

F 320 – Termodinâmica – Lista 6

P.01. [P.10.8 and 10.9, Lemons]

(a) Starting from the identities $T = (\partial U/\partial S)_V$ and $p = -(\partial U/\partial V)_S$ and the equations of state for an ideal gas, $pV = nRT$ and $U = C_V T$ with C_V being a constant, show that

$$U(S, V) = U_0 \left(\frac{V_0}{V} \right)^{nR/C_V} e^{(S-S_0)/C_V},$$

where $U_0 = U(S_0, V_0)$.

(b) Starting from $\mu = (U - TS + pV)/n$, show that, for an ideal gas,

$$\mu(S, V, n) = u_0 \left(\frac{nv_0}{V} \right)^{R/c_v} \left[1 - \frac{S - nR}{nc_v} \right] \exp \left(\frac{S - ns_0}{nc_v} \right),$$

where $u_0 = U/n$, $s_0 = S/n$, $v_0 = V_0/n$, and $c_v = C_V/n$.

(c) The chemical potential of an ideal gas $\mu = \mu(S, V, n)$ may be derived directly from the partial derivative $(\partial U/\partial n)_{S,V}$ of the energy of an ideal gas $U(S, V, n)$ in which the system mole number enters as an explicit variable. To do so, one must first rewrite $U(S, V)$ as found in item (a) in terms of specific quantities c_v , u_0 , s_0 , and v_0 that are independent of the variables S , V , and n . Then, show that $\mu = (\partial U/\partial n)_{S,V}$ reproduces the result $\mu = G/n$ found in item (b).

P.02. [P.10.10, Lemons] Show that the chemical potential of cavity radiation is zero by showing that the Gibbs free energy of cavity radiation is zero. The fact that the Gibbs free energy of cavity radiation vanishes identically is a sign that the variables T and p of cavity radiation cannot both be independent variables.

03. [P.10.12, Lemons] Prove the following relations among variables describing a single-phase, open fluid system.

$$(a) \quad \left(\frac{\partial T}{\partial n}\right)_{S,p} = \left(\frac{\partial \mu}{\partial S}\right)_{p,n} \quad \text{and} \quad \left(\frac{\partial V}{\partial n}\right)_{S,p} = \left(\frac{\partial \mu}{\partial S}\right)_{S,n}.$$

$$(b) \quad \left(\frac{\partial S}{\partial n}\right)_{T,V} = \left(\frac{\partial \mu}{\partial T}\right)_{V,n} \quad \text{and} \quad \left(\frac{\partial p}{\partial n}\right)_{T,V} = \left(\frac{\partial \mu}{\partial V}\right)_{T,n}.$$

$$(c) \quad \left(\frac{\partial S}{\partial n}\right)_{T,p} = \left(\frac{\partial \mu}{\partial T}\right)_{p,n} \quad \text{and} \quad \left(\frac{\partial V}{\partial n}\right)_{T,p} = \left(\frac{\partial \mu}{\partial p}\right)_{T,n}.$$

04. [P.11.14, Zemansky] From $dH = TdS + Vdp + \mu dn$ derive the relation

$$\left(\frac{\partial S}{\partial p}\right)_{H,n} = -\frac{V}{T}.$$

For the ideal gas, the entropy as a function of H , p , and n has the form

$$S(H, p, n) = R \ln \frac{f(H, n)}{p^n},$$

where $f(H, n)$ is a function of the enthalpy H and the number of moles n . Using the result from part (a), derive the ideal-gas equation of state.

05. [P.15.4, Zemansky] There are n_1 moles of an ideal monatomic gas at temperature T_1 and pressure p in one compartment of an insulated container. In an adjoining compartment separated by an insulating partition are n_2 moles of another ideal monatomic gas at temperature T_2 and pressure p . When the partition is removed:

- Show that the final pressure of the mixture is p .
- Calculate the entropy change when the gases are identical.
- Calculate the entropy change when the gases are different.

P.06. [P.15.5, Zemansky] There are n_1 moles of an ideal gas at pressure p_1 and temperature T in one compartment of an insulated container. In an adjoining compartment separated by a partition are n_2 moles of an ideal gas at pressure p_2 and temperature T . When the partition is removed:

- Calculate the final pressure of the mixture.
- Calculate the entropy change when the gases are identical.
- Calculate the entropy change when the gases are different.
- Prove that the entropy change in part (c) is the same as that which would be produced by two independent free expansions.

P.07. [P.15.8, Zemansky]

- Show that the molar Helmholtz function f of an ideal gas is

$$f = u_0 + \int c_v dT' - T \int \frac{c_v}{T'} dT' - T s_0 - RT \ln v.$$

- Consider N inert ideal gases separated from one another by suitable partitions, all gases at the same temperature T and pressure p . Show that, after the diffusion, the Helmholtz function of the mixture of the inert ideal gases is

$$F = \sum_i n_i (\phi_i + RT \ln x_i),$$

where $\phi_i = \phi_i(T, p)$.

- Show that the change in the Helmholtz function due to diffusion is

$$F_F - F_I = RT \sum_i n_i \ln x_i.$$

08. [P.15.14, Zemansky] Show that, for an ideal gas in a mixture of ideal gases,

$$d\mu_i = \frac{\mu_i - h_i}{T} dT + v_i dp + RT d \ln x_i.$$

09. [P.11.3, Adkins] A liquid is in equilibrium with a gas phase consisting of a mixture of its vapour and of an insoluble gas whose partial pressure is p' . Assuming that the components in the gaseous phase behave like ideal gases, show that the vapour pressure of the liquid, p , is changed by the presence of the insoluble gas, the change, if it is not too large, being given by

$$\frac{\Delta p}{p_0} = \frac{v_L}{RT} p',$$

where p_0 is the vapour pressure in the absence of the gas and v_L is the molar volume of the liquid.

P.10. [P.11.4 and P.11.5, Zemansky and P.7.14, Sears]

(a) Show that the Clausius-Clapeyron equation can be derived from one of the TdS equations.

(b) Show that a substance with a negative slope for its fusion curve, such as ordinary ice or bismuth, contracts upon melting.

(c) Prove that in the $p - T$ plane the slope of the sublimation curve at the triple point is greater than that of the vaporization curve at the same point.

11. [P.11.8, Zemansky] Prove that, during a first-order phase transition:

(a) the entropy of the entire system is a linear function of the total volume and

(b) the change of internal energy is given by

$$\Delta U = \Delta H \left(1 - \frac{d \ln T}{d \ln p} \right).$$

12. [P.12.2 and P.12.3, Lemons] The lever rule relates the fraction in each phase of a two-phase system to its volume V relative to parameters at each end of the isotherm-isobar. The relation is that of a lever with "masses" n_L and n_V balanced at distances $(V - V_L)$ and $(V_V - V)$, respectively, from a pivot at V . Thus,

$$n_L(V - V_L) = n_V(V_V - V).$$

Derive the lever rule from the idea encapsulated in the equations $n = n_L + n_V$ and $V = n_L v_L + n_V v_V$ that each phase coexisting in a two-phase system is the phase of a purely saturated fluid.

(b) One hundred grams of H_2O are at atmospheric pressure and 100°C . If 5 g are in vapor phase and 95 g in liquid phase, what is the total volume of the system? Use the specific volumes $v_L = 1.04 \text{ cm}^3/\text{g}$ and $v_V = 1.67 \times 10^3 \text{ cm}^3/\text{g}$.

P.13. [P.12.7, Lemons] Assume that the volume of a saturated liquid is ignorably small compared with the volume of the saturated vapor at the same temperature and that the ideal gas equation of state $pV = nRT$ describes the saturated vapor. Given these assumptions, derive an expression for $p(T)$ within a region of the vapor dome for which the heat of transition $Q_{L \rightarrow V}$ is a constant independent of temperature. Use the initial condition $p = p_0$ when $T = T_0$ to evaluate the integration constant.

P.14. [P.10.5, Adkins] If c_1 and c_2 are the specific heat capacities of a liquid and of its saturated vapour respectively, and l is the specific latent heat of vaporization, show that

$$c_2 - c_1 = \frac{dl}{dT} - \frac{l}{T}.$$

What is the physical significance of the fact that c_2 for saturated steam is negative?

15. [P.10.6, Adkins] Show that when the saturated vapour of an incompressible liquid is expanded adiabatically, some liquid condenses out if

$$C_p + T \frac{d}{dT} \left(\frac{L}{T} \right) < 0,$$

where C_p is the heat capacity of the liquid (which is assumed constant) and L the latent heat of vaporization.

16. [P.7.28, Sears] In a second-order phase transition $s_i = s_f$ or $v_i = v_f$ at a particular temperature and pressure where f and i denote the final and initial phase. Show that in these cases the Clausius-Clapeyron equation can be written as

$$\frac{dp}{dT} = \frac{1}{Tv} \frac{c_{pf} - c_{pi}}{\beta_f - \beta_i} \quad \text{or} \quad \frac{dp}{dT} = \frac{\beta_f - \beta_i}{\kappa_f - \kappa_i},$$

respectively. Hint: Begin with an appropriate TdS relation.

17. [P.10.7, Adkins] Show that for a system consisting of two phases in equilibrium,

$$\left(\frac{\partial p}{\partial V} \right)_S = -\frac{T}{C_V} \left(\frac{dp}{dT} \right)^2,$$

where dp/dT is the slope of the phase equilibrium curve.

18. [P.11.11, Zemansky]

(a) Prove that, for a single phase,

$$\left(\frac{\partial p}{\partial T} \right)_S = \frac{c_p}{Tv\beta}.$$

(b) Calculate $(\partial p/\partial T)_S$ for ice at $T = -3^\circ\text{C}$, where $c_p = 2.01 \text{ kJ/kg K}$, $\beta = 1.58 \times 10^{-4} \text{ K}^{-1}$, and $v = 1.09 \times 10^{-3} \text{ m}^3/\text{kg}$.

(c) Ice is initially at $T = -3^\circ\text{C}$ and $1.01 \times 10^5 \text{ Pa}$. The pressure is increased adiabatically until the ice reaches the melting point. At what temperature and pressure is this melting point?

Hint: At what point does a line whose slope is $(\partial p/\partial T)_S$ cut a line whose slope is that of the fusion curve, $-1.35 \times 10^7 \text{ Pa/K}$?

P.19. [P.7.23, Sears]

(a) Calculate the slope of the fusion curve of ice in Pa/K at the temperature $T = -2^\circ\text{C}$. The heat of fusion at this temperature is 3.34×10^5 J/kg and the change in specific volume on melting is -9.05×10^{-5} m³/Kg.

(b) Ice at $T = -2^\circ\text{C}$ and atmospheric pressure is compressed isothermally. Find the pressure at which the ice starts to melt.

(c) Calculate $(\partial p/\partial T)_v$ for ice at $T = -2^\circ\text{C}$. Consider that $\beta = 15.7 \times 10^{-5}$ K⁻¹ and $\kappa = 120 \times 10^{-12}$ Pa⁻¹.

(d) Ice at $T = -2^\circ\text{C}$ and atmospheric pressure is kept in a container at constant volume, and the temperature is gradually increased. Find the temperature and pressure at which the ice starts to melt. Assume that the fusion curve and the rate of change of pressure with temperature, at constant volume, are both linear.

20. [P.11.9, Zemansky] When lead is melted at atmospheric pressure, the melting point is $T = 600$ K, the density decreases from 11.01 to 10.65 g/cm³, and the latent heat of fusion $\Delta H = 24.5$ J/g. What is the melting point at the pressure $p = 1.01 \times 10^7$ Pa?

P.21. [P.11.6, Zemansky] Saturated liquid carbon dioxide at a temperature $T_1 = 293$ K and a pressure $p_1 = 5.72 \times 10^6$ Pa experiences throttling to a pressure $p_2 = 1.01 \times 10^5$ Pa. The temperature of the resulting mixture of solid and vapor is $T = 195$ K. What fraction is vaporized? The enthalpy of saturated liquid at the initial state is 24200 J/mol, and the enthalpy of saturated solid at the final state is 6750 J/mol. The heat of sublimation at the final state is 25100 J/mol.

22. [P.10.3, Adkins] In the transition from ferromagnetic to paramagnetic nickel at the Curie point $T_C = 631$ K, the heat capacity at constant pressure changes by 6.7 J/K mol and the volume expansivity by 5.5×10^{-6} K⁻¹. The molar volume of nickel is 6.6×10^{-6} m³. Calculate the effect of pressure on the Curie point assuming the transition to be second order.

P.23. [P.13.1, Lemons] Many of the equations of state discussed incorporate a constant heat capacity C_V appropriate only for high-temperature systems. However, the equations of state for cavity radiation should obtain for all temperatures, including those down to the $T \rightarrow 0$ limit. Show that cavity radiation observes the following limits:

$$\left(\frac{\partial S}{\partial V}\right)_T \rightarrow 0, \quad \left(\frac{\partial p}{\partial T}\right)_V \rightarrow 0, \quad C_V \rightarrow 0 \quad \text{as} \quad T \rightarrow 0.$$

24. [P.12.1, Adkins] Show that the e.m.f. of a reversible electric cell becomes constant as $T \rightarrow 0$.

25. [P.12.3, Adkins] For a superconductor, the specific heat capacity in the superconducting and normal states may be written

$$c_s = c_e + aT^3 \quad \text{and} \quad c_n = \gamma T + aT^3,$$

where a and γ are constants. Show that

$$\int_0^1 \frac{c_e}{\gamma T} dt = 1,$$

where $t = T/T_c$ is the reduced temperature.

26. [P.12.4, Adkins] According to Debye's theory, the heat capacity of a crystalline solid may be expressed in the form

$$C_V = f(T/\Theta),$$

where Θ is independent of temperature but depends on volume according to the law $\Theta \propto V^{-\gamma}$ with γ being a constant. Show that the cubic expansivity β and the isothermal compressibility κ satisfy the relation

$$\beta = \gamma C_V \kappa / V.$$