



UPSC PHYSICS OPTIONAL for CSE & IFoS

ABHI PHYSICS

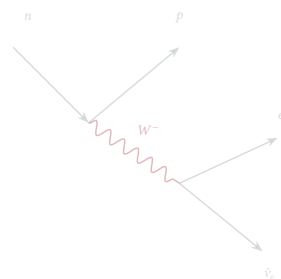
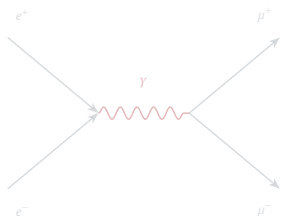
$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi$$

$$[\hat{x}, \hat{p}] = i\hbar$$

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

$$E_n = -\frac{13.6}{n^2} \text{ eV}$$

PREVIOUS YEAR QUESTIONS



41 YEARS QUESTION BANK | 1986-2026

CSE + IFoS

SUBJECT

Thermal Physics

10 SOLVED QUESTIONS • CSE + IFoS

$$n \rightarrow p + e^- + \bar{\nu}_e$$

$$E^2 = p^2 c^2 + m^2 c^4$$

$$\partial_\mu j^\mu = 0$$

SUBJECT-WISE • TOPIC-WISE • SOURCE-TAGGED

For Civil Services and Indian Forest Service Examinations

Sample Preview extbar 10 Solved Questions

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Q1. What are the limitations of the first law of thermodynamics? One mole of a gas, assumed to be perfect, at 0 °C is heated at constant pressure till its volume is twice its initial value. Calculate the amount of heat absorbed. Given, $C_v = 20 \cdot 9 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $R = 8 \cdot 3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

INTRODUCTION:

The first law of thermodynamics is the principle of conservation of energy applied to a thermodynamic system. With heat supplied to the gas taken as positive and work done by the gas taken as positive, it is written as

$$\Delta U = Q - W, \quad \text{or} \quad Q = \Delta U + W.$$

It relates heat, work and the change in internal energy, but by itself does not specify whether a process can occur spontaneously or in which direction it will proceed.

For the calculation, the gas is assumed to remain ideal and in quasistatic equilibrium while being heated at constant pressure. Let T_1, V_1 and T_2, V_2 denote its initial and final temperatures and volumes. The given middle dots in the numerical data are interpreted as decimal points:

$$C_v = 20.9 \text{ J mol}^{-1} \text{K}^{-1}, \quad R = 8.3 \text{ J mol}^{-1} \text{K}^{-1}.$$

The initial absolute temperature is

$$T_1 = 273.15 \text{ K},$$

and the final volume satisfies $V_2 = 2V_1$.

SOLUTION:

The limitations of the first law are as follows:

1. It gives only an energy balance; it does not indicate the natural direction of a process. For example, it does not explain why heat flows spontaneously from a hotter body to a colder body and not conversely.
2. It provides no criterion for spontaneity or thermodynamic equilibrium. Processes having the same energy balance may differ in whether they can actually occur.
3. It does not distinguish between reversible and irreversible processes and gives no measure of the degradation or quality of energy.
4. It places no restriction, by itself, on the conversion of heat into work. Although it forbids a perpetual-motion machine of the first kind, which would create energy, it cannot rule out a

hypothetical cyclic engine that converts all the heat received from a single reservoir into work. That restriction follows from the second law.

5. It does not determine the maximum possible efficiency of a heat engine or the coefficient of performance of a refrigerator.
6. It does not introduce entropy and hence cannot account for entropy production in irreversible processes.
7. It gives no information about the rate at which a permitted process occurs.

For the numerical part, the ideal-gas equation is

$$PV = nRT.$$

Since P and n remain constant,

$$\frac{V_2}{V_1} = \frac{T_2}{T_1}.$$

Using $V_2 = 2V_1$,

$$\frac{T_2}{T_1} = 2, \quad T_2 = 2T_1 = 2(273.15 \text{ K}) = 546.30 \text{ K}.$$

Therefore,

$$\Delta T = T_2 - T_1 = 546.30 - 273.15 = 273.15 \text{ K}.$$

For one mole of an ideal gas,

$$\Delta U = nC_v \Delta T.$$

The work done during constant-pressure expansion is

$$W = P(V_2 - V_1).$$

Using $PV = nRT$ at the initial and final states,

$$P(V_2 - V_1) = nR(T_2 - T_1) = nR\Delta T.$$

Hence, from the first law,

$$Q = \Delta U + W = nC_v \Delta T + nR\Delta T = n(C_v + R)\Delta T.$$

Thus the constant-pressure molar heat capacity is

$$C_p = C_v + R = 20.9 + 8.3 = 29.2 \text{ J mol}^{-1} \text{K}^{-1}.$$

The heat absorbed is therefore

$$\begin{aligned} Q &= nC_p \Delta T \\ &= (1.00 \text{ mol})(29.2 \text{ J mol}^{-1} \text{K}^{-1})(273.15 \text{ K}) \\ &= 7975.98 \text{ J} \\ &\approx 7.98 \times 10^3 \text{ J}. \end{aligned}$$

For physical consistency, both $\Delta U = nC_v \Delta T$ and $W = nR\Delta T$ are positive because the gas is heated and expands. Consequently $Q = \Delta U + W > 0$, as required for heat absorbed by the gas.

CONCLUSION:

The first law expresses conservation of energy but does not determine the direction or spontaneity of a process, distinguish reversible from irreversible change, introduce entropy, set the maximum efficiency of heat engines, rule out complete cyclic conversion of heat from a single reservoir into work, or predict process rates.

At constant pressure, doubling the volume of the ideal gas doubles its absolute temperature. Thus

$$\begin{aligned} T_2 &= 546.30 \text{ K} \\ \Delta T &= 273.15 \text{ K} \\ C_p &= 29.2 \text{ J mol}^{-1} \text{ K}^{-1}. \end{aligned}$$

Therefore, the amount of heat absorbed by one mole of the gas is

$$Q \approx 7.98 \times 10^3 \text{ J} = 7.98 \text{ kJ}.$$

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Q2. Two solids *A* and *B* have Debye temperatures 200 K and 300 K respectively. At $T = 20 \text{ K}$, compare their specific heats.

INTRODUCTION:

The temperature is much smaller than either Debye temperature:

$$\frac{T}{\Theta_{D,A}} = \frac{20}{200} = 0.10, \quad \frac{T}{\Theta_{D,B}} = \frac{20}{300} = 0.0667.$$

Hence the low-temperature Debye T^3 law is applicable. The comparison is understood to be between the molar lattice specific heats of the two solids, with the same number of vibrational degrees of freedom per mole. Their electronic contributions, if any, are neglected.

SOLUTION:

For a three-dimensional Debye solid at $T \ll \Theta_D$, the molar heat capacity at constant volume is

$$C_V = \frac{12\pi^4}{5} R \left(\frac{T}{\Theta_D} \right)^3.$$

At the same temperature, all factors except the Debye temperature cancel in the ratio:

$$\frac{C_{V,A}}{C_{V,B}} = \frac{(T/\Theta_{D,A})^3}{(T/\Theta_{D,B})^3} = \left(\frac{\Theta_{D,B}}{\Theta_{D,A}} \right)^3.$$

Substituting the given Debye temperatures,

$$\frac{C_{V,A}}{C_{V,B}} = \left(\frac{300 \text{ K}}{200 \text{ K}} \right)^3 = \left(\frac{3}{2} \right)^3 = \frac{27}{8} = 3.375.$$

Numerically, using

$$\frac{12\pi^4}{5} R \approx 1.944 \times 10^3 \text{ J mol}^{-1} \text{ K}^{-1},$$

one obtains

$$C_{V,A} \approx 1.944 \times 10^3 \left(\frac{20}{200} \right)^3 = 1.944 \text{ J mol}^{-1} \text{ K}^{-1},$$

and

$$C_{V,B} \approx 1.944 \times 10^3 \left(\frac{20}{300} \right)^3 = 0.576 \text{ J mol}^{-1} \text{ K}^{-1}.$$

Thus the solid with the lower Debye temperature has the larger low-temperature lattice heat capacity, because a larger fraction of its phonon modes is thermally excited.

CONCLUSION:

At 20 K, within the low-temperature Debye approximation,

$$C_{V,A} : C_{V,B} = 27 : 8$$

or

$$C_{V,A} = 3.375 C_{V,B}.$$

The corresponding molar lattice heat capacities are approximately

$$C_{V,A} \approx 1.94 \text{ J mol}^{-1} \text{ K}^{-1}, \quad C_{V,B} \approx 0.576 \text{ J mol}^{-1} \text{ K}^{-1}.$$

Therefore, solid *A* has about 3.4 times the specific heat of solid *B* at the stated temperature, provided lattice vibrations dominate and $T \ll \Theta_D$.

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Q3. Calculate the pressure at which water will boil at 150°C , given that the change in specific volume when 1 gram of water is converted into steam is 1676 cm^3 . Given, latent heat of vaporization for steam = 540 cal per gram , $J = 4.2 \times 10^7 \text{ ergs/cal}$ and one atmospheric pressure = 10^6 dynes/cm^2 .

INTRODUCTION:

The required quantity is the absolute pressure p_2 at which liquid water and steam coexist in equilibrium at

$$T_2 = 150^\circ \text{C} = 423 \text{ K}.$$

At the normal boiling point,

$$T_1 = 100^\circ \text{C} = 373 \text{ K}, \quad p_1 = 1 \text{ atm} = 10^6 \text{ dyn cm}^{-2}.$$

For liquid–vapour equilibrium, the variation of saturation pressure with temperature is governed by the Clapeyron equation

$$\frac{dp}{dT} = \frac{L}{T\Delta v},$$

where L is the latent heat of vaporization per unit mass and

$$\Delta v = v_{\text{steam}} - v_{\text{water}}.$$

The sign convention is

$$\Delta v > 0, \quad \Delta p = p_2 - p_1.$$

Thus $dp/dT > 0$, as expected for vaporization.

Because only one value each of L and Δv is supplied, both are assumed constant over the interval 373–423 K. The phases are assumed to remain in thermodynamic equilibrium along the saturation curve.

SOLUTION:

The latent heat in cgs mechanical units is

$$L = 540 \frac{\text{cal}}{\text{g}} \times 4.2 \times 10^7 \frac{\text{erg}}{\text{cal}} = 2.268 \times 10^{10} \text{ erg g}^{-1}.$$

The given specific-volume change is

$$\Delta v = 1676 \text{ cm}^3 \text{ g}^{-1}.$$

With L and Δv constant, the Clapeyron equation must be integrated while retaining its $1/T$ dependence:

$$dp = \frac{L}{\Delta v} \frac{dT}{T}.$$

Integrating between the normal boiling point (p_1, T_1) and the required state (p_2, T_2),

$$\int_{p_1}^{p_2} dp = \frac{L}{\Delta v} \int_{T_1}^{T_2} \frac{dT}{T},$$

and hence

$$p_2 - p_1 = \frac{L}{\Delta v} \ln\left(\frac{T_2}{T_1}\right).$$

Now,

$$\frac{L}{\Delta v} = \frac{2.268 \times 10^{10} \text{ erg g}^{-1}}{1676 \text{ cm}^3 \text{ g}^{-1}} = 1.3532 \times 10^7 \text{ erg cm}^{-3}.$$

Since

$$1 \text{ erg} = 1 \text{ dyne cm},$$

it follows that

$$1 \text{ erg cm}^{-3} = 1 \text{ dyne cm}^{-2},$$

so

$$\frac{L}{\Delta v} = 1.3532 \times 10^7 \text{ dyn cm}^{-2}.$$

Therefore,

$$p_2 - p_1 = 1.3532 \times 10^7 \ln\left(\frac{423}{373}\right) \text{ dyn cm}^{-2}.$$

Using

$$\ln\left(\frac{423}{373}\right) = \ln(1.13405) \approx 0.12579,$$

we obtain

$$p_2 - p_1 \approx (1.3532 \times 10^7)(0.12579) \text{ dyn cm}^{-2} \approx 1.702 \times 10^6 \text{ dyn cm}^{-2}.$$

Thus

$$p_2 = p_1 + (p_2 - p_1) = (1.000 + 1.702) \times 10^6 \text{ dyn cm}^{-2},$$

or

$$p_2 \approx 2.702 \times 10^6 \text{ dyn cm}^{-2}.$$

Since $1 \text{ atm} = 10^6 \text{ dyn cm}^{-2}$,

$$p_2 \approx 2.70 \text{ atm}.$$

The result has the required physical sign: because $L > 0$, $\Delta v > 0$, and $T_2 > T_1$, the saturation pressure increases. Moreover, for a very small temperature change,

$$\ln\left(\frac{T_2}{T_1}\right) \approx \frac{T_2 - T_1}{T_1},$$

so the integrated result reduces to the local Clapeyron form, as it should.

CONCLUSION:

Under the approximation that the latent heat and specific-volume change remain constant between 100°C and 150°C, water boils at 150°C when the absolute pressure is

$$p_2 \approx 2.70 \times 10^6 \text{ dyn cm}^{-2} \approx 2.70 \text{ atm}.$$

Thus the boiling point rises to 150°C when the external pressure is increased to approximately 2.70 atmospheres.

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Q4. Why does the specific heat of solids depend on material at low temperatures but become independent of material at high temperatures?

INTRODUCTION:

The temperature dependence follows from the quantization of lattice vibrations. A crystalline solid containing N atoms has $3N$ normal vibrational modes, which may be treated, in the harmonic approximation, as independent quantum oscillators of angular

frequencies ω_s . Their frequencies depend on the elastic constants, atomic masses, crystal structure, and interatomic forces; hence the vibrational spectrum is material-dependent.

Let C_V denote the heat capacity at constant volume, k_B the Boltzmann constant, and

$$\Theta_D = \frac{\hbar\omega_D}{k_B}$$

the Debye temperature corresponding to the maximum Debye frequency ω_D . The low- and high-temperature regimes mean $T \ll \Theta_D$ and $T \gg \Theta_D$, respectively. The discussion primarily concerns the lattice heat capacity of a non-magnetic crystalline solid. In metals, an additional electronic contribution is relevant at sufficiently low temperatures.

SOLUTION:

For a normal mode of frequency ω , the allowed energies are

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega, \quad n = 0, 1, 2, \dots$$

Its temperature-dependent mean energy is

$$\bar{E}(\omega, T) = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/(k_B T)} - 1}.$$

The zero-point term $\hbar\omega/2$ is independent of T and therefore does not contribute to the heat capacity. Differentiation gives the heat capacity of one mode:

$$c_\omega = k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\hbar\omega/(k_B T)}}{(e^{\hbar\omega/(k_B T)} - 1)^2}.$$

At low temperature, a mode with $\hbar\omega \gg k_B T$ has an exponentially small thermal occupation. Thus only long-wavelength acoustic modes of sufficiently low frequency are appreciably excited. In the Debye approximation, their density of states is

$$g(\omega) = \frac{9N}{\omega_D^3} \omega^2, \quad 0 \leq \omega \leq \omega_D,$$

where the normalization satisfies

$$\int_0^{\omega_D} g(\omega) d\omega = 3N.$$

The thermal lattice energy is therefore

$$U_{\text{th}} = \int_0^{\omega_D} \frac{\hbar\omega}{e^{\hbar\omega/(k_B T)} - 1} g(\omega) d\omega.$$

On introducing

$$x = \frac{\hbar\omega}{k_B T}, \quad \frac{\hbar\omega_D}{k_B T} = \frac{\Theta_D}{T},$$

one obtains

$$U_{\text{th}} = 9Nk_B T \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx.$$

Hence

$$C_V = 9Nk_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx.$$

For $T \ll \Theta_D$, the upper limit can be replaced by infinity. Using

$$\int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15},$$

the energy and heat capacity become

$$U_{\text{th}} = \frac{3\pi^4}{5} Nk_B \frac{T^4}{\Theta_D^3},$$

and

$$C_V = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\Theta_D} \right)^3.$$

Thus the Debye T^3 law is obtained. Since

$$\omega_D = v_D (6\pi^2 n)^{1/3}, \quad \Theta_D = \frac{\hbar v_D}{k_B} (6\pi^2 n)^{1/3},$$

where $n = N/V$ is the number density and v_D is an appropriate average sound velocity, Θ_D depends on density, atomic mass, and elastic constants. Consequently, the coefficient of T^3 ,

$$\frac{C_V}{T^3} = \frac{12\pi^4}{5} \frac{Nk_B}{\Theta_D^3},$$

is different for different materials. This is the origin of the strong material dependence at low temperature.

For a metal, thermally excited electrons near the Fermi surface add a term proportional to T , so that at sufficiently low temperature

$$C_V = \gamma T + \beta T^3, \quad \beta = \frac{12\pi^4}{5} \frac{Nk_B}{\Theta_D^3}.$$

Both γ , which depends on the electronic density of states at the Fermi energy, and β are material-dependent.

At high temperature, $T \gg \Theta_D$, one has

$$x = \frac{\hbar\omega}{k_B T} \ll 1$$

for essentially every lattice mode. Since

$$e^x - 1 \simeq x,$$

the mean thermal energy of each mode approaches

$$\frac{\hbar\omega}{e^{\hbar\omega/(k_B T)} - 1} \simeq k_B T.$$

This is also the classical equipartition result: each harmonic mode has one quadratic kinetic term and one quadratic potential term, contributing

$$\frac{1}{2}k_B T + \frac{1}{2}k_B T = k_B T.$$

Because a solid of N atoms has $3N$ vibrational modes,

$$U_{th} \approx 3Nk_B T,$$

and hence

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \approx 3Nk_B.$$

For one mole, $N = N_A$, and therefore

$$C_{V,m} \approx 3N_A k_B = 3R \approx 24.9 \text{ J mol}^{-1} \text{ K}^{-1}.$$

This is the Dulong–Petit law. The mode frequencies, and hence the microscopic material properties, disappear from the leading high-temperature result because all $3N$ modes are fully thermally excited and each contributes the same classical amount k_B .

The statement of material independence applies to heat capacity per atom or per mole of atoms. If “specific heat” means heat capacity per unit mass, then

$$c_V = \frac{C_{V,m}}{M} \approx \frac{3R}{M},$$

where M is the molar mass. It therefore retains a dependence on molar mass even in the classical high-temperature limit. Moreover, strong anharmonicity, thermal expansion, phase changes, or differences between C_P and C_V can produce corrections to the ideal Dulong–Petit value.

CONCLUSION:

At low temperatures, only low-frequency acoustic phonons are excited, and their spectrum is fixed by material-specific atomic masses, number density, elastic constants, and sound velocities. Consequently,

$$C_V \approx \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\Theta_D} \right)^3, \quad T \ll \Theta_D,$$

with an additional material-dependent electronic term γT in metals.

At high temperatures, every one of the $3N$ lattice modes reaches the classical equipartition limit and contributes k_B , giving

$$C_V \approx 3Nk_B, \quad C_{V,m} \approx 3R \approx 24.9 \text{ J mol}^{-1} \text{ K}^{-1}, \quad T \gg \Theta_D.$$

Thus the high-temperature lattice heat capacity per atom, or molar heat capacity per mole of atoms, is approximately independent of material because it depends only on the number of vibrational degrees of freedom. The heat capacity per unit mass remains $3R/M$ and is not strictly material-independent.

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Q5. A reversible heat engine operates with three reservoirs at 300 K, 400 K and 1200 K. It absorbs 1200 kJ energy as heat from the reservoir at 1200 K and delivers 400 kJ work. Determine the heat interactions with the other two reservoirs.

INTRODUCTION:

The heat interactions are determined by applying both the first law of thermodynamics and the Clausius equality for a reversible cyclic heat engine.

Let Q_T denote the heat transferred to the engine from a reservoir at absolute temperature T . The sign convention is

$$Q_T > 0$$

for heat absorbed by the engine

$$Q_T < 0$$

for heat rejected by the engine.

Let $W > 0$ denote work delivered by the engine. The given quantities are

$$Q_{1200} = 1200 \text{ kJ}, \quad W = 400 \text{ kJ}.$$

The unknown heat interactions are Q_{300} and Q_{400} . The engine is assumed to complete a thermodynamic cycle, so its changes in internal energy and entropy over one cycle are both zero. Since the engine is reversible, the total entropy change of the reservoirs and engine is zero.

SOLUTION:

For a cyclic heat engine, the first law gives

$$\sum Q = W.$$

Therefore,

$$Q_{300} + Q_{400} + Q_{1200} = W.$$

Substituting the given values,

$$Q_{300} + Q_{400} + 1200 \text{ kJ} = 400 \text{ kJ},$$

and hence

$$Q_{300} + Q_{400} = -800 \text{ kJ}. \quad (1)$$

Because the cycle is reversible, the Clausius equality is

$$\oint \frac{\delta Q_{rev}}{T} = 0.$$

As each heat interaction occurs with a constant-temperature reservoir,

$$\frac{Q_{300}}{300 \text{ K}} + \frac{Q_{400}}{400 \text{ K}} + \frac{Q_{1200}}{1200 \text{ K}} = 0.$$

Substituting $Q_{1200} = 1200 \text{ kJ}$,

$$\frac{Q_{300}}{300 \text{ K}} + \frac{Q_{400}}{400 \text{ K}} + \frac{1200 \text{ kJ}}{1200 \text{ K}} = 0,$$

so that

$$\frac{Q_{300}}{300 \text{ K}} + \frac{Q_{400}}{400 \text{ K}} = -1 \text{ kJ K}^{-1}. \quad (2)$$

Multiplying equation (2) by 1200 K gives

$$4Q_{300} + 3Q_{400} = -1200 \text{ kJ}. \quad (3)$$

Multiplying equation (1) by 3 gives

$$3Q_{300} + 3Q_{400} = -2400 \text{ kJ}. \quad (4)$$

Subtracting equation (4) from equation (3),

$$Q_{300} = (-1200 + 2400) \text{ kJ} = 1200 \text{ kJ}.$$

Using equation (1),

$$Q_{400} = -800 \text{ kJ} - 1200 \text{ kJ} = -2000 \text{ kJ}.$$

The energy balance is verified by

$$1200 \text{ kJ} + 1200 \text{ kJ} - 2000 \text{ kJ} = 400 \text{ kJ} = W.$$

Thus, the total heat absorbed is 2400 kJ, of which 2000 kJ is rejected and the remaining 400 kJ appears as work.

The entropy balance is

$$\frac{1200}{1200} + \frac{1200}{300} - \frac{2000}{400} = (1 + 4 - 5) \text{ kJ K}^{-1} = 0,$$

as required for a reversible cycle. Every term Q/T has units of entropy, kJ K^{-1} , so the entropy equation is dimensionally consistent.

The positive value of Q_{300} means that the engine absorbs heat even from the lowest-temperature reservoir. This is physically possible because the device is not a simple two-reservoir heat engine: part of the high-temperature energy enables reversible heat transfer from the 300 K reservoir to the 400 K reservoir while the composite device delivers net work.

CONCLUSION:

Subject to the stated assumptions of cyclic operation and complete reversibility,

$$Q_{300} = +1200 \text{ kJ}, \quad Q_{400} = -2000 \text{ kJ}.$$

Therefore, the engine absorbs 1200 kJ of heat from the 300 K reservoir and rejects 2000 kJ of heat to the 400 K reservoir. Together with the given absorption of 1200 kJ from the 1200 K reservoir, these interactions conserve energy, produce 400 kJ of work, and generate zero net entropy.

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Q6. A ternary system consists of three components (A , B and C) in equilibrium with two phases. Determine the number of degrees of freedom using the Gibb's phase rule and discuss the effect of pressure and temperature variations on the phase equilibrium.

INTRODUCTION:

The demand is to determine the number of independent intensive variables required to specify the equilibrium state and to explain how variations of temperature and pressure affect the two-phase equilibrium.

Assume that the system is non-reacting, that A , B , and C are chemically independent components, and that the two phases are homogeneous bulk phases in complete thermal, mechanical, and chemical equilibrium. Surface, gravitational, electric, and magnetic effects are neglected.

Let C = number of independent components,

P = number of phases,

F = number of degrees of freedom.

For the present system,

$$C = 3, \quad P = 2.$$

The phases will be denoted by 1 and 2, with mole fractions

$$x_i^{(1)}, \quad x_i^{(2)}, \quad i = A, B, C.$$

Temperature T and pressure p are common to both phases. The thermodynamic pressure convention is that $dp > 0$ denotes an increase in pressure. Differences between the partial molar properties of the phases are defined by

$$\Delta \bar{s}_i = \bar{s}_i^{(2)} - \bar{s}_i^{(1)}, \quad \Delta \bar{v}_i = \bar{v}_i^{(2)} - \bar{v}_i^{(1)}.$$

The governing principle is Gibbs' phase rule,

$$F = C - P + 2,$$

which follows from counting the independent intensive variables and subtracting the independent chemical-equilibrium conditions.

SOLUTION:

For each phase α , the mole fractions satisfy

$$x_A^{(\alpha)} + x_B^{(\alpha)} + x_C^{(\alpha)} = 1.$$

Therefore, only $C - 1$ mole fractions are independent in each phase. Before imposing chemical equilibrium, the complete intensive description contains:

1. the common temperature T ;
2. the common pressure p ;
3. $C - 1$ independent composition variables for each of the P phases.

Thus, the number of intensive variables before imposing the equilibrium constraints is

$$N_{\text{var}} = 2 + P(C - 1).$$

Chemical equilibrium requires that every component have the same chemical potential in all coexisting phases:

$$\mu_i^{(1)} = \mu_i^{(2)} = \dots = \mu_i^{(P)}, \quad i = 1, 2, \dots, C.$$

For any one component, equality among P phases supplies $P - 1$ independent equations. Consequently, the number of independent chemical-equilibrium constraints is

$$N_{\text{con}} = C(P - 1).$$

The number of degrees of freedom is therefore

$$\begin{aligned} F &= N_{\text{var}} - N_{\text{con}} \\ &= [2 + P(C - 1)] - C(P - 1) \\ &= 2 + PC - P - CP + C \\ &= C - P + 2. \end{aligned}$$

For the ternary two-phase system,

$$F = 3 - 2 + 2 = 3.$$

Hence the system is *trivariant*. Three independent intensive variables can be specified while retaining two-phase equilibrium. One convenient choice is T , p , and one independent parameter identifying the pair of equilibrium phase compositions. Once these three variables are fixed, the remaining intensive composition variables are determined by

$$\mu_A^{(1)} = \mu_A^{(2)}, \quad \mu_B^{(1)} = \mu_B^{(2)}, \quad \mu_C^{(1)} = \mu_C^{(2)}.$$

The result under commonly imposed restrictions is as follows:

1. If both temperature and pressure are variable, then

$$F = 3.$$

2. If pressure is fixed externally, one degree of freedom has already been specified. The reduced phase rule gives

$$F_p = C - P + 1 = 3 - 2 + 1 = 2.$$

Thus, temperature and one independent compositional parameter may be varied within the two-phase equilibrium region.

3. If temperature is fixed externally,

$$F_T = C - P + 1 = 2.$$

Pressure and one independent compositional parameter remain variable.

4. If both temperature and pressure are fixed,

$$F_{T,p} = C - P = 3 - 2 = 1.$$

Thus there remains one independent intensive compositional parameter. The compositions of the two phases cannot be chosen independently; they must satisfy all three chemical-potential equalities.

The total or overall composition is distinct from the equilibrium composition of either phase. Once the equilibrium phase compositions are known, changing the overall composition along the appropriate two-phase combination generally changes the relative amounts of the phases rather than their equilibrium intensive compositions. If n_1 and n_2 are the amounts of the two phases, material balance gives

$$z_i = \frac{n_1 x_i^{(1)} + n_2 x_i^{(2)}}{n_1 + n_2}, \quad i = A, B, C,$$

where z_i is the overall mole fraction. Thus, phase amounts are extensive variables and are not counted in F .

For each component in a multicomponent phase,

$$d\mu_i = -\bar{s}_i dT + \bar{v}_i dp + \sum_{j=1}^{C-1} \left(\frac{\partial \mu_i}{\partial x_j} \right)_{T,p} dx_j,$$

where $\bar{s}_i$ and $\bar{v}_i$ are the partial molar entropy and partial molar volume of component i . Subtracting this relation for phase 1 from that for phase 2 gives

$$\begin{aligned} d(\mu_i^{(2)} - \mu_i^{(1)}) &= -\Delta \bar{s}_i dT + \Delta \bar{v}_i dp \\ &+ \sum_{j=1}^{C-1} \left(\frac{\partial \mu_i^{(2)}}{\partial x_j^{(2)}} \right)_{T,p} dx_j^{(2)} - \sum_{j=1}^{C-1} \left(\frac{\partial \mu_i^{(1)}}{\partial x_j^{(1)}} \right)_{T,p} dx_j^{(1)}. \end{aligned}$$

For continued two-phase equilibrium this expression must vanish separately for

$$i = A, \quad B, \quad C,$$

because

$$\mu_i^{(2)} - \mu_i^{(1)} = 0.$$

At fixed pressure,

$$dp = 0,$$

so a change in temperature produces the direct contribution

$$d(\mu_i^{(2)} - \mu_i^{(1)})_{\text{fixed compositions}} = -\Delta \bar{s}_i dT.$$

Hence increasing T lowers the chemical potential of component i more strongly in the phase in which its partial molar entropy is larger. To restore equality of all three chemical potentials, the compositions $x_i^{(1)}$ and $x_i^{(2)}$ generally readjust. Therefore, temperature variation can shift the equilibrium phase compositions, alter the two-phase region, and, for a specified overall composition, change the relative amounts of the phases. If a phase boundary is crossed, one phase can disappear or an additional stable phase can appear.

At fixed temperature,

$$dT = 0,$$

and the direct pressure contribution is

$$d(\mu_i^{(2)} - \mu_i^{(1)})_{\text{fixed compositions}} = \Delta \bar{v}_i dp.$$

Thus increasing pressure raises the chemical potential of component i more strongly in the phase in which its partial molar volume is larger. The equilibrium compositions must again change so that

$$\mu_i^{(1)} = \mu_i^{(2)}$$

remains satisfied for every component. Pressure effects are usually relatively small when both phases are condensed and have similar partial molar volumes, but they may be substantial when one phase is gaseous or when the phases have appreciably different densities.

No universal statement that an entire phase is favoured merely because it has a larger molar entropy or molar volume can be made for arbitrary ternary phases of different compositions. The correct coexistence criterion is the component-wise equality of chemical potentials. A definite prediction of the direction and magnitude of the composition shifts requires the partial molar entropies, partial molar volumes, and composition dependence of the three chemical potentials.

As a dimensional check,

$$[\mu_i] = \text{J mol}^{-1},$$

while

$$[\bar{s}_i dT] = \text{J mol}^{-1} \text{K}^{-1} \text{K} = \text{J mol}^{-1},$$

and

$$[\bar{v}_i dp] = \text{m}^3 \text{mol}^{-1} \text{Pa} = \text{J mol}^{-1}.$$

Thus every term in $d\mu_i$ has the correct dimensions.

As a limiting check, setting $C = 1$ and $P = 2$ gives

$$F = 1 - 2 + 2 = 1,$$

which is the familiar result that two phases of a pure substance coexist along a one-parameter curve: choosing either T or p fixes the other. This confirms the consistency of the phase-rule counting.

CONCLUSION:

For a non-reacting ternary system containing two homogeneous phases in equilibrium,

$$F = C - P + 2 = 3.$$

The system is therefore trivariant. The corresponding restricted degrees of freedom are

$$F_p = 2, \quad F_T = 2, \quad F_{T,p} = 1.$$

Temperature affects equilibrium through the partial molar entropy terms

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,x} = -\bar{s}_i,$$

whereas pressure affects it through the partial molar volume terms

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,x} = \bar{v}_i.$$

Consequently, variations in T or p generally shift the compositions of the two coexisting phases so that

$$\mu_i^{(1)} = \mu_i^{(2)}, \quad i = A, B, C$$

continues to hold. For a specified overall composition, these shifts can also alter the relative phase amounts, and sufficiently large variations can cause a phase boundary to be crossed. The result is valid provided there are three independent non-reacting components, two bulk equilibrium phases, and no additional externally imposed thermodynamic constraints.

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Q7. Discuss briefly the considerations which led Van der Waals to modify the gas equation. What are the critical constants of a gas? Calculate the values of these constants in terms of the constants of the Van der Waals equation.

INTRODUCTION:

The ideal-gas equation for one mole,

$$PV_m = RT,$$

is based on two simplifying assumptions: the molecules occupy negligible volume, and no intermolecular forces act between them except during perfectly elastic collisions. Real gases depart appreciably

from this equation at high pressure and low temperature, where molecular size and intermolecular attraction become important.

Van der Waals therefore introduced two corrections. If b is the excluded molar volume, the volume actually available for molecular motion is $V_m - b$, rather than V_m . If a measures the strength of intermolecular attraction, the observed pressure is smaller than the pressure that would exist without attraction. The corresponding pressure correction for one mole is a/V_m^2 . Thus the Van der Waals equation is

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT,$$

or

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}.$$

Here P is the pressure, T the absolute temperature, V_m the molar volume, R the universal gas constant, and $a, b > 0$ are characteristic constants of the gas.

The critical constants are the critical temperature T_c , critical pressure P_c , and critical molar volume V_c . At T_c , the distinction between the liquid and vapour phases disappears. The critical isotherm has a stationary point of inflection at (P_c, V_c) ; hence

$$\left(\frac{\partial P}{\partial V_m}\right)_{T_c, V_c} = 0, \quad \left(\frac{\partial^2 P}{\partial V_m^2}\right)_{T_c, V_c} = 0.$$

SOLUTION:

The reasons for modifying the ideal-gas equation are as follows.

1. Finite molecular volume:

Real molecules are not point particles. At sufficiently high pressure, their own volume is no longer negligible compared with the volume of the vessel. Moreover, because two molecules cannot occupy the same region of space, the volume available for translational motion is smaller than the measured molar volume. Van der Waals represented this reduction by replacing

$$V_m \longrightarrow V_m - b.$$

2. Intermolecular attraction:

A molecule well inside the gas is attracted approximately equally in all directions, so the resultant force on it is nearly zero. A molecule approaching a wall, however, is attracted predominantly back into the gas. Its momentum transfer to the wall, and hence the measured pressure, is therefore reduced.

The reduction is proportional both to the number density of molecules near the wall and

to the number density of molecules attracting them. It consequently varies as the square of the density:

$$\Delta P \propto \left(\frac{1}{V_m}\right)^2.$$

Writing the proportionality constant as a ,

$$P_{\text{ideal interaction-free}} = P + \frac{a}{V_m^2}.$$

Combining the pressure and volume corrections gives

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT.$$

To calculate the critical constants, write the equation of state explicitly as

$$P(V_m, T) = \frac{RT}{V_m - b} - \frac{a}{V_m^2}.$$

At the critical point, the first derivative of pressure with respect to molar volume at constant temperature vanishes:

$$\left(\frac{\partial P}{\partial V_m}\right)_T = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3}.$$

Therefore,

$$-\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0,$$

so that

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3}. \quad (1)$$

The second derivative is

$$\left(\frac{\partial^2 P}{\partial V_m^2}\right)_T = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4}.$$

At the critical point,

$$\frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0,$$

or

$$\frac{RT_c}{(V_c - b)^3} = \frac{3a}{V_c^4}. \quad (2)$$

Dividing equation (2) by equation (1) eliminates T_c :

$$\frac{1}{V_c - b} = \frac{3a/V_c^4}{2a/V_c^3} = \frac{3}{2V_c}.$$

Hence

$$2V_c = 3(V_c - b),$$

which gives

$$\boxed{V_c = 3b}.$$

Substituting $V_c = 3b$ into equation (1),

$$\frac{RT_c}{(3b - b)^2} = \frac{2a}{(3b)^3}.$$

Thus

$$\frac{RT_c}{4b^2} = \frac{2a}{27b^3},$$

and therefore

$$T_c = \frac{8a}{27Rb}.$$

The critical pressure follows from the equation of state:

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2}.$$

Using $V_c = 3b$ and $RT_c = 8a/(27b)$,

$$P_c = \frac{8a/(27b)}{3b - b} - \frac{a}{(3b)^2}.$$

Therefore,

$$P_c = \frac{8a}{54b^2} - \frac{a}{9b^2} = \frac{4a}{27b^2} - \frac{3a}{27b^2},$$

so

$$P_c = \frac{a}{27b^2}.$$

These expressions satisfy the critical-point derivative conditions explicitly. For example,

$$\left(\frac{\partial P}{\partial V_m} \right)_c = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = -\frac{2a}{27b^3} + \frac{2a}{27b^3} = 0,$$

and

$$\left(\frac{\partial^2 P}{\partial V_m^2} \right)_c = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = \frac{2a}{27b^4} - \frac{2a}{27b^4} = 0.$$

The dimensional checks are

$$[a] = [P][V_m]^2, \quad [b] = [V_m].$$

Consequently,

$$\left[\frac{a}{b^2} \right] = [P], \quad \left[\frac{a}{Rb} \right] = [T],$$

as required for P_c and T_c .

A further consistency check is the critical compressibility factor:

$$Z_c = \frac{P_c V_c}{RT_c} = \frac{(a/27b^2)(3b)}{8a/(27b)} = \frac{3}{8}.$$

Thus the Van der Waals equation predicts the same dimensionless critical compressibility factor for all gases. In the dilute-gas limit $V_m \gg b$, with a/V_m^2 negligible, the equation reduces to

$$PV_m \simeq RT,$$

recovering ideal-gas behaviour.

CONCLUSION:

Van der Waals modified the ideal-gas equation to account for the finite size of molecules through the excluded-volume constant b , and for intermolecular attraction through the pressure correction a/V_m^2 . For one mole,

$$\left(P + \frac{a}{V_m^2} \right) (V_m - b) = RT.$$

The critical constants obtained from the stationary-inflection conditions on the critical isotherm are

$$V_c = 3b, \quad P_c = \frac{a}{27b^2}, \quad T_c = \frac{8a}{27Rb}.$$

They also obey

$$\frac{P_c V_c}{RT_c} = \frac{3}{8}.$$

Hence the Van der Waals parameters determine the pressure, temperature, and molar volume at which the liquid and gaseous phases become indistinguishable.

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Q8. Explain why, at equilibrium, the chemical potential of a component must be the same in all coexisting phases. Derive the equilibrium condition for a binary liquid-vapour system in terms of chemical potential.

INTRODUCTION:

The chemical potential of component i in a phase is the partial molar Gibbs free energy,

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}}.$$

It therefore measures the change in Gibbs free energy when an infinitesimal amount of that component is added to the phase at fixed temperature and pressure.

Consider a closed, non-reacting system containing homogeneous coexisting phases. The phases are assumed to have a common temperature T and pressure P , and interfacial, gravitational, and other finite-size contributions are neglected. The total amount of each component is conserved, but matter may pass between phases. At fixed T and P , stable equilibrium requires the total Gibbs free energy to be stationary against every allowed infinitesimal transfer and to be

a minimum with respect to finite admissible variations.

For the binary liquid-vapour system, let the components be 1 and 2, and use superscripts l and v for the liquid and vapour phases. Thus,

$$\mu_i^l = \mu_i^l(T, P, x_1, x_2), \quad \mu_i^v = \mu_i^v(T, P, y_1, y_2),$$

where x_i and y_i are the liquid- and vapour-phase mole fractions, with

$$x_1 + x_2 = 1, \quad y_1 + y_2 = 1.$$

The required equilibrium conditions follow by minimizing the total Gibbs free energy subject to conservation of both components.

SOLUTION:

For a multicomponent homogeneous phase, the fundamental Gibbs relation is

$$dG = -S dT + V dP + \sum_i \mu_i dn_i.$$

At fixed T and P , this reduces to

$$dG = \sum_i \mu_i dn_i.$$

Consider first one component i distributed between two coexisting phases α and β . Let a positive infinitesimal amount dn_i be transferred from phase α to phase β . Conservation of the total amount of component i gives

$$dn_i^\alpha = -dn_i, \quad dn_i^\beta = +dn_i.$$

The corresponding change in the total Gibbs free energy is

$$\begin{aligned} dG_{\text{tot}} &= \mu_i^\alpha dn_i^\alpha + \mu_i^\beta dn_i^\beta \\ &= -\mu_i^\alpha dn_i + \mu_i^\beta dn_i \\ &= (\mu_i^\beta - \mu_i^\alpha) dn_i. \end{aligned}$$

At equilibrium, an allowed infinitesimal transfer in either direction must produce no first-order change in G_{tot} . Since dn_i is arbitrary,

$$dG_{\text{tot}} = 0 \implies \boxed{\mu_i^\alpha = \mu_i^\beta}.$$

The physical meaning can also be seen from the sign of dG_{tot} . If

$$\mu_i^\alpha > \mu_i^\beta,$$

then transfer from α to β gives

$$dG_{\text{tot}} = (\mu_i^\beta - \mu_i^\alpha) dn_i < 0,$$

so the transfer is spontaneous. Thus a component moves, in the thermodynamic sense, from a phase of

higher chemical potential to one of lower chemical potential. Such transfer ceases only when its chemical potentials are equal. For more than two coexisting phases,

$$\boxed{\mu_i^{(1)} = \mu_i^{(2)} = \dots = \mu_i^{(r)}}$$

for every component i .

Now consider a binary liquid-vapour system. Its total Gibbs free energy is

$$G = G^l(T, P, n_1^l, n_2^l) + G^v(T, P, n_1^v, n_2^v).$$

Because the system is closed and non-reacting, the total amount of each component is fixed:

$$n_1^l + n_1^v = N_1, \quad n_2^l + n_2^v = N_2.$$

Hence the allowed variations satisfy

$$dn_1^v = -dn_1^l, \quad dn_2^v = -dn_2^l.$$

At fixed T and P , the variation of the total Gibbs free energy is

$$dG = \mu_1^l dn_1^l + \mu_2^l dn_2^l + \mu_1^v dn_1^v + \mu_2^v dn_2^v.$$

Using the conservation constraints,

$$\begin{aligned} dG &= \mu_1^l dn_1^l + \mu_2^l dn_2^l - \mu_1^v dn_1^l - \mu_2^v dn_2^l \\ &= (\mu_1^l - \mu_1^v) dn_1^l + (\mu_2^l - \mu_2^v) dn_2^l. \end{aligned}$$

The amounts of components 1 and 2 may be independently redistributed between the two phases while their respective total amounts remain fixed. Therefore dn_1^l and dn_2^l are independent admissible variations. The equilibrium condition $dG = 0$ for every such variation requires the coefficient of each variation to vanish:

$$\boxed{\mu_1^l(T, P, x_1, x_2) = \mu_1^v(T, P, y_1, y_2)},$$

$$\boxed{\mu_2^l(T, P, x_1, x_2) = \mu_2^v(T, P, y_1, y_2)}.$$

Together with

$$T^l = T^v, \quad P^l = P^v,$$

these are the conditions for thermal, mechanical, and diffusive equilibrium, respectively.

The result may equivalently be obtained with constrained minimization. Introduce Lagrange multipliers λ_1 and λ_2 for conservation of the two components:

$$\Phi = G^l + G^v - \lambda_1(n_1^l + n_1^v - N_1) - \lambda_2(n_2^l + n_2^v - N_2).$$

Stationarity with respect to the four independently varied phase amounts gives

$$\frac{\partial \Phi}{\partial n_1^l} = \mu_1^l - \lambda_1 = 0, \quad \frac{\partial \Phi}{\partial n_1^v} = \mu_1^v - \lambda_1 = 0,$$

and

$$\frac{\partial \Phi}{\partial n_2^l} = \mu_2^l - \lambda_2 = 0, \quad \frac{\partial \Phi}{\partial n_2^v} = \mu_2^v - \lambda_2 = 0.$$

Consequently,

$$\mu_1^l = \lambda_1 = \mu_1^v, \quad \mu_2^l = \lambda_2 = \mu_2^v,$$

which reproduces the equilibrium conditions.

For a general non-ideal mixture, the chemical potential may be expressed in terms of fugacity:

$$\mu_i(T, P, \text{composition}) = \mu_i^\circ(T) + RT \ln\left(\frac{f_i}{f^\circ}\right).$$

At the same temperature, equality of chemical potentials is therefore equivalent to equality of component fugacities:

$$\mu_i^l = \mu_i^v \iff f_i^l = f_i^v, \quad i = 1, 2.$$

Thus the binary phase-equilibrium relations can also be written as

$$f_1^l(T, P, x_1, x_2) = f_1^v(T, P, y_1, y_2)$$

$$f_2^l(T, P, x_1, x_2) = f_2^v(T, P, y_1, y_2).$$

As a check, if $\mu_i^l - \mu_i^v > 0$, transferring component i from liquid to vapour gives

$$dG = (\mu_i^v - \mu_i^l) dn_i^v < 0,$$

so vaporization is favoured. If $\mu_i^l - \mu_i^v < 0$, condensation is favoured. When the two chemical potentials are equal, neither direction lowers the Gibbs free energy, as required at phase equilibrium. Dimensionally, μ_i has units of energy per mole, and $\mu_i dn_i$ has units of energy, consistent with its contribution to dG .

CONCLUSION:

At fixed common temperature and pressure, the equilibrium state minimizes the total Gibbs free energy subject to conservation of every component. An infinitesimal transfer of component i between two phases changes the Gibbs free energy by the chemical-potential difference multiplied by the transferred amount. Therefore, diffusive equilibrium requires

$$\mu_i^\alpha = \mu_i^\beta$$

for each component in every pair of coexisting phases.

For a closed, non-reacting binary liquid-vapour system with homogeneous bulk phases and negligible interfacial and gravitational effects, the complete phase-equilibrium conditions are

$$T^l = T^v, \quad P^l = P^v,$$

$$\mu_1^l(T, P, \mathbf{x}) = \mu_1^v(T, P, \mathbf{y}), \quad \mu_2^l(T, P, \mathbf{x}) = \mu_2^v(T, P, \mathbf{y}),$$

where $\mathbf{x} = (x_1, x_2)$, $\mathbf{y} = (y_1, y_2)$, $x_1 + x_2 = 1$, and $y_1 + y_2 = 1$. Equivalently,

$$f_1^l = f_1^v, \quad f_2^l = f_2^v.$$

A chemical-potential inequality produces net transfer from the phase of higher chemical potential to that of lower chemical potential; equality signifies that neither vaporization nor condensation of either component can lower the Gibbs free energy.

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Q9. For silver, the specific heat at constant pressure in the range of 50 K to 100 K is given by : $C_p = 0.076 T - 0.00026 T^2 - 0.15 \text{ cal mol}^{-1} \text{ deg}^{-1}$. If 2 moles of silver are heated from 50 K to 100 K, calculate the change in entropy.

INTRODUCTION:

The demand is to calculate the entropy change of $n = 2$ moles of silver when its temperature increases from

$$T_1 = 50 \text{ K} \quad \text{to} \quad T_2 = 100 \text{ K}$$

at constant pressure.

Entropy is a state function. Hence its change may be evaluated along a reversible constant-pressure path between the same equilibrium states. For reversible heating,

$$dS = \frac{\delta Q_{\text{rev}}}{T},$$

and, at constant pressure with no phase transition or additional non- pV work,

$$\delta Q_{\text{rev}} = nC_p(T) dT.$$

Therefore,

$$\Delta S = n \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT.$$

Here $C_p(T)$ is the molar heat capacity, T is the absolute temperature, and $\Delta S = S_2 - S_1$. We use the laboratory thermodynamic frame and the sign convention that heat absorbed by the silver is positive; consequently, heating with $C_p > 0$ should give $\Delta S > 0$. The empirical expression is assumed valid throughout $50 \leq T \leq 100 \text{ K}$, with no phase change in this interval. Since a temperature interval of one kelvin equals one Celsius degree, $\text{cal mol}^{-1} \text{ deg}^{-1}$ may be used as $\text{cal mol}^{-1} \text{ K}^{-1}$.

SOLUTION:

The given molar heat capacity is

$$C_p(T) = 0.076T - 0.00026T^2 - 0.15 \text{ cal mol}^{-1} \text{ K}^{-1}.$$

Dividing by the absolute temperature,

$$\frac{C_p(T)}{T} = 0.076 - 0.00026T - \frac{0.15}{T}.$$

Thus,

$$\Delta S = 2 \int_{50}^{100} \left(0.076 - 0.00026T - \frac{0.15}{T} \right) dT.$$

Integrating term by term gives

$$\Delta S = 2 \left[0.076T - \frac{0.00026}{2}T^2 - 0.15 \ln T \right]_{50}^{100}.$$

Equivalently,

$$\Delta S = 2 \left[0.076(T_2 - T_1) - 0.00013(T_2^2 - T_1^2) - 0.15 \ln \left(\frac{T_2}{T_1} \right) \right].$$

Substituting $T_1 = 50 \text{ K}$ and $T_2 = 100 \text{ K}$,

$$\begin{aligned} \Delta S &= 2 \left[0.076(100 - 50) - 0.00013(100^2 - 50^2) - 0.15 \ln \left(\frac{100}{50} \right) \right] \text{ cal K}^{-1} \\ &= 2 [0.076(50) - 0.00013(10000 - 2500) - 0.15 \ln 2] \text{ cal K}^{-1} \\ &= 2 [3.800 - 0.00013(7500) - 0.15(0.693147)] \text{ cal K}^{-1} \\ &= 2 [3.800 - 0.975 - 0.103972] \text{ cal K}^{-1} \\ &= 2(2.72103) \text{ cal K}^{-1} \\ &= 5.44206 \text{ cal K}^{-1}. \end{aligned}$$

In SI units, using $1 \text{ cal} = 4.184 \text{ J}$,

$$\Delta S = 5.44206 \text{ cal K}^{-1} \times 4.184 \text{ J cal}^{-1} = 22.77 \text{ J K}^{-1}.$$

The dimensions are consistent because

$$n \frac{C_p}{T} dT \sim \text{mol} \frac{\text{cal mol}^{-1} \text{ K}^{-1}}{\text{K}} \text{ K} = \text{cal K}^{-1},$$

which is the correct dimension of entropy.

As a plausibility check,

$$C_p(50) = 0.076(50) - 0.00026(50)^2 - 0.15 = 3.00 \text{ cal mol}^{-1} \text{ K}^{-1},$$

and

$$C_p(100) = 0.076(100) - 0.00026(100)^2 - 0.15 = 4.85 \text{ cal mol}^{-1} \text{ K}^{-1}.$$

Thus $C_p > 0$ throughout the interval, so heating must produce a positive entropy change, in agreement with the calculated sign. Also, in the limiting case $T_2 \rightarrow T_1$, every term in the integrated expression vanishes and $\Delta S \rightarrow 0$, as required.

CONCLUSION:

For 2 moles of silver heated at constant pressure from 50 K to 100 K,

$$\Delta S = +5.44 \text{ cal K}^{-1}$$

or, equivalently,

$$\Delta S = +22.8 \text{ J K}^{-1}.$$

The positive sign means that the entropy of the silver increases during heating. This result is valid provided the stated heat-capacity formula applies over 50–100 K, the initial and final states are equilibrium states, and no phase transition occurs in the interval.

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Q10. One gram of water (1 cm^3) becomes 1671 cm^3 of steam when boiled at constant pressure of 1 atm ($1.013 \times 10^5 \text{ Pa}$). The heat of vapourisation at this pressure is $L = 2.256 \times 10^6 \text{ J/kg}$. Calculate : (i) The work done by the water when it vapourizes, and; (ii) Increase in its internal energy.

INTRODUCTION:

We consider a closed system consisting of $m = 1 \text{ g} = 1.000 \times 10^{-3} \text{ kg}$ of water in the laboratory frame. State 1 is liquid water of volume $V_1 = 1 \text{ cm}^3$, and state 2 is steam of volume $V_2 = 1671 \text{ cm}^3$. The vapourization occurs at the constant external pressure

$$P = 1.013 \times 10^5 \text{ Pa}.$$

The heat supplied to the system is positive, and the boundary work W is defined as positive when done by the water on its surroundings. With this convention, the first law of thermodynamics is

$$\Delta U = Q - W.$$

We neglect changes in the macroscopic kinetic and gravitational potential energies. Since the phase change occurs at constant pressure and the stated latent heat L is for that pressure,

$$Q = mL.$$

The expansion work is obtained from

$$W = \int_{V_1}^{V_2} P_{\text{ext}} dV = P(V_2 - V_1),$$

because the external pressure is constant.

SOLUTION:

(i) The increase in volume is

$$\Delta V = V_2 - V_1 = (1671 - 1) \text{ cm}^3 = 1670 \text{ cm}^3.$$

Using

$$1 \text{ cm}^3 = 10^{-6} \text{ m}^3,$$

we obtain

$$\Delta V = 1670 \times 10^{-6} \text{ m}^3 = 1.670 \times 10^{-3} \text{ m}^3.$$

Therefore, the work done by the water is

$$\begin{aligned} W &= P\Delta V \\ &= (1.013 \times 10^5 \text{ Pa}) (1.670 \times 10^{-3} \text{ m}^3) \\ &= 1.69171 \times 10^2 \text{ Pa m}^3. \end{aligned}$$

Since $1 \text{ Pa m}^3 = 1 \text{ J}$,

$$W = 1.692 \times 10^2 \text{ J} \approx 169.2 \text{ J}.$$

The positive sign is consistent with the physical process: the water expands and does work on the surroundings.

(ii) The heat absorbed during vapourization is

$$\begin{aligned} Q &= mL \\ &= (1.000 \times 10^{-3} \text{ kg}) (2.256 \times 10^6 \text{ J kg}^{-1}) \\ &= 2.256 \times 10^3 \text{ J} \\ &= 2256 \text{ J}. \end{aligned}$$

Applying the first law,

$$\begin{aligned} \Delta U &= Q - W \\ &= 2256 \text{ J} - 169.171 \text{ J} \\ &= 2086.829 \text{ J}. \end{aligned}$$

Hence,

$$\Delta U = 2.087 \times 10^3 \text{ J} \approx 2.087 \text{ kJ}.$$

Equivalently, at constant pressure the latent heat supplies the enthalpy increase:

$$mL = \Delta H = \Delta U + P\Delta V,$$

which reproduces the same result.

The dimensions are consistent:

$$[P\Delta V] = \text{Pa m}^3 = \frac{\text{N}}{\text{m}^2} \text{m}^3 = \text{N m} = \text{J}.$$

Moreover,

$$0 < W < Q,$$

so the internal energy increases while part of the supplied heat is transferred outward as expansion work. Numerically,

$$\frac{W}{Q} \approx 0.0750,$$

so about 7.50% of the latent heat becomes expansion work and about 92.5% increases the internal energy. As a limiting check, if the volume change were negligible, $P\Delta V \rightarrow 0$, the first law would give $\Delta U \rightarrow Q$, as expected.

CONCLUSION:

At $1.013 \times 10^5 \text{ Pa}$, the vapourizing water expands by $1.670 \times 10^{-3} \text{ m}^3$. Thus,

$$(i) \text{ Work done by the water on the surroundings} = 1.692 \times 10^2 \text{ J}$$

and

$$(ii) \text{ Increase in internal energy} = 2.087 \times 10^3 \text{ J} = 2.087 \text{ kJ}.$$

These results assume constant external pressure, negligible changes in bulk kinetic and potential energies, and the stated latent heat at the specified pressure. The water transfers approximately 169.2 J outward as mechanical work, while its internal energy increases by approximately 2.087 kJ; hence most of the absorbed latent heat increases the molecular internal energy of the steam.



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