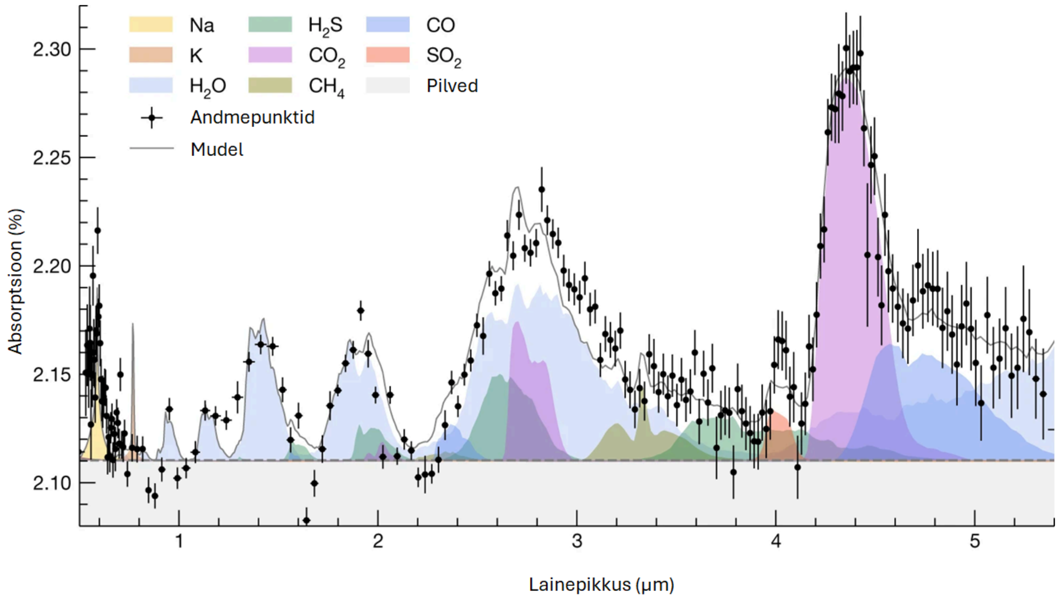


The figure below shows the JWST infrared absorption spectrum from the exoplanet WASP-39 b. The regions of vibrational modes for the molecules marked in the spectrum are indicated in different colors.



WASP-39 b is a gas giant whose atmosphere contains several hydrogen-bearing substances such as H_2, H_2S, CH_4 and H_2O. According to this spectrum, the amounts of H_2S and CH_4 are much lower than expected. The presence of SO_2 is also surprising. It is believed that since WASP-39 b is very close to its system's central star, SO_2 is the product of certain photochemical catalysis.

d) Write and balance the equation for the photochemical formation of SO_2 that could occur in the atmosphere of WASP-39 b. (1)

The vibrational modes of gaseous H_2 are absent from the spectrum.

e) Choose the correct ending to the statement: "The vibrational modes of H_2 do not appear in the spectrum because… (1)

- ☐ …H_2 reacts photocatalytically with CO and CO_2 in the Sabatier process."
- ☐ …H_2 does not acquire an electric dipole. Therefore, the molecule does not interact with photons."

- ☐ …the electric dipole of H_2 does not change during vibration. Therefore, the molecule does not interact with photons."
- ☐ …H_2 reacts with O_2 (whose spectral lines are also absent), forming H_2O."

4. Fire starter from milk **(10 p)**

Mikk read the label on a milk carton and noticed the word "magnesium." While hiking, he usually uses a magnesium fire stick, and he wondered if magnesium found in milk could be used to make a fire stick. Mikk found that the best source of magnesium is dried whey—milk from which almost all the fat has been removed. To determine the magnesium content, he dissolved 6 g of whey in a volumetric flask with distilled water and adjusted the volume to exactly 100 cubic centimeters. He then took a 10.0 cm^3 sample of the solution, added a buffer, and titrated it with a 0.200 M EDTA solution to the stoichiometric point. On average, it took 1.11 cm^3 of the EDTA solution to titrate one sample. The reaction occurring with both calcium and magnesium is:

$$M^{2+} + EDTA^{4-} \rightarrow MEDTA^{2-}$$

a) Calculate the total amount of Mg^{2+} and Ca^{2+} ions in 6 g of whey (mol). (1.5)

b) Calculate how many mg of magnesium are in 500.0 g of whey if the amount of magnesium in milk is 10 times less by mass compared to calcium. (3)

To Mikk's disappointment, there was not enough magnesium in the whey he purchased to make a fire stick, but he decided to isolate pure magnesium. To do this, Mikk dissolved 500.0 g of whey in distilled water and added calcium hydroxide to the solution, causing the magnesium ions to react with the hydroxide ions and precipitate out of the solution.

c) Write and balance the equation for the reaction that occurred. (1)

Mikk filtered and dried the resulting precipitate and added hydrochloric acid to obtain magnesium chloride. He then decided to electrolyze the resulting salt solution to obtain pure magnesium. He believed that magnesium should precipitate at one electrode while chlorine would evolve at the other, but gas evolved at both electrodes.

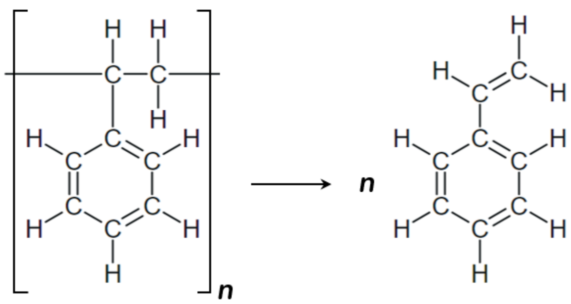
d) Write and balance the equations for the following reactions:

- **i)** anode reaction; (1)
- **ii)** cathode reaction; (1)
- **iii)** overall electrolysis reaction. (1)

e) Mikk used a battery with a current of 2 A for the electrolysis and electrolyzed the solution for one minute. Calculate how many cm^3 of gaseous chlorine Mikk produced, given that the loss during electrolysis was 90%. *Hint: The reaction was conducted at a temperature of 0 °C, $n = (I \cdot t)/(z \cdot F)$, $F = 96485\ C \cdot mol^{-1}$.* (1.5)

5. Cinnamon Rolls from Styrofoam **(9 p)**

Hobby chemist Jesse wanted to bake cinnamon rolls but discovered that he was out of cinnamon. However, Jesse had a large amount of styrofoam, which consists of polystyrene. The young chemistry enthusiast knew that polystyrene is made up of a number of n styrene (C_6H_5–CH=CH_2) monomers, which can be synthesized into cinnamaldehyde. Cinnamaldehyde gives cinnamon its characteristic taste and smell. To break down the polystyrene into styrene, Jesse needed magnesium oxide as a catalyst:

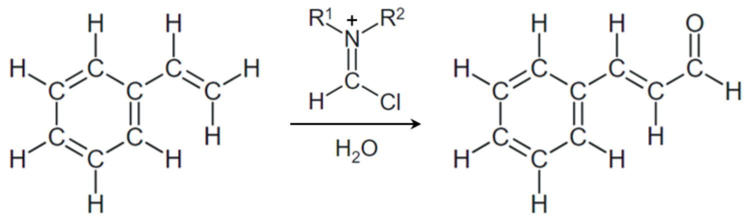


a) Write and balance the equation for the formation of magnesium oxide, using simple substances as reactants. (1)

The average molar mass of polystyrene is 350 kg·mol^{-1}.

b) Calculate how many styrene molecules on average can be obtained from breaking down one molecule of polystyrene. (1)

For one tray of cinnamon rolls, 5 teaspoons (1 tsp. = 5 cm^3) of cinnamon is needed. The density of cinnamon is ρ = 0.446 g·cm^{-3} and 1 g of cinnamon contains approximately 18 mg of cinnamaldehyde. Cinnamaldehyde can be synthesised from styrene using the Vilsmeier-Haack reaction shown below:



c) Calculate how many cm^3 of polystyrene (ρ = 28.0 kg·m^{-3}) Jesse needs to bake one tray of cinnamon rolls, assuming the synthesis yield is 40%. (3.5)

To make the dough rise, Jesse had to choose between three gas-producing reactions – fermenting glucose with yeast to produce ethanol, the thermal decomposition of baking soda (sodium bicarbonate), or a reaction of baking powder. Baking powder contains ammonium bicarbonate and diprotic tartaric acid.

d) Complete and balance the equations for reactions **i)–iii)**. (3)

i) $C_6H_{12}O_6 \rightarrow C_2H_5OH + \ldots$

ii) $NaHCO_3 \rightarrow \ldots + \ldots + \ldots$

iii) $NH_4HCO_3 + C_4H_6O_6 \rightarrow \ldots + \ldots + \ldots$

Jesse decided to use the chemical reaction that would produce the most gas per mole of reactant to make the dough rise.

e) Choose, whether Jesse used the glucose fermentation reaction, the thermal decomposition of baking soda, or baking powder to obtain the greatest amount of gas. (0.5)

6. Poisonous gases (10 p)

Compound **X**, which in its pure form is a volatile oily liquid at room temperature, consists of four elements: carbon, nitrogen, oxygen, and chlorine. In a container with a volume of 0.50 dm^3 2.25 g of **X** was fully vaporized at 110 °C. It was found that the pressure exerted by the gas in the container was 0.8604 atm. The gas constant R = 0.0821 dm^3·atm/mol^{-1}·K^{-1}.

a) Calculate the molar mass of gas **X**. (2)

The molecule of **X** contains a total of seven atoms, none of which are bonded to another atom of the same element. The atoms of the two elements with the lowest electronegativity form four bonds. Upon pyrolysis of **X** a chlorine-containing poisonous gas **Y** (M = 99.01 g·mol^{-1}) that was widely used during World War I, nitrogen monoxide, and chlorine are produced (**reaction 1**). When 0.10 g of gaseous **Y** is dissolved in 55.00 cm^3 of water, all the chlorine in the compound hydrolyzes into hydrochloric acid, and carbon dioxide is released (**reaction 2**).

b) Determine the mass percentage of chlorine in compound **Y** and the molecular formula of **Y** through calculations, assuming that titration of the acidic aqueous solution requires 23.63 cm^3 0.0855 M sodium hydroxide solution. Assume that the titrant reacts only with the hydrochloric acid present in the solution. (3)

c) Determine the molecular formula of compound **X**. (1)

d) Write and balance the equations corresponding to **reactions 1–2**. (2)

e) Draw the structure formulas of **X** ja **Y**. Clearly show all chemical bonds between atoms, and charges where necessary. (2)

7. Poisoning of the hatter **(10 p)**

Metal **X** is named after the ancient Roman god of commerce, and due to its unusual state of matter, it has been used in thermometers. Both the vapors of this metal and its compounds are highly toxic, and alchemists believed that **X** could turn other metals into gold.

a) Write the symbol and name of metal **X**. (1)

A few hundred years ago, assassin Z007 was tasked with using metal **X** to kill the town's hatter. The person ordering the murder knew that such a death wouldn't raise suspicion because hatters used compounds of metal **X** in their work. Z007 learned from pharmacists that chloride salt **Y** of metal **X** had been used as a treatment for constipation. Thus, Z007 decided to prepare a medicinal compound with a higher dose of poison.

First, Z007 tried reacting metal **X** with hydrochloric acid, but there was no reaction. To make sure the problem wasn't with the metal, he dropped a piece of metal into a solution of nitric acid. Bubbles of a gas consisting of two elements began to form from the solution, confirming that the issue was with the hydrochloric acid (**reactions 1 ja 2** – in both parallel reactions, the products include nitrates of metal **X**, where the oxidation states of **X** differ). Z007 found in an alchemy book that metal **X** reacts with aqua regia (a mixture of hydrochloric acid and nitric acid in a volume ratio of 3 : 1), producing a chloride salt where **X** has an oxidation state of +II, along with nitrosyl chloride and water (**reaction 3)**.

b) Write and balance the equations for **reactions 1–3**. (6)

To prepare the compound in the medicine, Z007 took the chloride salt obtained from reaction 3 and heated it with metal **X**, producing salt **Y** (**reaction 4**), in which the mass percentage of chlorine is 15.02%.

c) Write and balance the equation for this reaction. (2)

When dissolved in water, the cation of salt **Y** undergoes disproportionation into the $\mathbf{X}^{2+}$ ion and elemental **X**, which results in the toxic effect of the salt (**reaction 5**).

d) Write and balance the ionic equation for the disproportionation reaction. (1)

8. Unit cells **(10 p)**

In solid substances, particles can be arranged in various ways. The concept of a "unit cell," which is the smallest repeating unit in a crystal structure, is used to describe the structures of crystalline materials. At 20 °C, the unit cell formed by nickel atoms is cubic, and the length of the unit cell edge is 0.352 nm. The density of nickel is 8.94 $g \cdot cm^{-3}$.

a) Calculate the number of nickel atoms in one unit cell, given that $N_A = 6.022 \cdot 10^{23}$ mol^{-1}. (2)

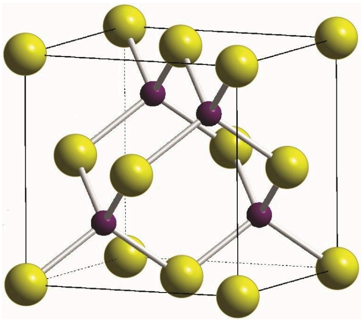
Since the atoms are spherical, but the nickel crystal lattice is cubic, the nickel atoms only occupy 74.0% of the volume of the crystal lattice.

b) Calculate the radius of a nickel atom. *Hint: The volume of a sphere* $V = 4/3\pi r^3$. (2)

c) Choose how the density of nickel changed with increasing temperature. (1)

- ☐ The density increased.
- ☐ The density decreased.
- ☐ The density did not change.

The concept of a unit cell can also be applied to crystals made of several different elements. An unknown metal **M** forms a crystal with sulfur, and the unit cell of this crystal is shown in the diagram. The edge length of the cubic unit cell is 540.6 pm and the crystal's density is 4.098 $g \cdot cm^{-3}$.



d) Calculate how many sulfur (yellow) and metal **M** (purple) ions are in one unit cell. *Hint: An ion at the corner of a unit cell counts as ⅛ in the unit cell, an ion on the edge counts as ½, and an ion inside the unit cell counts as one.* (1)

e) Identify metal **M** through calculations. (4)

9. From liquid to gas (10 p)

The state of a pure substance (solid, liquid, or gas) depends on both the system's temperature and pressure. An important concept for understanding these states is vapor pressure, which is the pressure exerted by the vapor in equilibrium with its liquid or solid phase at a given temperature. For example, liquid water in equilibrium with its vapor at 298 K has a vapor pressure of 3.17 kPa. When the vapor pressure equals the surrounding environmental pressure, the substance begins to boil or sublimate.

a) The boiling point of ethanol at standard pressure is 351.4 K. Write down the vapor pressure of ethanol at its boiling point. (1)

b) The vapor pressure of propane is 586 kPa at 280 K and 1020 kPa at 300 K. Determine whether propane is in the gaseous or liquid state under the following conditions: (1)

Pressure, P (kPa)	Temperature, T (K)	State
500	280	gas/liquid
500	300	gas/liquid
1000	280	gas/liquid
1000	300	gas/liquid

In solutions with two or more substances, each component has its own vapor pressure, known as the partial vapor pressure of that component. The total vapor pressure of the solution equals the sum of the vapor pressures of its components. To calculate partial vapor pressures, Raoult's law is used, where P_i^0 is the vapor pressure of the pure substance and X_i is the mole fraction of the component in the solution:

$$P_i = P_i^0 X_i$$

At 300 K, the vapor pressure of acetone (C_3H_6O) is 33.3 kPa, and the vapor pressure of methanol (CH_3OH) is 18.7 kPa. The solution contains 5.00 g of acetone and 5.00 g of methanol.

c) Calculate the partial vapor pressures of acetone and methanol, and the total vapor pressure of the solution. (5)

d) Calculate the mole fraction of acetone in the vapor above the mixture, based on the partial vapor pressures calculated in the previous question. (1)

Raoult's law and the dependence of vapor pressure on temperature explain why non-volatile solutes raise the boiling point of the solvent. This phenomenon is known as the boiling point elevation of solutions. 30.0 g of sodium chloride was dissolved in 100 g of water.

e) Calculate the mole fraction of the solute in the solution. (1)

f) Which of the following statements correctly explains why non-volatile solutes raise the boiling point of the solvent? (1)

- ☐ Non-volatile solutes increase the vapor pressure of the solution, making it easier for the solvent to enter the gas phase.

- ☐ Non-volatile solutes decrease the vapor pressure of the solution, making it harder for the solvent to enter the gas phase.
- ☐ Dissolved particles weaken the intermolecular forces between solvent molecules, increasing the energy required to vaporize the solution.