Problem and solution Blundell and Blundell Concept of Thermal Physics Chapter 28 Phase transitions Masatsugu Sei Suzuki, SUNY at Binghamton (Date: November 10, 2019)

<mark>28-1</mark>

(28.1) When lead is melted at atmospheric pressure, the melting point is 327.0° C, the density decreases from 1.101×10^{4} to 1.065×10^{4} kg m⁻³ and the latent heat is 24.5 kJ kg⁻¹. Estimate the melting point of lead at a pressure of 100 atm.

((Solution))

$$\rho_{s} = 1.101 \times 10^{4} \text{ kg/m}^{3}, \qquad \rho_{l} = 1.065 \times 10^{4} \text{ kg/m}^{3},$$

$$V_{s} = \frac{1}{\rho_{s}} = 0.90827 \times 10^{-4} \text{ m}^{3}/\text{kg}, \qquad V_{l} = \frac{1}{\rho_{l}} = 0.938971 \times 10^{-4} \text{ m}^{3}/\text{kg},$$

$$L_{f} = 24.5 \text{ kJ/kg} \qquad \text{(latent heat of fusion for lead)}$$

$$T_{M} = 327 + 273 = 600 \text{ K}$$

$$\frac{dP}{dT} = \frac{S_{l} - S_{s}}{V_{l} - V_{s}} = \frac{1}{T} \frac{L_{f}}{V_{l} - V_{s}} = \frac{1}{600} \frac{24.5 \times 10^{3}}{0.0307 \times 10^{-4}} = 1.33 \times 10^{7} \text{ Pa/K} = 131.3 \text{ atm/K}$$

where

1 atm = 1.01315×10^5 Pa.

When $\Delta P = 99$ atm,

$$\Delta T = \frac{dP}{131.3} = \frac{99}{131.3} = 0.75 \text{ C}$$

which means that the melting temperature increases as

<mark>28-2</mark>

(28.2) Some tea connoisseurs claim that a good cup of tea cannot be brewed with water at a temperature less than 97°C. Assuming this to be the case, is it possible for an astronomer, working on the summit of Mauna Kea in Hawaii (elevation 4194 m, though you don't need to know this to solve the problem) where the air pressure is 615 mbar, to make a good cup of tea without the aid of a pressure vessel?

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((Solution))

L: latent heat of vaporization

 $\Delta V = V_g - V_l$

Thus we have the Clausius-Clapeyron equation,

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

Two approximations:

(i) $V_g >> V_l$

$$\Delta N = V_g - V_l \approx V_g$$

(ii)

$$PV_g = nRT$$
 (ideal gas law)

Using these two approximations, we have

$$\frac{dP}{dT} = \frac{L}{T\Delta V} = \frac{L}{TV_g} = \frac{LP}{nRT^2} = \frac{L_v P}{RT^2}$$

where L_v is the latent heat of vaporization per mol. Suppose that L_v is independent of T.

$$\int \frac{dP}{P} = \frac{L_v}{R} \int \frac{dT}{T^2}$$

or

$$\ln P = -\frac{L_v}{RT} + \text{constant}$$

or

$$P(T) = P_0 \exp(-\frac{L_v}{RT})$$

or

$$\ln P = \ln P_0 - \frac{L_v}{RT}$$

At P = 1 atm = 1013 mbar, T = 373 K. At P = 615 mbar, what is the temperature T?

$$\ln(1013) = \ln P_0 - \frac{L_v}{R} \frac{1}{373}$$
$$\ln(615) = \ln P_0 - \frac{L_v}{R} \frac{1}{(273 + x)}$$

Then we have

$$\ln(\frac{1013}{615}) = -\frac{L_{\nu}}{R}(\frac{1}{373} - \frac{1}{273 + x})$$

with

$$R = 8.3144598 \text{ J/(mol K)}$$

$$L_v = 2260 \text{ kJ/kg} = (2260 \text{ x } 18) \text{ J/mol} = 40.680 \text{ kJ/mol}$$

So we have the boiling temperature as

$$T = 359.329 \text{ K} = 86.3 \text{ C}.$$

((Another approach))

$$\frac{dP}{dT} = \frac{L_v}{T(\frac{1}{\rho_{steam}} - \frac{1}{\rho_{water}})} \approx \frac{2257 \times 10^3 J / kg}{(373K)(1.672m^3/kg)} = 3620 \text{ Pa/K} = 0.0357 \text{ atm/K}$$

When the pressure is 615 mbar, the corresponding pressure is

$$P = \frac{615}{1013.25} = 0.607 \text{ atm}$$

The phase of change is

 $\Delta P = 0.607 - 1 = -0.393$ atm

The change of the boiling temperature is

$$T_B' = 100 - 11 = 89$$
 C.

since

$$\Delta T = \frac{\Delta P}{0.0357 \text{atm/K}} = \frac{-0.393 atm}{0.0357 \text{atm/K}} = -11$$

((Note))

The specific volumes of water and steam at 100 C and 1 atm are

$$\frac{1}{\rho_{water}} = 1.043 \times 10^{-3} \text{ m}^{3}/\text{kg}$$
$$\frac{1}{\rho_{steam}} = 1.672 \text{ m}^{3}/\text{kg}$$

Latent heat of vaporization:

$$L_v = 2257 \text{ kJ/ kg}$$

One atmosphere

1 atm=1.01325 x 10⁵ Pa

Triple point (TP) of water:

REFERENCE

A. Rex, Finn's Thermal Physics, CRC Press (2017)

<mark>28-3</mark>

(28.3) The gradient of the melting line of water on a p-T diagram close to 0° C is $-1.4 \times 10^7 \text{ Pa K}^{-1}$. At 0° C, the specific volume of water is $1.00 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ and of ice is $1.09 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$. Using this information, deduce the latent heat of fusion of ice.

In winter, a lake of water is covered initially by a uniform layer of ice of thickness 1 cm. The air temperature at the surface of the ice is -0.5° C. Es-

timate the rate at which the layer of ice begins to thicken, assuming that the temperature of the water just below the ice is 0° C. You can also assume steady state conditions and ignore convection.

The temperature of the water at the bottom of the lake, depth 1 m, is maintained at 2°C. Find the thickness of ice which will eventually be formed. [The thermal conductivity of ice is $2.3 \text{ W m}^{-1} \text{ K}^{-1}$ and of water is $0.56 \text{ W m}^{-1} \text{ K}^{-1}$.]

((Solution))

(i) Clapeyron-Clausius equation for fusion

$$T = 273 K$$

$$V_{l} = 1.00 \times 10^{-3} \text{ m}^{3}/\text{kg}, \qquad V_{s} = 1.09 \times 10^{-3} \text{ m}^{3}/\text{kg},$$

$$\frac{dP}{dT} = \frac{S_{l} - S_{s}}{V_{l} - V_{s}} = \frac{1}{T} \frac{L_{f}}{V_{l} - V_{s}} = -\frac{1}{273} \frac{L_{f}}{0.09 \times 10^{-3}} = -1.4 \times 10^{7} \text{ Pa/K}$$

$$L_{f} = 273 \times 0.09 \times 1.4 \times 10^{4} \text{ Pa} = 343.98 \times 10^{3} \text{ J/kg}$$

We consider the equation of thermal diffusion: $\wp = \frac{dQ}{dt} = -\kappa A \frac{dT}{dx}$



(ii) Thermal diffusion equation

$$\frac{dQ}{dt} = L_f \rho_{ice} A \frac{dx}{dt} = \kappa_{ice} A \frac{\Delta T}{x}$$

or

$$\frac{dx}{dt} = \frac{\kappa_{ice}}{L_f \rho_{ice}} \frac{\Delta T}{x} = \frac{2.3 \times 0.5}{3.4398 \times 10^5 \times 0.9174 \times 10^3 \times 10^{-2}} = 0.364 \times 10^{-6} \text{ m/s}$$

or

$$\frac{dx}{dt} = 3.14 \text{ cm/day}$$

where

$$x = x_0 = 1.0 \text{ cm at } t = 0$$

$$\Delta T = 0.5 \text{ K}$$

$$\rho_{ice} = \frac{1}{1.09} \times 10^3 = 0.9174 \text{ x } 10^3 \text{ kg/m}^3$$

$$L_f = 3.4398 \text{ x } 10^5 \text{ J/kg}$$

$$\kappa_{ice} = 2.3 \text{ W/(m K)}.$$

(iii) Thermal equilibrium



 $\kappa_{\text{water}} = 0.56 \text{ W/(m K)}.$

In thermal equilibrium (heat flux-1 is equal to heat flux-2)

$$\kappa_{ice} \frac{0.5}{x} = \kappa_{water} \frac{2}{1-x}$$
$$x = 0.51 \text{ m}$$

<mark>28.5</mark>

(28.5) The equilibrium vapour pressure p of water as a function of temperature is given in the following table:

T (°C)	p (Pa)
0 10 20 30 40 50	611 1228 2339 4246 7384 12349

Deduce a value for the latent heat of evaporation $L_{\rm v}$ of water. State clearly any simplifying assumptions that you make.

Estimate the pressure at which ice and water are in equilibrium at -2° C given that ice cubes float with 4/5 of their volume submerged in water at the triple point (0.01°C, 612 Pa).

[Latent heat of sublimation of ice at the triple point, $L_{\rm s} = 2776 \times 10^3 \, {\rm J \, kg^{-1}}$.]

((Solution))

L: latent heat of vaporization/mole

$$\Delta v = v_g - v_l$$

Thus we have the Clausius-Clapeyron equation,

$$\frac{dP}{dT} = \frac{l_v}{T\Delta v}$$

Two approximations:

(i)
$$v_g \gg v_l$$

$$\Delta v = v_g - v_l \approx v_g = \frac{V_g}{N_g}$$

(ii)

$$PV_g = N_g k_B T$$
 (ideal gas law)

or

$$Pv_g = k_B T$$

Using these two approximations, we have

$$\frac{dP}{dT} = \frac{l_v}{T\Delta v} = \frac{l_v}{Tv_g} = \frac{l_v P}{k_B T^2} = \frac{N_A l_v P}{N_A k_B T^2} = \frac{L_v P}{R_B T^2}$$

where L_{ν} is the heat of vaporization per mol,

$$L_v = N_A l_v$$
.

Suppose that L_v is independent of *T*.

$$\int \frac{dP}{P} = \frac{L_v}{k_B} \int \frac{dT}{T^2}$$

or

$$\ln P = -\frac{L_v}{k_B T} + \text{constant}$$

or

$$P(T) = P_0 \exp(-\frac{L_v}{k_B T})$$

or

$$P(T) = P_0 \exp(-\frac{L_v}{RT}).$$

or

$$\ln P = \ln P_0 - \frac{L_v}{RT}$$

where L_{ν} is the latent heat per mol.





The least-squares fit of the data to a straight line yields

$$\frac{L_v}{R} = 5302.0 \pm 17.6$$

where R = 8.3144596 J/(K mol). Then we have

$$L_v = 5302 \times 8.3144596 = 4.4083 \text{ x } 10^4 \text{ J/mol}$$

For water 1 kg = 1000/18 mol = 55.5555 mol

$$L_v = \frac{1000}{18} \times 4.4083 \times 10^4 = 2.449 \times 10^6$$
 J/kg

We consider the latent heat around the tri-critical point (T_c , P_c , V_c) at which the three phases (sold=ice, gas, and water) meet together.

$$L_v = T_c(S_g - S_l)$$
, $L_s = T_c(S_g - S_s) = 2.776 \times 10^6$ J/kg; latent heat for sublimation

Then we have the latent heat L_f at the tri-critical point,

$$L_s - L_v = T_c(S_l - S_s) = L_f = (2.776 - 2.449) \times 10^6 = 3.27 \times 10^5 \text{ J/kg}$$

We note that

$$L_f(J/mol) = \frac{1000}{18} L_f(J/kg) = 181.667 \text{ (J/mol)}$$

The buoyant force is balanced with the gravitational force,

$$\rho_l V_1 g = \rho_s (V_1 + V_2) g$$

where the total volume of ice is $V_s = V_1 + V_2$, and the volume of ice submerged in the water is V_1 . So we have

$$\frac{\rho_l}{\rho_s} = 1 + \frac{V_2}{V_1} = 1 + \frac{1}{4} = \frac{5}{4}$$

leading to

$$\rho_l = 1.00 \times 10^3 \text{ kg/m}^3, \qquad \rho_s = 0.80 \times 10^3 \text{ kg/m}^3,$$
$$V_l = 1.00 \times 10^{-3} \text{ m}^3/\text{kg}, \qquad V_s = 1.25 \times 10^{-3} \text{ m}^3/\text{kg},$$

$$\frac{dP}{dT} = \frac{S_l - S_s}{V_l - V_s} = \frac{1}{T} \frac{L_f}{V_l - V_s} = -\frac{1}{273} \frac{3.27 \times 10^5}{0.25 \times 10^{-3}} = -4.79121 \times 10^6 \text{ Pa/K}$$

When the temperature drops from 0 C to -2 C, the pressure P increases to

$$\Delta P = 9.58242 \times 10^6$$
 Pa = 94.58 atm

where

 $1 \text{ atm} = 1.01315 \text{ x} 10^5 \text{ Pa.}$

<mark>28.6</mark>

(28.6) It is sometimes stated that the weight of a skater pressing down on their thin skates is enough to melt ice, so that the skater can glide around on a thin film of liquid water. Assuming an ice rink at -5°C, do some estimates and show that this mechanism won't work. [In fact, frictional heating of ice is much more important, see S.C. Colbeck, Am. J. Phys. 63, 888 (1995) and S. C. Colbeck, L. Najarian, and H. B. Smith Am. J. Phys. 65, 488 (1997).]

((Solution))

 $\rho_{l} = 1.00 \times 10^{3} \text{ kg/m}^{3}, \qquad \rho_{s} = 0.917 \times 10^{3} \text{ kg/m}^{3},$ $V_{l} = \frac{1}{\rho_{l}} = 1.00 \times 10^{-3} \text{ m}^{3}/\text{kg}, \qquad V_{s} = 1.091 \times 10^{-3} \text{ m}^{3}/\text{kg},$ $L_{f} = 334 \text{ kJ/kg} \qquad \text{(latent heat of fusion for water)}$ $\frac{dP}{dT} = \frac{S_{l} - S_{s}}{V_{l} - V_{s}} = \frac{1}{T} \frac{L_{f}}{V_{l} - V_{s}} = -\frac{1}{273} \frac{3.34 \times 10^{5}}{0.091 \times 10^{-3}} = -1.34 \times 10^{7} \text{ Pa/K} = -132.2 \text{ atm/K}.$

where

$$1 \text{ atm} = 1.01315 \text{ x} 10^5 \text{ Pa.}$$

For a very heavy skater (100 kg), only making the contact with ice over an area 10 cm x 1 mm = 10^{-4} m².

$$\Delta P = \frac{100 \times 9.8}{10^{-4}} = 9.8 \text{ x } 10^6 \text{ Pa} = 96.7 \text{ atm}$$

Then



Fig. TP (triple point): T = 0 C (273.16 K) and P = 0.00637 atm. The stating point α : T = -5 C and P = 1 atm.

We now suppose that the temperature is -5 C. At 1 atmosphere, the ice is in the state α on the *P*-*T* plane. There is no water present. When the ice skater puts pressure on the ice, the state moves

along the constant temperature line $(\alpha - \beta - \gamma)$. In theory, as soon as the phase boundary is reached at the state γ , some ice melts so that the edge of the skate sinks in fractionally, with the load now spread over a large area stabilizing the pressure. The state thus remains fixed at γ , with the liberated water acting as a lubricant.

The question must be asked: Is 106.7 atm or so sufficient to achieve this goal? From

$$\frac{dP}{dT} = -132.2 \text{ atm/K}.$$

So a pressure increase of (132.2 atm/K) x 5 K = 661 atm would be required to go to from α to γ . Thus this explanation for the success of the skater appears inadequate.

((Note))

Thermal conductivity:

$$\kappa_{ice} = 2.3 \text{ W/(m K)}$$

 $\kappa_{water} = 0.56 \text{ W/(m K)}$

The gas constan:

$$R = 8.3145 \text{ J/(K mol)}$$

Latent heat of fusion:

$$L_f = 334 \text{ kJ/kg}$$

Latent heat of vaporization:

$$L_v = 2260 \text{ kJ/ kg}$$

The density

$$\rho_{water} = 1.00 \times 10^3 \text{ kg/m}^3.$$

 $\rho_{ice} = 0.917 \times 10^3 \text{ kg/m}^3.$

$$\frac{1}{\rho_{ice}} - \frac{1}{\rho_{water}} = 0.0951 \times 10^{-3} \text{ m}^3/\text{kg}$$