

Assigned questions for Lecture 14 are listed below. The questions occur in the following editions of “Physical Chemistry” by P.W. Atkins:

11th edition	10th edition	9th edition	8th edition
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Note: The letter “P” in front of a number indicates that the question is in the “Problem” category as opposed to the “Exercise” category in Atkins’ books. Updates are highlighted in yellow. Most things are a match here, with a few missing problems.

Question 14.01

4A.1	4A.1	4.1	n/a
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Missing from 8th and earlier Eds.

4A.1(a) How many phases are present at each of the points marked in Fig. 4.1a?

4A.1(b) How many phases are present at each of the points marked in Fig. 4.1b?

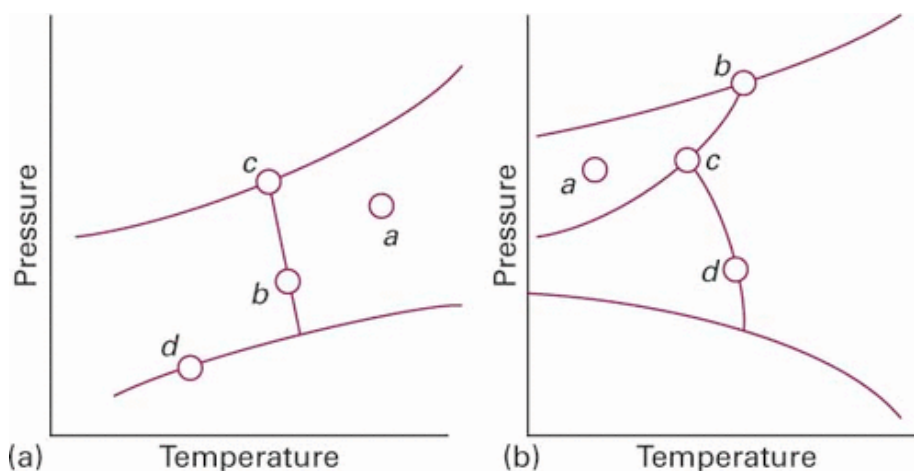


Figure 4.1 The phase diagrams referred to in (a) Exercise 4A.1(a) and (b) Exercise 4A.1(b).

Question 14.02

4B.3	4B.3	4.6	n/a
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Same questions, missing from 8th Ed.

4B.3(a) By how much does the chemical potential of copper change when the pressure exerted on a sample is increased from 100 kPa to 10 MPa?

4B.3(b) By how much does the chemical potential of benzene change when the pressure exerted on a sample is increased from 100 kPa to 10 MPa?

Question 14.03

4B.6	4B.6	4.9	4.1
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Same questions.

4B.6(a) The vapour pressure of dichloromethane at 24.1 °C is 53.3 kPa and its enthalpy of vaporization is 28.7 kJ mol⁻¹. Estimate the temperature at which its vapour pressure is 70.0 kPa

4B.6(b) The vapour pressure of a substance at 20.0 °C is 58.0 kPa and its enthalpy of vaporization is 32.7 kJ mol⁻¹. Estimate the temperature at which its vapour pressure is 66.0 kPa.

Question 14.04

4B.5	4B.5	4.8	4.2
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Same questions.

4B.5(a) The molar volume of a certain solid is 161.0 cm³ mol⁻¹ at 1.00 atm and 350.75 K, its melting temperature. The molar volume of the liquid at this temperature and pressure is 163.3 cm³ mol⁻¹. At 100 atm the melting temperature changes to 351.26 K. Calculate the enthalpy and entropy of fusion of the solid.

4B.5(b) The molar volume of a certain solid is 142.0 cm³ mol⁻¹ at 1.00 atm and 427.15 K, its melting temperature. The molar volume of the liquid at this temperature and pressure is 152.6 cm³ mol⁻¹. At 1.2 MPa the melting temperature changes to 429.26 K. Calculate the enthalpy and entropy of fusion of the solid.

Question 14.05

4B.8	4B.8	4.11	4.4
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Same questions.

4B.8(a) The vapour pressure of benzene between 10 °C and 30 °C fits the expression $\log(p/\text{Torr}) = 7.960 - 1780/(T/K)$. Calculate (i) the enthalpy of vaporization and (ii) the normal boiling point of benzene.

4B.8(b) The vapour pressure of a liquid between 15 °C and 35 °C fits the expression $\log(p/\text{Torr}) = 8.750 - 1625/(T/K)$. Calculate (i) the enthalpy of vaporization and (ii) the normal boiling point of the liquid.

Question 14.06

4B.9	4B.9	4.12	4.5
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Same questions. Addition in grey text in the 11th Ed.

4B.9(a) When benzene freezes at 5.5 °C its density changes from 0.879 g cm⁻³ to 0.891 g cm⁻³. Its enthalpy of fusion is 10.59 kJ mol⁻¹. Estimate the freezing point of benzene at 1000 atm.

4B.9(b) When a certain liquid (with $M = 46.1$ g mol⁻¹) freezes at -3.65 °C its density changes from 0.789 g cm⁻³ to 0.801 g cm⁻³. Its enthalpy of fusion is 8.68 kJ mol⁻¹. Estimate the freezing point of the liquid at 100 MPa.

Question 14.07

4B.11	4B.10	4.13	4.6
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Same questions.

4B.11(a) In July in Los Angeles, the incident sunlight at ground level has a power density of 1.2 kW m^{-2} at noon. A swimming pool of area 50 m^2 is directly exposed to the sun. What is the maximum rate of loss of water? Assume that all the radiant energy is absorbed.

4B.11(b) Suppose the incident sunlight at ground level has a power density of 0.87 kW m^{-2} at noon. What is the maximum rate of loss of water from a lake of area 1.0 ha ? ($1 \text{ ha} = 10^4 \text{ m}^2$.) Assume that all the radiant energy is absorbed.

Question 14.08*

n/a	n/a	n/a	DQ4.4
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Same question.

(DQ 4.4, 8th Ed.) Use the phase diagram below (Fig. 4.4, 8th ed.) to state what would be observed when a sample of carbon dioxide, initially at 1.0 atm and 298 K , is subjected to the following cycle: (a) isobaric (constant-pressure) heating to 320 K , (b) isothermal compression to 100 atm , (c) isobaric cooling to 210 K , (d) isothermal decompression to 1.0 atm , (e) isobaric heating to 298 K .

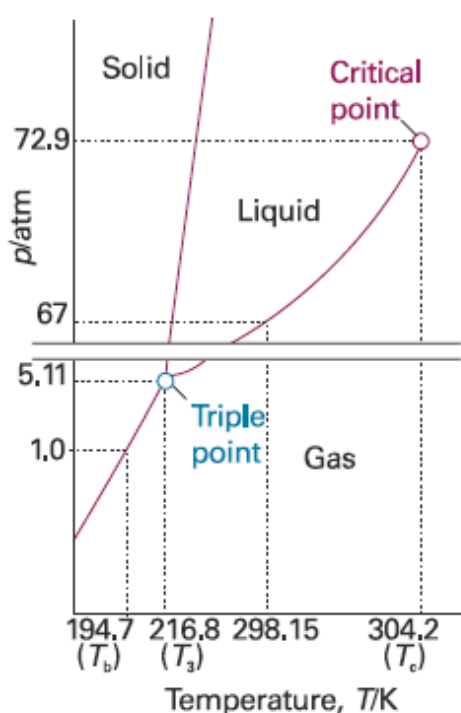


Fig. 4.4 The experimental phase diagram for carbon dioxide. Note that, as the triple point lies at pressures well above atmospheric, liquid carbon dioxide does not exist under normal conditions (a pressure of at least 5.11 atm must be applied).

Question 14.09

4B.12a	4B.11a	4.14a	4.7a
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Same questions. Slightly different wording in 11th Ed.

4B.12(a) An open vessel containing (i) water, (ii) benzene, (iii) mercury stands in a laboratory measuring 5.0 m × 5.0 m × 3.0 m at 25 °C. What mass of each substance will be found in the air if there is no ventilation? (The vapour pressures are (i) 3.2 kPa, (ii) 13.1 kPa, (iii) 0.23 Pa.)

Question 14.10

4B.13	4B.12	4.15	4.8
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Same questions. Addition in grey text in the 11th Ed.

4B.13(a) Naphthalene, C₁₀H₈, melts at 80.2 °C. If the vapour pressure of the liquid is 1.3 kPa at 85.8 °C and 5.3 kPa at 119.3 °C, use the Clausius–Clapeyron equation to calculate (i) the enthalpy of vaporization, (ii) the normal boiling point, and (iii) the enthalpy of vaporization at the boiling point.

4B.13(b) The normal boiling point of hexane is 69.0 °C. Estimate (i) its enthalpy of vaporization and (ii) its vapour pressure at 25 °C and 60 °C. (*Hint: You will need to use Trouton's rule.*)

Question 14.11

4B.14	4B.13	4.16	4.9
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10th Ed. and earlier.

4B.13(a) Calculate the melting point of ice under a pressure of 50 bar. Assume that the density of ice under these conditions is ca. 0.92 g cm⁻³ and that of liquid water is 1.00 g cm⁻³.

4B.13(b) Calculate the melting point of ice under a pressure of 10 MPa. Assume that the density of ice under these conditions is ca. 0.915 g cm⁻³ and that of liquid water is 0.998 g cm⁻³.

11th Ed. (more or less the same, slight wording changes).

4B.14(a) Estimate the melting point of ice under a pressure of 50 bar. Assume that the mass density of ice under these conditions is ca. 0.92 g cm⁻³ and that of liquid water is 1.00 g cm⁻³. The enthalpy of fusion of water is 6.008 kJ mol⁻¹ at the normal melting point.

4B.14(b) Estimate the melting point of ice under a pressure of 10 MPa. Assume that the mass density of ice under these conditions is ca. 0.915 g cm⁻³ and that of liquid water is 0.998 g cm⁻³. The enthalpy of fusion of water is 6.008 kJ mol⁻¹ at the normal melting point.

Question 14.12

P4B.1	4B.14	4.17	4.1
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Same questions.

P4B.1(a) What fraction of the enthalpy of vaporization of water is spent on expanding the water vapour?

P4B.1(b) What fraction of the enthalpy of vaporization of ethanol is spent on expanding its vapour?

Question 14.13*

n/a	n/a	n/a	4.1
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Missing after 8th Ed.

(DQ 4.6 in 8th edition) Explain the significance of the Clapeyron equation and of the Clausius-Clapeyron equation (no answer posted for this, please see notes, or see write up at end of this document).

Question 14.14*

n/a	n/a	n/a	n/a
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Missing after 7th Ed.

(Ex. 6.2a, 7th edition) Refer to the figure below (**Fig. 4.5, 8th ed.**) and describe the changes that would be observed when water vapour at 1.0 atm and 400 K is cooled at constant pressure to 260 K. Suggest the appearance of the cooling curve, which is a plot of temperature vs. time.

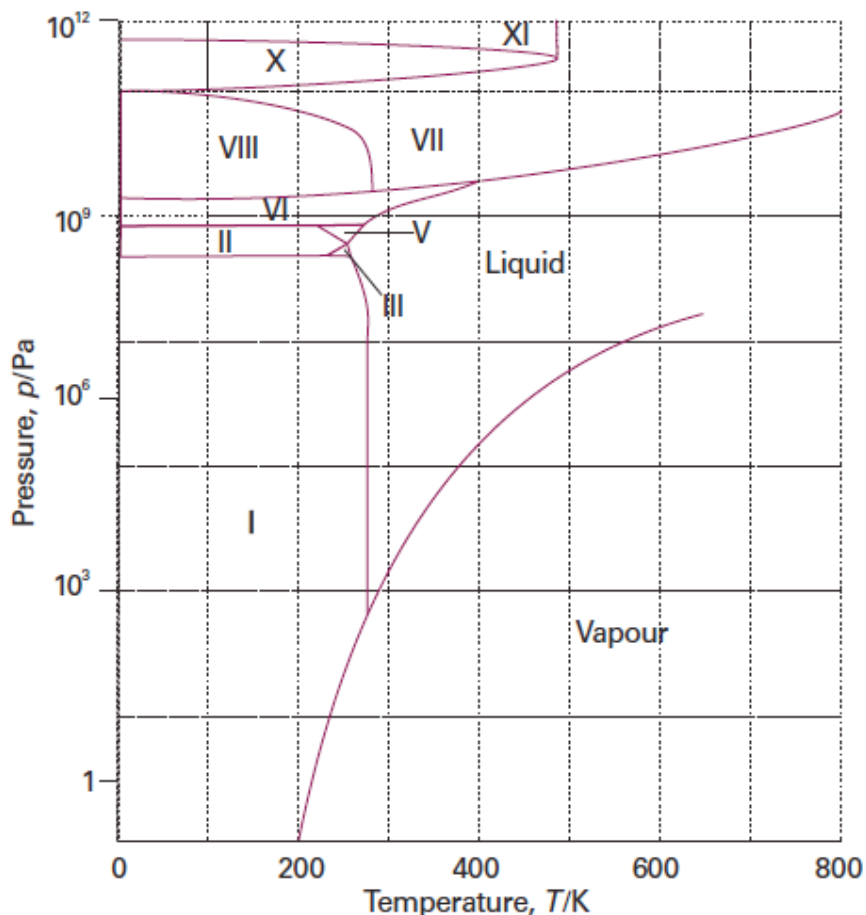


Fig. 4.5 The experimental phase diagram for water showing the different solid phases.

Answer 14.01*

4A.1	4A.1	4.1	n/a
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Missing from 8th and earlier Eds.

- 4.1(b)** The phase rule (eqn 4.1) relates the number of phases (P), components (C), and degrees of freedom (F) of a thermodynamic system:

$$F = C - P + 2$$

Restricting to pure substances ($C = 1$) and rearranging for phases gives

$$P = 3 - F$$

Areas in the phase diagram have two degrees of freedom; one can vary pressure and temperature independently (within limits) and stay within the area. Thus, $F = 2$ and $P = 1$ in areas. Lines have one degree of freedom; one can vary pressure or temperature, but to stay on the line the value of the other is determined by the line. Thus, $F = 1$ and $P = 2$ on lines. Points on the phase diagram have zero degrees of freedom; one can vary neither pressure nor temperature on a given point. Thus, $F = 0$ and $P = 3$ on points.

(a) is in an area, so there is a single phase. (b) and (c) are points, so there are three phases present.

(d) is on a line, so there are two phases present.

Answer 14.02*

4B.3	4B.3	4.6	n/a
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Same questions, missing from 8th Ed.

E4.6(a) Eqn 4.3 shows how the chemical potential changes with pressure

$$d\mu = \left(\frac{\partial \mu}{\partial p} \right)_T dp = V_m dp = \frac{M}{\rho} dp$$

$$\text{so } \Delta\mu = \int \frac{M}{\rho} dp = \frac{M}{\rho} \Delta p = \frac{63.55 \text{ g mol}^{-1}}{8.960 \text{ g cm}^{-3}} \times (10 \times 10^6 - 100 \times 10^3) \text{ Pa} \times \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} = \boxed{70 \text{ J mol}^{-1}}$$

Note: we assumed that the sample is incompressible.

E4.6(b) Eqn 4.3 shows how the chemical potential changes with pressure

$$d\mu = \left(\frac{\partial \mu}{\partial p} \right)_T dp = V_m dp = \frac{M}{\rho} dp$$

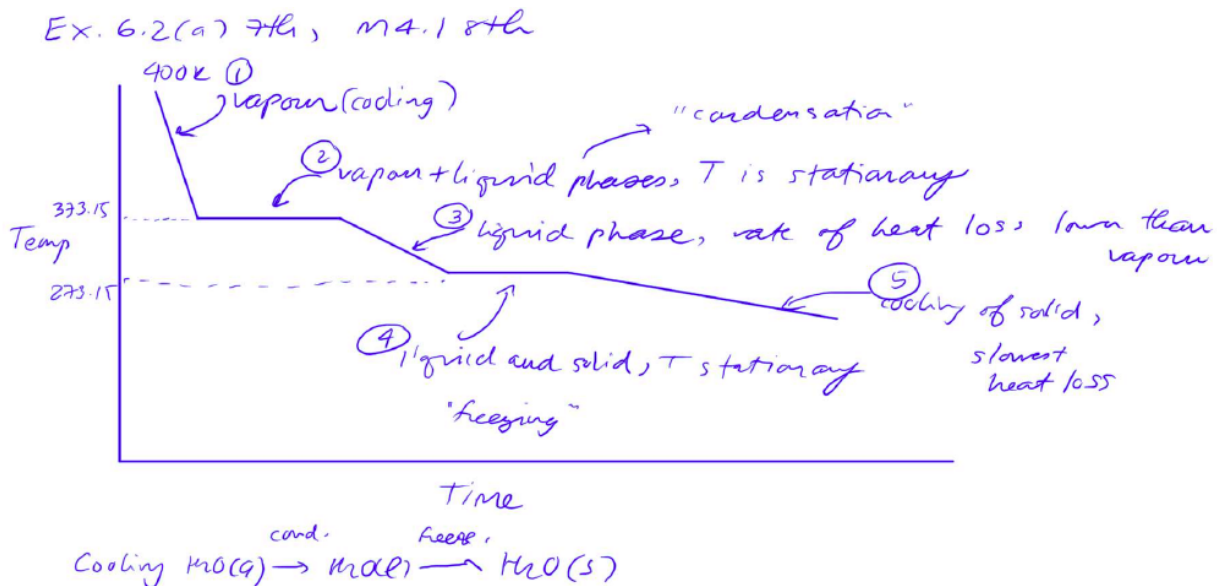
$$\begin{aligned} \text{so } \Delta\mu &= \int \frac{M}{\rho} dp = \frac{M}{\rho} \Delta p = \frac{78.11 \text{ g mol}^{-1}}{0.879 \text{ g cm}^{-3}} \times (10 \times 10^6 - 100 \times 10^3) \text{ Pa} \times \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \\ &= \boxed{8.8 \times 10^2 \text{ J mol}^{-1}} = \boxed{0.088 \text{ kJ mol}^{-1}} \end{aligned}$$

Note: We assumed that the sample is incompressible.

Answer 14.14*

n/a	n/a	n/a	n/a
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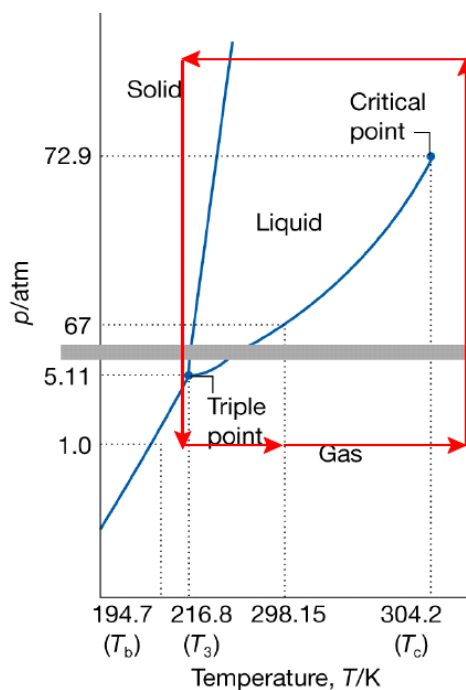
Missing after 8th Ed.



Answer 14.08*

n/a	n/a	n/a	DQ4.4
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(a) System remains gaseous, but heats up. (b) Isothermal compression creates the supercritical fluid. (c) Sample is cooled to a solid, no liquid phase in between. (d) Sample sublimates into the vapour phase. (e) System back to original vapour state.

**Answer 14.13***

n/a	n/a	n/a	n/a	4.1
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Missing after 8th Ed.

The Clapeyron equation is exact and applies rigorously to all first-order phase transitions. It shows how p and T vary w.r.t. each other along the phase boundary line, and defines the line. The Clausius-Clapeyron equation is not exact, and its derivations involves approximations, including the perfect gas law holds for solid-gas and liquid-gas phase transitions. It only holds for these types of transitions.

Extra solutions from the 9th Ed. solutions manual - courtesy of David Hirsh!

Answer 14.01*

4A.1	4A.1	4.1	n/a
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Missing from 8th and earlier Eds.

- E4.1(a)** The phase rule [eqn 4.1] relates the number of phases (P), components (C), and degrees of freedom (F) of a thermodynamic system:

$$F = C - P + 2$$

Restricting to pure substances ($C = 1$) and rearranging for phases gives

$$P = 3 - F$$

Areas in the phase diagram have two degrees of freedom; one can vary pressure and temperature independently (within limits) and stay within the area. Thus, $F = 2$ and $P = 1$ in areas. Lines have one degree of freedom; one can vary pressure or temperature, but to stay on the line the value of the other is determined by the line. Thus, $F = 1$ and $P = 2$ on lines. Points on the phase diagram have zero degrees of freedom; one can vary neither pressure nor temperature and on a given point. Thus, $F = 0$ and $P = 3$ on points.

- (a) is in an area, so there is a single phase. (b) and (d) are on lines, so there are two phases present.
 (c) is a point, so there are three phases present.

Answer 14.03

4B.6	4B.6	4.9	4.1
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Same questions.

- E4.9(a)** On the assumption that the vapour is a perfect gas and that $\Delta_{\text{vap}}H$ is independent of temperature, we may write

$$p = p^* e^{-\chi}, \quad \chi = \left(\frac{\Delta_{\text{vap}}H}{R} \right) \times \left(\frac{1}{T} - \frac{1}{T^*} \right) [4.12], \quad \ln \frac{p^*}{p} = \chi$$

$$\begin{aligned} \frac{1}{T} &= \frac{1}{T^*} + \frac{R}{\Delta_{\text{vap}}H} \ln \frac{p^*}{p} \\ &= \frac{1}{297.25 \text{ K}} + \left(\frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}{28.7 \times 10^3 \text{ J mol}^{-1}} \right) \ln \frac{53.3 \text{ kPa}}{70.0 \text{ kPa}} = 3.285 \times 10^{-3} \text{ K}^{-1} \end{aligned}$$

Hence, $T = \boxed{304 \text{ K}} = \boxed{31^\circ\text{C}}$.

- E4.9(b)** Assume that the vapour is a perfect gas and $\Delta_{\text{vap}}H$ is independent of temperature

$$p = p^* e^{-\chi}, \quad \chi = \left(\frac{\Delta_{\text{vap}}H}{R} \right) \times \left(\frac{1}{T} - \frac{1}{T^*} \right) [4.12], \quad \ln \frac{p^*}{p} = \chi$$

$$\begin{aligned} \frac{1}{T} &= \frac{1}{T^*} + \frac{R}{\Delta_{\text{vap}}H} \ln \frac{p^*}{p} \\ &= \frac{1}{293.2 \text{ K}} + \frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}{32.7 \times 10^3 \text{ J mol}^{-1}} \times \ln \left(\frac{58.0}{66.0} \right) = 3.378 \times 10^{-3} \text{ K}^{-1} \end{aligned}$$

Hence, $T = \frac{1}{3.378 \times 10^{-3} \text{ K}^{-1}} = 296 \text{ K} = \boxed{23^\circ\text{C}}$

Answer 14.04

4B.5	4B.5	4.8	4.2
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Same questions.

E4.8(a) Use the Clapeyron equation [4.6]

$$\frac{dp}{dT} = \frac{\Delta_{\text{trs}}S}{\Delta_{\text{trs}}V}$$

Assume that $\Delta_{\text{fus}}S$ and $\Delta_{\text{fus}}T$ are independent of temperature:

$$\Delta_{\text{fus}}S = \Delta_{\text{fus}}V \times \left(\frac{dp}{dT} \right) \approx \Delta_{\text{fus}}V \times \frac{\Delta p}{\Delta T}$$

$$\Delta_{\text{fus}}S = [(163.3 - 161.0) \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}] \times \left(\frac{(100 - 1) \times (1.013 \times 10^5 \text{ Pa})}{(351.26 - 350.75) \text{ K}} \right) = \boxed{+45.23 \text{ J K}^{-1} \text{ mol}^{-1}}$$

At the melting temperature

$$\Delta_{\text{fus}}H = T_f \Delta_{\text{fus}}S = (350.75 \text{ K}) \times (45.23 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{+16 \text{ kJ mol}^{-1}}$$

E4.8(b) Use the Clapeyron equation (eqn 4.6)

$$\frac{dp}{dT} = \frac{\Delta_{\text{trs}}S}{\Delta_{\text{trs}}V}$$

Assume that $\Delta_{\text{fus}}S$ and $\Delta_{\text{fus}}T$ are independent of temperature:

$$\Delta_{\text{fus}}S = \Delta_{\text{fus}}V \times \left(\frac{dp}{dT} \right) \approx \Delta_{\text{fus}}V \times \frac{\Delta p}{\Delta T}$$

$$\Delta_{\text{fus}}S = (152.6 \text{ cm}^3 \text{ mol}^{-1} - 142.0 \text{ cm}^3 \text{ mol}^{-1}) \times \frac{(1.2 \times 10^6 \text{ Pa} - 1.01 \times 10^5 \text{ Pa})}{429.26 \text{ K} - 427.15 \text{ K}}$$

$$= (10.6 \text{ cm}^3 \text{ mol}^{-1}) \times \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \right) \times (5.21 \times 10^5 \text{ Pa K}^{-1})$$

$$= 5.52 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} = \boxed{+5.5 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Answer 14.05

4B.8	4B.8	4.11	4.4
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Same questions.

E4.11(a) (a) The indefinitely integrated form of eqn 4.11 is used as in Exercise 4.10(a).

$$\ln p = \text{constant} - \frac{\Delta_{\text{vap}}H}{RT}, \quad \text{or} \quad \log p = \text{constant} - \frac{\Delta_{\text{vap}}H}{2.303 RT}$$

$$\begin{aligned} \text{Therefore, } \Delta_{\text{vap}}H &= (2.303) \times (1780 \text{ K}) \times R = (2.303) \times (1780 \text{ K}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= \boxed{+34.08 \text{ kJ mol}^{-1}} \end{aligned}$$

(b) The normal boiling point corresponds to $p = 1.000 \text{ atm} = 760 \text{ Torr}$,

$$\text{so } \log 760 = 7.960 - \frac{1780 \text{ K}}{T_b}$$

$$\text{and } T_b = \boxed{350.5 \text{ K}}.$$

E4.11(b) (a) The indefinitely integrated form of eqn 4.11 is used as in Exercise 4.10(a).

$$\ln p = \text{constant} - \frac{\Delta_{\text{vap}}H}{RT} \quad \text{or} \quad \log p = \text{constant} - \frac{\Delta_{\text{vap}}H}{2.303 RT}$$

$$\begin{aligned} \text{Thus, } \Delta_{\text{vap}}H &= 1625 \text{ K} \times R \times 2.303 = 1625 \text{ K} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 2.303 \\ &= \boxed{31.11 \text{ kJ mol}^{-1}} \end{aligned}$$

(b) The normal boiling point corresponds to $p = 1.000 \text{ atm} = 760 \text{ Torr}$,

$$\text{so } \log 760 = 8.750 - \frac{1625 \text{ K}}{T}$$

$$\text{and } T = \frac{1625 \text{ K}}{8.750 - \log 760} = \boxed{276.9 \text{ K}}$$

Answer 14.06

4B.9	4B.9	4.12	4.5
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Same questions.

$$\begin{aligned}
 \text{E4.12(a)} \quad \Delta T &\approx \frac{\Delta_{\text{fus}}V}{\Delta_{\text{fus}}S} \times \Delta p \text{ [4.6 and Exercise 4.8(a)]} \\
 &\approx \frac{T_f \Delta_{\text{fus}}V}{\Delta_{\text{fus}}H} \times \Delta p = \frac{T_f M \Delta p}{\Delta_{\text{fus}}H} \times \Delta \left(\frac{1}{\rho} \right) \quad [V_m = M/\rho] \\
 &\approx \frac{278.6 \text{ K} \times 999 \text{ atm} \times 78.11 \text{ g mol}^{-1}}{10.59 \times 10^3 \text{ J mol}^{-1}} \times \left(\frac{1}{0.879 \text{ g cm}^{-3}} - \frac{1}{0.891 \text{ g cm}^{-3}} \right) \\
 &\quad \times \left(\frac{1.013 \times 10^5 \text{ Pa}}{1 \text{ atm}} \right) \times \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \right) \\
 &\approx 3.2 \text{ K}
 \end{aligned}$$

Therefore, at 1000 atm, $T_f = (278.6 + 3.2) \text{ K} = \boxed{281.8 \text{ K}}$ or $\boxed{8.7^\circ\text{C}}$.

$$\begin{aligned}
 \text{E4.12(b)} \quad \Delta T &\approx \frac{\Delta_{\text{fus}}V}{\Delta_{\text{fus}}S} \times \Delta p \text{ [4.6 and Exercise 4.8(a)]} \\
 &\approx \frac{T_f \Delta_{\text{fus}}V}{\Delta_{\text{fus}}H} \times \Delta p = \frac{T_f M \Delta p}{\Delta_{\text{fus}}H} \times \Delta \left(\frac{1}{\rho} \right) \quad [V_m = M/\rho]
 \end{aligned}$$

Normal freezing point is $T_f = (273.15 - 3.65) \text{ K} = 269.50 \text{ K}$ at a pressure of 1 atm, which is about 0.1 MPa. Thus, to the nearest MPa, $\Delta p = 100 \text{ MPa} = 1.00 \times 10^8 \text{ Pa}$

$$\Delta T \approx \frac{269.50 \text{ K} \times 46.1 \text{ g mol}^{-1} \times (1.00 \times 10^8 \text{ Pa})}{8.68 \times 10^3 \text{ J mol}^{-1}} \times \left(\frac{1}{0.789 \text{ g cm}^{-3}} - \frac{1}{0.801 \text{ g cm}^{-3}} \right) \approx 2.7 \text{ K}$$

Therefore, at 100 MPa, $T_f = (269.50 + 2.7) \text{ K} = \boxed{27.2 \text{ K}}$ or $\boxed{-1.0^\circ\text{C}}$.

Answer 14.07

4B.11	4B.10	4.13	4.6
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Same questions.

E4.13(a) The rate of loss of mass of water may be expressed as

$$\frac{dm}{dt} = \frac{d}{dt}(nM), \quad \text{where} \quad n = \frac{q}{\Delta_{\text{vap}}H}$$

$$\text{Thus,} \quad \frac{dn}{dt} = \frac{dq/dt}{\Delta_{\text{vap}}H} = \frac{(1.2 \times 10^3 \text{ W m}^{-2}) \times (50 \text{ m}^2)}{44.0 \times 10^3 \text{ J mol}^{-1}} = 1.4 \text{ mol s}^{-1}$$

$$\text{and} \quad \frac{dm}{dt} = (1.4 \text{ mol s}^{-1}) \times (18.02 \text{ g mol}^{-1}) = \boxed{25 \text{ g s}^{-1}}$$

E4.13(b) The rate of loss of mass of water may be expressed as

$$\frac{dm}{dt} = \frac{d}{dt}(nM), \quad \text{where} \quad n = \frac{q}{\Delta_{\text{vap}}H}$$

$$\text{Thus,} \quad \frac{dn}{dt} = \frac{dq/dt}{\Delta_{\text{vap}}H} = \frac{(0.87 \times 10^3 \text{ W m}^{-2}) \times (10^4 \text{ m}^2)}{44.0 \times 10^3 \text{ J mol}^{-1}} = 200 \text{ mol s}^{-1}$$

$$\text{and} \quad \frac{dm}{dt} = (200 \text{ mol s}^{-1}) \times (18.02 \text{ g mol}^{-1}) = \boxed{3.6 \text{ kg s}^{-1}}$$

Answer 14.09

4B.12a	4B.11a	4.14a	4.7a
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*Same questions.*E4.14(a) Assume perfect-gas behaviour. The volume is 75 m³.

$$n = \frac{pV}{RT} = \frac{m}{M} \quad \text{so} \quad m = \frac{pVM}{RT}$$

$$\text{(a)} \quad m = \frac{(3.2 \times 10^3 \text{ Pa}) \times (75 \text{ m}^3) \times (18.02 \text{ g mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = \boxed{1.7 \times 10^3 \text{ g}} \text{ water}$$

$$\text{(b)} \quad m = \frac{(13.1 \times 10^3 \text{ Pa}) \times (75 \text{ m}^3) \times (78.11 \text{ g mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = \boxed{31 \times 10^3 \text{ g}} \text{ benzene}$$

$$\text{(c)} \quad m = \frac{(0.23 \text{ Pa}) \times (75 \text{ m}^3) \times (200.59 \text{ g mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = \boxed{1.4 \text{ g}} \text{ mercury}$$

Answer 14.10

4B.13	4B.12	4.15	4.8
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Same questions.

E4.15(a) The Clausius–Clapeyron equation [4.11] integrates to the form [4.12] that may be rewritten as

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta_{\text{vap}}H}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\begin{aligned} \text{(a)} \quad \Delta_{\text{vap}}H &= R \ln\left(\frac{p_2}{p_1}\right) \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1} \\ &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\left(\frac{5.3 \text{ kPa}}{1.3 \text{ kPa}}\right) \times \left(\frac{1}{359.0 \text{ K}} - \frac{1}{392.5 \text{ K}}\right)^{-1} \\ &= \boxed{+4.9 \times 10^4 \text{ J mol}^{-1}} = \boxed{+49 \text{ kJ mol}^{-1}} \end{aligned}$$

(b) Rearrange the equation above to isolate a temperature

$$\frac{R}{\Delta_{\text{vap}}H} \ln\left(\frac{p_2}{p_1}\right) + \frac{1}{T_2} = \frac{1}{T_1}$$

The normal boiling point (T_1 in this equation) corresponds to a vapour pressure of 101.3 kPa. Using the data at 119.3°C (T_2), we have

$$\left(\frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}{+4.9 \times 10^4 \text{ J mol}^{-1}}\right) \ln\left(\frac{5.3 \text{ kPa}}{101.3 \text{ kPa}}\right) + \frac{1}{392.5 \text{ K}} = 2.05 \times 10^{-3} \text{ K}^{-1} = \frac{1}{488 \text{ K}}$$

Thus, the estimated boiling point is 488 K = $\boxed{215^\circ\text{C}}$

The accepted value is 218°C.

(c) At the boiling point

$$\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T_b} \approx \frac{+49 \times 10^3 \text{ J mol}^{-1}}{488 \text{ K}} = \boxed{+101 \text{ J K}^{-1} \text{ mol}^{-1}}$$

E4.15(b) (a) According to Trouton's rule (Section 3.3(b))

$$\Delta_{\text{vap}}H \approx 85 \text{ J K}^{-1} \text{ mol}^{-1} \times T_b = 85 \text{ J K}^{-1} \text{ mol}^{-1} \times 342.2 \text{ K} = \boxed{29.1 \text{ kJ mol}^{-1}}$$

(b) Use the integrated form of the Clausius–Clapeyron equation (eqn 4.12) rearranged to

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta_{\text{vap}}H}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

At $T_1 = 342.2 \text{ K}$, $p_1 = 1.000 \text{ atm}$ [normal boiling point]; thus, at 25°C

$$\ln\left(\frac{p_2}{1.000 \text{ atm}}\right) = \left(\frac{2.91 \times 10^4 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{342.2 \text{ K}} - \frac{1}{298.2 \text{ K}}\right) = -1.51$$

$$\text{and } p_2 = e^{-1.51} \text{ atm} = \boxed{0.22 \text{ atm}}$$

$$\text{At } 60^\circ\text{C}, \ln\left(\frac{p_2}{1.000 \text{ atm}}\right) = \left(\frac{2.91 \times 10^4 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{342.2 \text{ K}} - \frac{1}{333.2 \text{ K}}\right) = -0.276$$

$$\text{and } p_2 = e^{-0.276} \text{ atm} = \boxed{0.76 \text{ atm}}$$

Answer 14.11

4B.14	4B.13	4.16	4.9
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Same questions.

$$\text{E4.16(a)} \quad \Delta T \approx \frac{T_f M \Delta p}{\Delta_{\text{fus}} H} \times \Delta \left(\frac{1}{\rho} \right) \quad [\text{Exercise 4.12(a)}]$$

$$\Delta T \approx \left(\frac{(273.15 \text{ K}) \times (49 \times 10^5 \text{ Pa}) \times (18.0 \text{ g mol}^{-1})}{6.01 \times 10^3 \text{ J mol}^{-1}} \right) \times \left(\frac{1}{1.00 \text{ g cm}^{-3}} - \frac{1}{0.92 \text{ g cm}^{-3}} \right) \times \frac{1 \text{ m}^3}{10^6 \text{ cm}^3}$$

$$= -0.35 \text{ K}$$

$$T_f(50 \text{ bar}) = (273.15 - 0.35) \text{ K} = \boxed{272.80 \text{ K}}$$

$$\text{E4.16(b)} \quad \Delta T = T_f(10 \text{ MPa}) - T_f(0.1 \text{ MPa}) = \frac{T_f \Delta p M}{\Delta_{\text{fus}} H} \Delta \left(\frac{1}{\rho} \right) \quad [\text{Exercise 4.12(b)}]$$

$$\Delta T = \left(\frac{(273.15 \text{ K}) \times 9.9 \times 10^6 \text{ Pa} \times 18.0 \text{ g mol}^{-1}}{6.01 \times 10^3 \text{ J mol}^{-1}} \right) \times \left(\frac{1}{0.998 \text{ g cm}^{-3}} - \frac{1}{0.915 \text{ g cm}^{-3}} \right) = -0.74 \text{ K}$$

$$T_f(10 \text{ MPa}) = (273.15 - 0.74) \text{ K} = \boxed{272.41 \text{ K}}$$

Answer 14.12

P4B.1	4B.14	4.17	4.1
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Same questions.

$$\text{E4.17(a)} \quad \Delta_{\text{vap}} H = \Delta_{\text{vap}} U + \Delta_{\text{vap}}(pV) = 40.656 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{vap}}(pV) = p \Delta_{\text{vap}} V = p(V_{\text{gas}} - V_{\text{liq}}) \approx pV_{\text{gas}} = RT \quad [\text{perfect gas}]$$

$$\Delta_{\text{vap}}(pV) \approx (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (373.2 \text{ K}) = 3102 \text{ J mol}^{-1}$$

$$\text{Fraction} = \frac{\Delta_{\text{vap}}(pV)}{\Delta_{\text{vap}} H} = \frac{3.102 \text{ kJ mol}^{-1}}{40.656 \text{ kJ mol}^{-1}} = \boxed{0.0763} = 7.63\%$$

$$\text{E4.17(b)} \quad \Delta_{\text{vap}} H = \Delta_{\text{vap}} U + \Delta_{\text{vap}}(pV) = 43.5 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{vap}}(pV) = p \Delta_{\text{vap}} V = p(V_{\text{gas}} - V_{\text{liq}}) \approx pV_{\text{gas}} = RT \quad [\text{perfect gas}]$$

$$\Delta_{\text{vap}}(pV) \approx (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (352 \text{ K}) = 2.93 \times 10^3 \text{ J mol}^{-1}$$

$$\text{Fraction} = \frac{\Delta_{\text{vap}}(pV)}{\Delta_{\text{vap}} H} = \frac{2.93 \text{ kJ mol}^{-1}}{43.5 \text{ kJ mol}^{-1}} = \boxed{0.0673} = 6.73\%$$