18

Phase equilibrium and solutions

Answers to worked examples

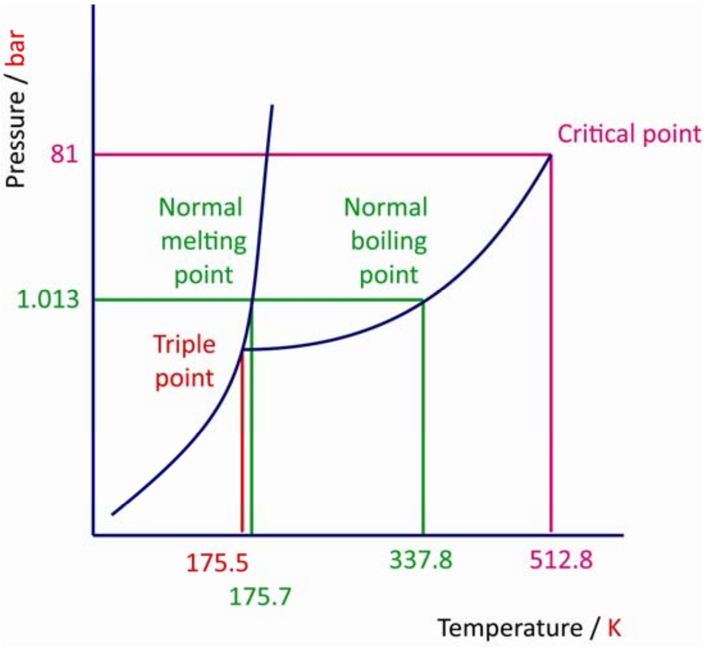
WE 18.1 Using a phase diagram

The normal melting and boiling points for methanol (CH_3OH) are 175.7 K and 337.8 K, respectively. The critical temperature and pressure are 512.8 K and 81 bar. The triple point occurs at 175.5 K. Sketch (not to scale) the single-component phase diagram for methanol.

Strategy

Consider Figure 18.4, which shows a typical phase diagram for a one-component system. Remember that the normal melting and boiling points correspond to a pressure of 1 atm = 1.013 bar.

Solution



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WE 18.3 Using the Clausius–Clapeyron equation

Find the vapour pressure of benzene at 325 K.

Strategy

Apply the particular form of the Clausius–Clapeyron equation, Equation 18.8, for the calculation of the vapour pressure, using the value for the enthalpy of vaporization from the Worked Example.

Solution

The integrated form of the Clausius–Clapeyron equation, Equation 18.7,

$$\ln\frac{p_2}{p_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

becomes Equation 18.8, if the normal boiling temperature is known

$$\ln\frac{1.01325 \times 10^5\,\mathrm{Pa}}{p} = \frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_\mathrm{b}}\right)$$

Rearranging this equation gives an expression for the vapour pressure at a particular temperature

$$\begin{aligned}\ln(p/1.01325 \times 10^5\,\mathrm{Pa}) &= -\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_\mathrm{b}}\right)\\ &= -\frac{30.8 \times 10^3\,\mathrm{J\ mol^{-1}}}{8.3145\ \mathrm{J\ K^{-1} mol^{-1}}}\left(\frac{1}{325\ \mathrm{K}} - \frac{1}{353\ \mathrm{K}}\right)\\ &= -0.904\end{aligned}$$

Thus,

$$p = e^{-0.904} \times 1.01325 \times 10^5\,\mathrm{Pa} = 41.0 \times 10^3\,\mathrm{Pa} = 41.0\ \mathrm{kPa}$$

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WE 18.5 Deviations from Raoult's law

In a mixture of ethanol and trichloromethane, the mole fraction of ethanol is 0.6. The vapour pressure of ethanol above the mixture is 0.087 bar and that of trichloromethane is 0.256 bar. Calculate the activity coefficient of each component.

(At the same temperature, the saturated vapour pressures of the pure components are: ethanol 0.137 bar and trichloromethane 0.393 bar.)

Strategy

Rearrange Equation 18.25, which defines the vapour pressure of a real component in terms of the mole fraction in the liquid, the vapour pressure when pure and the activity coefficient.

Solution

From Equation 18.25,

$$p_{\mathrm{E}}(\mathrm{real}) = \gamma_{\mathrm{E}} x_{\mathrm{E}} p_{\mathrm{E}}$$

then

$$\gamma_{\mathrm{E}} = p_{\mathrm{E}}(\mathrm{real})/x_{\mathrm{E}} p_{\mathrm{E}} = 0.087\ \mathrm{bar}/(0.6 \times 0.137\ \mathrm{bar}) = 1.06$$

There are only two components, so that

$$x_{\mathrm{E}} + x_{\mathrm{T}} = 1$$

and therefore

$$x_{\mathrm{T}} = 1 - x_{\mathrm{E}} = 1 - 0.6 = 0.4$$

Hence

$$\gamma_{\mathrm{T}} = p_{\mathrm{T}}(\mathrm{real})/x_{\mathrm{T}} p_{\mathrm{T}} = 0.256\ \mathrm{bar}/(0.4 \times 0.393\ \mathrm{bar}) = 1.63$$

WE 18.7 Using osmosis to find relative molecular mass, M_r

Lysozyme is a protein with M_r = 16 500. What is the osmotic pressure generated at 298 K by a solution of 1.00 g of lysozyme in 50.00 cm^3 of water?

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Strategy

Calculate the molar concentration and use Equation 18.28 to determine the osmotic pressure.

Solution

A mass of 1.00 g of lysozyme corresponds to an amount

$$n_\mathrm{L} = m_\mathrm{L}/M_\mathrm{L} = 1.00\ \mathrm{g}/16500\ \mathrm{g\ mol^{-1}} = 6.06 \times 10^{-5}\mathrm{mol}$$

and therefore a concentration of

$$c = n_\mathrm{L}/V = 6.06 \times 10^{-5}\mathrm{mol}/50.00\ \mathrm{cm^3} = 1.21 \times 10^{-6}\mathrm{mol\ cm^{-3}} = 1.21\ \mathrm{mol\ m^{-3}}$$

Using Equation 18.28, the osmotic pressure is

$$\begin{aligned}\pi &= cRT\\ &= 1.21\ \mathrm{mol\ m^{-3}} \times 8.3145\ \mathrm{J\ K^{-1}mol^{-1}} \times 298\ \mathrm{K}\\ &= 3000\ \mathrm{J\ m^{-3}} = 3000\ \mathrm{Pa} = 3.00\ \mathrm{kPa}\end{aligned}$$

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Answers to boxes

Box 18.1 Liquid crystals

Suggest some reasons why cyanobiphenyls form mesophases.

Strategy

Consider the structure of the molecules and the effect of the alkyl chains and polar head groups on the rigidity and polarity of the molecules.

Solution

The cyanobiphenyls are relatively flat molecules. The rigid biphenyl groups tend to line up to give an ordered crystalline material—but the alkyl chains introduce enough flexibility to stop well-ordered crystals forming at anything but low temperatures. The polar –CN group means that the molecules can be influenced by an electric field.

Box 18.5 Reverse osmosis and water purification

1 dm^3 of sea water contains about 35 g of dissolved substances. Assuming that this is all sodium chloride, estimate the minimum pressure needed for reverse osmosis to take place at 25 °C.

Strategy

Calculate the concentration of sodium chloride in sea water and apply Euqation 18.28.

Solution

The molar mass of sodium chloride is

$$M = (23.99 + 35.45)\ \mathrm{g\ mol^{-1}} = 59.44\ \mathrm{g\ mol^{-1}}$$

Thus, 35 g of dissolved substances, would correspond, from Equation 1.2, to an amount

$$n = m/M = 35\ \mathrm{g}/59.44\ \mathrm{g\ mol^{-1}} = 0.59\ \mathrm{mol}$$

This amount of sodium chloride would result in

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$$2 \times 0.59 \text{ mol} = 1.2 \text{ mol}$$

of ions, because every NaCl unit results in a Na^+ and a Cl^- ion. This is the amount dissolved in 1 dm^3, so that the concentration of ions in solution must be 1.2 mol dm^{-3}. From Equation 18.28, the osmotic pressure that would be generated by a solution with this concentration is

$$\pi = cRT = 1.2 \times 10^3 \text{ mol m}^{-3} \times 8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}$$
$$= 2.9 \times 10^6 \text{ Pa} = 2.9 \text{ MPa} = 29 \text{ bar}$$

A minimum pressure of 29 bar would be needed to prevent osmosis taking place and the pressure used would need to be somewhat higher to force water through the membrane against this osmotic pressure. In fact, sea water contains around 27 g dm^{-3} of NaCl, the remainder being other salts. The above calculation relies on the van't Hoff equation, Equation 18.28, which assumes ideal behaviour. Aqueous solutions of salt at high concentrations will not act ideally so that the pressure calculated here is only an estimate. However, it does show that high pressures are needed for reverse osmosis to operate efficiently.

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Answers to end of chapter questions

1. Figure 1 shows a generalised phase diagram.

(a) What phase(s) is/are present at W, X, Y and Z?

(b) What is the significance of points X, Y, T and C?

(c) What phase change would occur if you started at point U and

(i) increased the temperature with the pressure constant?

(ii) increased the pressure with the temperature constant?

Strategy

Compare the phase diagram with the typical single-component diagrams shown in Figure 18.4.

Solution

(a) W, solid; X, solid and liquid; Y, liquid and vapour; Z, vapour.

(b) X, normal melting point; Y, normal boiling point; T, triple point; C, critical point.

(c) (i) The liquid would boil at the temperature and pressure indicated by the liquid–vapour equilibrium curve between the triple point, T, and critical point C.

(ii) The liquid would eventually solidify, or freeze, at the pressure and temperature indicated by the solid–liquid equilibrium line that passes from the triple point, T, through X.

3. Mercury has a melting point of 234.3 K. At this temperature, the density of Hg (l) is 13.690 g cm^{-3} and that of Hg (s) is 14.193 g cm^{-3}. The enthalpy change of fusion is 9.75 J g^{-1}. Find the pressure needed to change the melting temperature by 1 K.

Strategy

Use the Clausius–Clapeyron equation, Equation 18.4. There is no need to calculate the molar volume change and molar enthalpy change using the molar mass. Instead, calculate the volume change per unit mass from the density and use the enthalpy change per unit mass as given.

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Solution

The Clapeyron equation, Equation 18.4, has the form

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{fus}}H}{T\Delta_{\mathrm{fus}}V}$$

The change in volume on melting of 1 g is

$$\Delta_{\mathrm{fus}}V = V(\mathrm{liquid}) - V(\mathrm{solid})$$

where, because the volume may be expressed in terms of the mass and the density as

$$V = 1/\rho$$

then

$$\begin{aligned}\Delta_{\mathrm{fus}}V &= 1/\rho_{\mathrm{m}}(\mathrm{liquid}) - 1/\rho_{\mathrm{m}}(\mathrm{solid})\\ &= (1/13.690\ \mathrm{g\ cm^{-3}} - 1/14.193\ \mathrm{g\ cm^{-3}})\\ &= +2.589\times10^{-3}\ \mathrm{cm^3\ g^{-1}}\\ &= +2.589\times10^{-9}\ \mathrm{m^3\ g^{-1}}\end{aligned}$$

Then, because the enthalpy change for 1 g is

$$\Delta_{\mathrm{fus}}H = +9.75\ \mathrm{J\ g^{-1}}$$

then, at a temperature of 234.3 K, the gradient of the pressure–temperature line on the phase diagram is

$$\begin{aligned}\frac{\mathrm{d}p}{\mathrm{d}T} &= \frac{+9.75\ \mathrm{J\ g^{-1}}}{234.3\ \mathrm{K}\times 2.589\times10^{-9}\ \mathrm{m^3\ mol^{-1}}}\\ &= 16.1\times10^{6}\ \mathrm{J\ m^{-3}K^{-1}} = 16.1\times10^{6}\ \mathrm{Pa\ K^{-1}}\end{aligned}$$

Assuming that the solid–liquid equilibrium forms a straight line on the pressure–temperature phase diagram, then

$$\frac{\Delta p}{\Delta T} = 16.1\times10^{6}\ \mathrm{Pa\ K^{-1}}$$

so that a temperature change of $\Delta T = +1$ K requires a change in pressure of

$$\Delta p = 16.1\ \times10^{6}\ \mathrm{Pa\ K^{-1}}\times\ \Delta T\ = 16.1\times10^{6}\ \mathrm{Pa\ K^{-1}}\times 1\ \mathrm{K} = 16.1\ \mathrm{MPa}$$

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5. Explain the observation that if a liquid evaporates from an open container, the temperature remains about constant but if it evaporates from an insulated flask, the temperature falls.

Strategy

Vaporization is an endothermic process. Consider from where the heat may be supplied in the two containers.

Solution

Vaporization is an endothermic process and so requires an input of energy. In an open container the energy can come from the surroundings so the temperature does not change very much. In an insulated container, the energy has to come from the liquid so that it cools down.

7. Mount Everest is the highest mountain on Earth with a height of 8850 m. At this altitude, the atmospheric pressure is about one-third that at sea-level. Find the melting and boiling temperatures of water at this pressure.

(The densities of ice and water at 0°C are 0.92 and 1.00 g cm^{-3}, respectively, and the enthalpy change of fusion of ice is +6.01 kJ mol^{-1}. The enthalpy change of vaporization of H_2O (l) at the normal boiling point is +40.7 kJ mol^{-1}.)

Strategy

For the melting temperature, calculate the molar volume change on melting and substitute into the Clapeyron equation, Equation 18.4. Use the Clausius–Clapeyron equation, Equation 18.7, for the boiling temperature.

Solution

The Clapeyron equation, Equation 18.4, has the form

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{trans}}H}{T\Delta_{\mathrm{trans}}V}$$

The change in molar volume on melting is

$$\Delta_{\mathrm{fus}}V = V(\mathrm{liquid}) - V(\mathrm{solid}) =$$

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where, because the molar volume may be expressed in terms of the molar mass and the density as

$$V_\mathrm{m} = M/\rho$$

then, because the molar mass of water is

$$M = [16.00 + (2 \times 1.01)]\ \mathrm{g\ mol^{-1}} = 18.02\ \mathrm{g\ mol^{-1}}$$

then

$$\begin{aligned}\Delta_\mathrm{fus} V_\mathrm{m} &= M/\rho_\mathrm{m}(\mathrm{liquid}) - M/\rho_\mathrm{m}(\mathrm{solid})\\ &= M/\big(1/\rho_\mathrm{m}(\mathrm{liquid}) - 1/\rho_\mathrm{m}(\mathrm{solid})\big)\\ &= 18.02\ \mathrm{g\ mol^{-1}}(1/1.00\ \mathrm{g\ cm^{-3}} - 1/0.92\ \mathrm{g\ cm^{-3}})\\ &= -1.57\ \mathrm{cm^3\ mol^{-1}}\\ &= -1.57 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}}\end{aligned}$$

Using the Clapeyron equation to find how melting temperature varies with pressure at 273 K

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_\mathrm{fus} H}{T\Delta_\mathrm{fus} V} = \frac{6.01 \times 10^3\mathrm{J\ mol^{-1}}}{273\ \mathrm{K} \times -1.57 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}}} = -14.0 \times 10^6\ \mathrm{Pa\ K^{-1}}$$

Hence, the change in melting temperature for a change in pressure is given by

$$\Delta T = -\Delta p/14.0 \times 10^6\ \mathrm{Pa\ K^{-1}}$$

Thus, if the pressure at the top of Mount Everest is a third of that at sea level,

$$\Delta p = 0.333\ \mathrm{atm} - 1.000\ \mathrm{atm} = -0.666\ \mathrm{atm}$$

which is equivalent to

$$\Delta p = 0.666\ \mathrm{atm} \times 1.01325 \times 10^5\mathrm{Pa\ atm^{-1}} = -67.5 \times 10^3\mathrm{Pa}$$

The melting temperature therefore changes by

$$\Delta T = -67.5 \times 10^3\mathrm{Pa}/-14.0 \times 10^6\ \mathrm{Pa\ K^{-1}} = +0.005\ \mathrm{K}$$

The melting temperature of ice therefore increases by 5 mK from sea level to the top of Mount Everest.

Using the Clausius–Clapeyron equation, Equation 18.7

$$\ln\frac{p_2}{p_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

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to determine the effect of the change in pressure on the boiling temperature, then, if the ratio of the pressures at sea level and at the top of Mount Everest is

$$\frac{p_2}{p_1} = \frac{0.333\ \text{atm}}{1.000\ \text{atm}} = 0.333$$

and the boiling temperature at sea level is 373 K, then substituting gives

$$\ln 0.333 = \frac{40.7 \times 10^3 \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\text{mol}^{-1}}\left(\frac{1}{373\ \text{K}} - \frac{1}{T_\text{b}}\right)$$

and solving for the unknown boiling temperature at the top of Mount Everest gives

$$T_\text{b} = 344\ \text{K}$$

The change in pressure therefore has a much greater effect on the boiling temperature than the melting temperature.

9. Which of the following pairs of compounds would you expect to have the higher enthalpy change of vaporization? Give the reason for your answer in each case.

(a) ethanol and methoxymethane

(b) propane and methoxymethane

(c) butane and propanone

(d) *E*-1,2-dichloroethene and *Z*-1,2-dichloroethene

Strategy

Consider the types of intermolecular interaction. Stronger interactions such as those arising from hydrogen bonding or between polar molecules will lead to higher values of enthalpy of vaporization.

Solution

(a) Ethanol can form hydrogen bonds whereas methoxymethane cannot. Hence ethanol would have the higher enthalpy change of vaporization.

(b) The two compounds are similar in size and so similar dispersion interactions would be expected. Methoxymethane is polar and has a dipole moment whereas propane is non polar. Methoxymethane would have the higher enthalpy change

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of vaporization.

(c) Butane is non-polar and has only dispersion interactions. Propanone has a similar size and so similar dispersion interactions might be expected. However, the carbonyl bond is polar and so propanone also has polar interactions. Propanone would thus have the higher enthalpy change of vaporization.

(d) *E*-1,2-dichloroethene is polar and so has dipole interactions. *Z*-1,2-dichloroethene has no overall dipole since the two individual dipoles cancel out. Hence *E*-1,2-dichloroethene would have the higher enthalpy change of vaporization.

11. The vapour pressure of pure $CHCl_3$ at 318 K is 58 kPa. What would be the partial vapour pressure of $CHCl_3$ above a mixture of 1 mol of $CHCl_3$ with 1 mol of ethanol, assuming the mixture behaves as an ideal solution? Comment on the fact that the measured value of the partial vapour pressure of $CHCl_3$ above the mixture is 42 kPa.

Strategy

Deduce the mole fraction of dichloromethane, $CHCl_3$, and use Raoult's law, Equation 18.23, along with the vapour pressures of the pure liquid to determine the total pressure.

Solution

The mixture is equimolar, so that

$$x_{\mathrm{C_2H_5OH}} = x_{\mathrm{CHCl_3}} = 0.5$$

Then, using Equation 18.23,

$$p_{\mathrm{CHCl_3}} = x_{\mathrm{CHCl_3}} p^{\mathrm{o}}_{\mathrm{CHCl_3}} = 0.5 \times 58\ \mathrm{kPa} = 29\ \mathrm{kPa}$$

The real vapour pressure, 42 kPa, is greater than the ideal value. This system therefore shows positive deviations from Raoult's law. Each component disrupts the polar interactions in the pure components so that interactions between dichloromethane and ethanol in the mixture are weaker than those in the pure components.

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13. In a solution of ethanol ($p°$ = 0.174 bar) and 2-methylhexane ($p°$ = 0.059 bar), the mole fraction of ethanol, x_{ethanol}, is 0.90. The vapour in equilibrium with the solution has a total vapour pressure of 0.248 bar. The mole fraction of ethanol in the vapour is 0.67. Calculate the activity coefficients of each component in the solution.

Strategy

Use Dalton's law to determine the partial pressure of ethanol, and hence 2-methylhexane, in the vapour. Then use Equation 18.25 to determine the activity coefficient for the two components.

Solution

The mole fraction of ethanol in the vapour phase is

$$y_{\mathrm{E}} = 0.67$$

and therefore of 2-methylhexane is

$$y_{\mathrm{M}} = 1 - y_{\mathrm{E}} = 1 - 0.67 = 0.33$$

The partial pressures of the two components are thus

$$p_{\mathrm{E}} = x_{\mathrm{E}} p_{\text{total}} = 0.67 \times 0.248\ \text{bar} = 0.166\ \text{bar}$$

and

$$p_{\mathrm{M}} = x_{M} p_{\text{total}} = 0.33 \times 0.248\ \text{bar} = 0.082\ \text{bar}$$

The mole fraction of ethanol in the liquid phase is

$$x_{\mathrm{E}} = 0.90$$

and therefore of 2-methylhexane is

$$x_{\mathrm{M}} = 1 - x_{\mathrm{E}} = 1 - 0.90 = 0.10$$

Then, from the definition of activity coefficients, Equation 18.25,

$$\gamma_{\mathrm{E}} = p_{\mathrm{E}}/x_{\mathrm{E}} p_{\mathrm{E}}^{\mathrm{o}} = 0.166\ \text{bar}/0.90 \times 0.174\ \text{bar} = 1.06$$

$$\gamma_{\mathrm{M}} = p_{\mathrm{E}}/x_{\mathrm{M}} p_{\mathrm{M}}^{\mathrm{o}} = 0.082\ \text{bar}/0.10 \times 0.059\ \text{bar} = 13.9$$

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15. The figure shows a sketch of the vapour-liquid phase diagram for mixtures of butanone and dichloromethane. For a solution with composition, $x_{\text{butanone}} = 0.4$ and $x_{\text{dichloromethane}} = 0.6$:

(a) estimate the boiling temperature of this mixture.

(b) estimate the composition of the vapour that boils from it.

(c) if this vapour was condensed, what would be the boiling temperature of the resulting liquid?

(d) if the boiling and condensing cycles continued, what would be the composition of (i) the distillate and (ii) the residue.

Strategy

(a) Draw a vertical line on the phase diagram at the appropriate composition and determine the point at which it intersects the liquid composition line, which is marked in red. (b) Draw a horizontal tie line and deduce the compositon of the vapour from the blue line. (c) Determine the temperature at which a liquid with this composition would boil from the liquid composition line in red. (d) Repeat the method until the mixture has been separated.

Solution

(a) The boiling temperature can be read from the liquid line, which is shown in red on the graph, as 332 K.

(b) Drawing a horizontal line at this temperature across to the vapour line, which is shown in blue, gives $x_{\text{dichloromethane}} \approx 0.82$.

(c) The boiling temperature of a liquid with this composition may be determined from the value of the red liquid composition line as 326 K.

(d) If the process is repeated, then the more volatile dicholormethane is collected as the distillate and the less volatile butanone as the residue.

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