I.7 Phase Equilibria and Solutions

Civil Services 2016–2026: **18** parts, **190** marks · IFoS 2016–2025: **17** parts, **160** marks

Syllabus. Clausius-Clapeyron equation; phase diagram for a pure substance; phase equilibria in binary systems, partially miscible liquids: upper and lower critical solution temperatures; partial molar quantities, their significance and determination; excess thermodynamic functions and their determination.

Marks	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026
CSE	15	10	10	15	20	40	20	20	15	10	15
IFoS	10	10	8	28	18	23	15	10	23	15	

How to use this chapter. Read every question once and mark the ones that repeat. Pick three, write them by hand against the clock (about 7 minutes for 10 marks), then compare with the model answers on vkcscience.com.

2026

CSE 2026 · Q1(e) Components and phases when NH_4Cl is heated [5 marks]

$NH_4Cl(s)$ decomposes when heated.
(i) How many components and phases are present when the salt is heated in a closed container?
(ii) Now, suppose additional NH_3 is also present in the container. How many components and phases will be present?

CSE 2026 · Q3(a)(ii) Cd–Bi simple eutectic: phase diagram and cooling curves [10 marks]

(ii) Cadmium (m. pt. = 321 °C) and bismuth (m. pt. = 271 °C) do not form solid solutions or compounds with one another. Their eutectic point lies at 61 weight percent of bismuth and 146 °C. Sketch their phase diagram and label each region to show what phases are present. Explain the cooling curves of this eutectic mixture.

2025

CSE 2025 · Q3(c) Phase diagram of butane and two compressions [10 marks]

You are given the following data for butane:
Normal melting point = −138 °C
Normal boiling point = 0 °C
Critical temperature = 152 °C
Critical pressure = 38 atm
Assume that the triple point is slightly lower in temperature than the melting point and that the vapour pressure at the triple point is 3×10^{-5} torr.
(i) Sketch a phase diagram for butane.
(ii) Butane at 1 atm and 140 °C is compressed to 40 atm. Are two phases present at any time during this process?
(iii) Butane at 1 atm and 200 °C is compressed to 40 atm. Are two phases present at any time during this process?

IFoS 2025 · Q4(a) Boiling point at reduced atmospheric pressure; Chemical potential of supercooled water [10 marks]

(i) For water, $\Delta H_{vaporization}$ is 40.65 kJ mol^{-1} and the normal boiling point is 373.15 K. Calculate the boiling point for water on the top of a mountain of height 5500 m, where normal barometric pressure is 380 torr. 5
(ii) By what amount does the chemical potential of water exceed that of ice at −5.00 °C and 1 atm pressure? [Given: $S^{\circ}_{H_2O,\,s}$ = 48.0 J mol^{-1} K^{-1} and $S^{\circ}_{H_2O,\,l}$ = 70.0 J mol^{-1} K^{-1}] 5

IFoS 2025 · Q4(b)(i) Incongruent melting and azeotropy [5 marks]

(i) Draw the phase diagrams for the following types of systems:
(1) Two-component, temperature-composition, solid-liquid diagram, one compound of formula AB_2 that melts incongruently, negligible solid-solid solubility
(2) Two-component, constant temperature-composition, liquid-vapour diagram, formation of an azeotrope at X_B = 0.333, complete miscibility
Label the regions and intersections of the diagrams, stating what materials (possibly compounds or azeotropes) are present and whether they are solid, liquid or gas. 5

2024

CSE 2024 · Q4(a) Triple point, stable phase and enthalpy of sublimation of a new drug [15 marks]

A new drug has been synthesized and its phase diagram is explored. It is found that near its triple point, vapour pressure over the liquid (P_l) and over the solid (P_s) are given by:

$$\ln P_l = -\frac{3010}{T} + 13.2 \qquad \ln P_s = -\frac{3820}{T} + 16.1$$

Calculate the triple point temperature and pressure.
Is the new drug solid, gas or liquid at 1 bar, 298 K?
What is $\Delta H_{\text{sublimation}}$? Explain.

IFoS 2024 · Q1(d) Components in ammonium chloride dissociation [8 marks]

Equivalent quantities of NH_3 and HCl form a one-component system, but when slight excess of NH_3 or HCl is added, it becomes a two-component system. Explain.

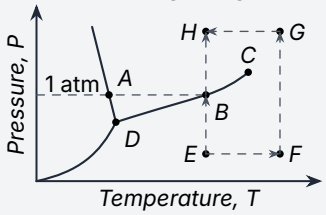
IFoS 2024 · Q4(a) Lead–silver eutectic and desilverisation [15 marks]

Draw the phase diagram of lead-silver system. Explain its significance in desilverization of lead.

2023

CSE 2023 · Q3(b) Reading a one-component phase diagram [20 marks]

Answer the following questions based on the phase diagram given below:



(i) How many components does this phase diagram represent?
(ii) Identify the points *A* to *D* with corresponding degrees of freedom.
(iii) Explain the changes expected in the paths $E \to B \to H$ and $E \to F \to G \to H$.

IFoS 2023 · Q4(b) Chemical potential versus temperature [10 marks]

(i) Show that the slope of μ versus T curve for a pure substance (existing in three phases—solid, liquid and gas) is always negative and is equal to $-S_m$.
(ii) Draw a schematic diagram of μ versus T curve for the above-mentioned three phases and show that for a pure substance, the slope follows the order

$$\left(\frac{\partial \mu(\text{s})}{\partial T}\right)_P > \left(\frac{\partial \mu(\text{l})}{\partial T}\right)_P \gg \left(\frac{\partial \mu(\text{g})}{\partial T}\right)_P$$

Locate the melting point and boiling point of the substance on the diagram.

2022

CSE 2022 · Q3(d) Phase diagram of water; critical point and triple point [10 marks]

Construct a phase-diagram for a one component system (water) and explain all the three curves. Also describe the significance of critical pressure, critical temperature and triple point.

CSE 2022 · Q4(b) Mean molar heat of vaporisation of water from two vapour pressures [10 marks]

The vapour pressure of water at 363.2 K is 529 torr. Use the Clausius-Clapeyron equation to determine the average value of molar heat of vaporization, $\Delta\bar{H}$, of water between 363.2 K and 373.2 K. [R = 8.314 J mol^{-1} K^{-1}]

IFoS 2022 · Q3(c) Sulfur phase diagram and metastability [15 marks]

Draw the phase diagram of Sulphur system and indicate the existence of the following metastable equilibria: $S_R \rightleftharpoons S_V$ and $S_L \rightleftharpoons S_V$. Explain the reasons behind these equilibria.

2021

CSE 2021 · Q1(d) Vapour pressure of water at 100 °C from its value at 95 °C [10 marks]

The vapour pressure of water at 95 °C is found to be 634 mm. What would be the vapour pressure at a temperature of 100 °C? The heat of vapourization in this range of temperature may be taken as 40593 J mol^{-1}. [R = 8.314 J K^{-1} mol^{-1}]

CSE 2021 · Q3(c)(i) Enthalpy of vaporisation from the triple point to the critical point [10 marks]

(i) Draw and explain the graph of enthalpy of vapourization from the triple point (T_p) to the critical point (T_c). 10

CSE 2021 · Q4(c) Phenol–water system and the importance of tie lines [20 marks]

Explain the phase diagram of phenol-water system by highlighting the importance of tie lines.

IFoS 2021 · Q1(d) Desilverisation of lead [8 marks]

Explain the application of phase rule in desilverization of lead.

IFoS 2021 · Q4(c) Clausius–Clapeyron equation [15 marks]

Derive Clausius–Clapeyron equation for a one component system at equilibrium, represented as

$$\text{water (liquid)} \rightleftharpoons \text{water (vapour)}$$

2020

CSE 2020 · Q1(d) Phenol–water: two liquid layers and the phase rule [10 marks]

Phenol and water are partially miscible liquids. By mixing these two liquids, we get two phases in equilibrium. Find the number of degrees of freedom of the system and mention them with the help of its phase diagram.

CSE 2020 · Q6(e) Sulfur melts but iodine sublimes on heating in an open vessel [10 marks]

Solid sulphur on heating in an open container melts, but solid iodine sublimes. Explain why.

IFoS 2020 · Q1(e) Smoke in horror films from the CO_2 phase diagram [8 marks]

How is the smoke in horror films made? Explain it with the help of phase diagram also.

IFoS 2020 · Q3(b) Deflated tyres on ice; comparing two binary phase diagrams [10 marks]

(i) Why does deflating the tyres on a car improve its road-holding on ice? 5

(ii) Compare the phase diagrams in Figure 1 and Figure 2, and comment briefly :

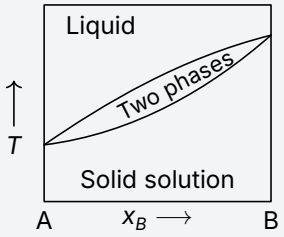


Figure 1

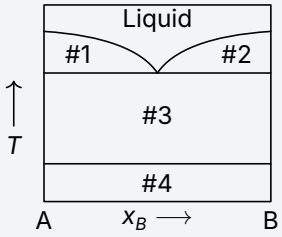


Figure 2

5

2019

CSE 2019 · Q7(a) Maximum number of coexisting phases from the phase rule [15 marks]

Predict the maximum number of phases that can coexist for

(i) 3 component system at constant P & T

(ii) 2 component system at constant T

(iii) one component system at constant T & P

IFoS 2019 · Q1(e) Clapeyron equation for sublimation [8 marks]

Derive Clapeyron equation applicable to sublimation process

$$\log \frac{p_1}{p_2} = -\frac{L}{2{\cdot}303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right],$$

where L is the latent heat per gm-mole.

IFoS 2019 · Q3(a) Critical solution temperature; steam distillation [20 marks]

(i) Define Critical Solution Temperature (CST). Write the degree of freedom (F) for the homogeneous phase of two-component CST system. List three examples of upper consolute temperature system. 12

(ii) The steam distillation of liquid A (Molar mass, M_A = 112·6 g . mol^{-1}) is determined to occur at a temperature of 91·3 °C when total pressure is 1·0 atm. Calculate the mass of liquid in 100 gm of distillate. The vapour pressure of water at 91·3 °C is 539·4 Torr.

(Assume complete miscibility of these liquids and total vapour pressure = 760 Torr.) 8

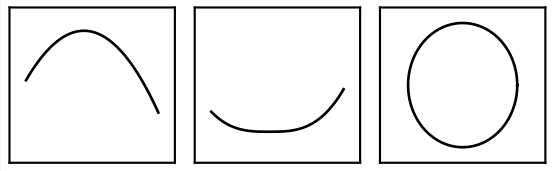
2018

CSE 2018 · Q4(d)(i) Slopes of the fusion and sublimation curves of water [5 marks]

Explain why fusion curve of ice has negative slope whereas sublimation curve has positive slope in the phase diagram.

CSE 2018 · Q4(d)(ii) Three liquid–liquid phase diagrams [5 marks]

Label and compare the phase diagrams given above:



IFoS 2018 · Q1(d) Why four phases of sulphur cannot coexist [8 marks]

Sulphur exists in four different (solid rhombic, solid monoclinic, liquid, and gaseous) phases under different conditions. Any two or three phases of sulphur may coexist in equilibrium, but all four phases do not coexist in equilibrium. Give reasons.

2017

CSE 2017 · Q1(d)(i) Four phases of sulfur cannot coexist [5 marks]

(i) Four-phase sulphur system (in equilibrium) is impossible. Explain.

CSE 2017 · Q1(d)(ii) On heating in an open vessel sulfur melts, iodine sublimes [5 marks]

(ii) In open container, on heating, solid sulphur melts, but solid iodine sublimes. Explain.

IFoS 2017 · Q4(b) P–T diagram of H_2O and the phase rule [10 marks]

Draw and discuss the pressure-temperature diagram for H_2O. Apply the phase rule to the diagram.

2016

CSE 2016 · Q2(b) Integrated Clausius–Clapeyron equation from the Clapeyron equation [15 marks]

Starting with the expression

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_2 - V_1)}$$

for the system consisting of two phases of a single substance in chemical equilibrium, derive the integrated form of the Clausius-Clapeyron equation.

IFoS 2016 · Q3(b)(i) Phase, component and degree of freedom [5 marks]

Just define the terms phase, component and degree of freedom involved in the statement of phase rule.

IFoS 2016 · Q3(b)(ii) Components of aqueous NaCl + KBr, then with KCl and NaBr [5 marks]

How many components are there in an aqueous solution of NaCl and KBr? If to this solution KCl and NaBr are added, how many components will be there?