

F 320 – Termodinâmica – Lista 4

P.01. [P.10.2, Zemansky] Show that, for an ideal gas:

$$(a) \quad F = \int C_V dT - T \int \frac{C_V}{T} dT - nRT \ln V - AT + B,$$

where A and B are constants, and

$$(b) \quad G = \int C_p dT - T \int \frac{C_p}{T} dT + nRT \ln p - A'T + B',$$

where A' and B' are constants.

02. [P.8.6, Lemons] We rewrite the fundamental constraint $dU = TdS - pdV$ in its equivalent entropy form $dS = (1/T)dU + (p/T)dV$.

(a) Find the forms of the two equations of state that follow from the entropy form of the fundamental constraint - that is, find the derivatives of the dependent variable S in terms of its proper independent variables U and V that give expressions for T and p .

(b) Use cross-differentiation to find the relation between the derivatives of T and p .

P.03. [P.10.3 and P.10.4, Zemansky]

(a) From the differential equation for the thermodynamic potential $F(T, V)$, derive expressions for pressure p , entropy S , internal energy U , heat capacity at constant volume C_V , heat capacity at constant pressure C_p , volume expansivity β , and isothermal compressibility κ .

(b) Derive the following equations:

$$U = F - T \left(\frac{\partial F}{\partial T} \right)_V, \quad C_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V,$$

$$H = G - T \left(\frac{\partial G}{\partial T} \right)_p, \quad C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p.$$

P.04. [P.10.5, Zemansky] Another set of characteristic functions for a single-substance system can be defined by performing the Legendre transformations on the entropy $S(U, V)$ rather than on the internal energy $U(V, S)$. The thermodynamic potentials turn out to be particularly useful in statistical mechanics and the theory of irreversible thermodynamics.

(a) Show that Legendre transformation of $S(U, V)$ that produces the characteristic function $J(1/T, V)$, known as the Massieu function, is given by

$$J = -\frac{U}{T} + S = -\frac{F}{T} \quad \text{and} \quad dJ = \frac{U}{T^2}dT + \frac{p}{T}dV.$$

(b) Show that Legendre transformation of $J(1/T, V)$ that produces the thermodynamic potential $Y(1/T, P/T)$, known as the Planck function, is defined by

$$Y = -\frac{H}{T} + S = -\frac{G}{T} \quad \text{and} \quad dY = \frac{H}{T^2}dT - \frac{V}{T}dp.$$

P.05. [P.10.8, Zemansky]

(a) Consider that the entropy $S = S(T, V)$ and derive the first TdS equation

$$TdS = C_V dT + T \left(\frac{\partial p}{\partial T} \right)_V dV.$$

(b) Consider that the entropy $S = S(T, p)$ and derive the second TdS equation

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp.$$

(c) Consider that the entropy $S = S(V, p)$ and derive the third TdS equation,

$$TdS = C_V \left(\frac{\partial T}{\partial p} \right)_V dp + C_p \left(\frac{\partial T}{\partial V} \right)_p dV.$$

(d) Show that the three TdS equations may be written as follows:

$$(a) \quad TdS = C_V dT + \frac{\beta T}{\kappa} dV;$$

$$(b) \quad TdS = C_p dT - V\beta T dp;$$

$$(c) \quad TdS = \frac{C_V \kappa}{\beta} dp + \frac{C_p}{\beta V} dV.$$

06. [P.10.12, Zemansky] Consider a gas that obeys the equation $p(v - b) = RT$, where b is constant and C_v is constant. Show that:

- (a) u is a function of T only;
- (b) γ is constant;
- (c) the relation $p(v - b)^\gamma = \text{const}$ holds for an adiabatic process.

07. [P.10.19, Zemansky] Derive the following equations:

$$(a) \quad C_V = -T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_S;$$

$$(b) \quad \left(\frac{\partial V}{\partial T} \right)_S = -\frac{C_V \kappa}{\beta T};$$

$$(c) \quad \left(\frac{\partial V}{\partial T} \right)_S \left(\frac{\partial T}{\partial V} \right)_p = \frac{1}{1 - \gamma}.$$

08. [P.8.13, Lemons] Starting from definitions of C_P and C_V , show that $C_P - C_V = TV\beta_p^2/\kappa_T$.

P.09. [P.8.11, Lemons] Derive the identity $\beta_V = \beta_p/p\kappa_T$, where

$$\beta_V = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_V,$$

from the reciprocity rule applied to the fluid variables.

P.10. [P.8.5, Lemons] Suppose the characterizing function of a fluid takes the form

$$U(S, V) = a \frac{S^2}{V},$$

where a is a constant that characterizes the particular hypothetical system.

(a) Determine the equations of state that assume the form $T = T(S, V)$ and $p = p(S, V)$.

(b) Verify the Maxwell relation $(\partial T/\partial V)_S = -(\partial p/\partial S)_V$.

11. [P.8.9, Lemons] Derive the following Maxwell relations from $(\partial T/\partial V)_S = -(\partial p/\partial S)_V$ and the reciprocal, reciprocity, and chain rules. List each rule as it is invoked.

(a) $(\partial T/\partial p)_S = (\partial V/\partial S)_p$;

(b) $(\partial T/\partial V)_p = -(\partial p/\partial S)_T$;

(c) $(\partial T/\partial p)_V = -(\partial V/\partial S)_T$.

12. [P.7.3, Adkins] A cylinder contains 0.1 kg of water at 15°C. A piston increases the pressure on the water isothermally from 1 atm to 100 atm. Find

- (a) the work done on the water by the piston,
- (b) the heat removed from the water,
- (c) the change in the internal energy of the water.

What would be the change in temperature of the water if the increase in pressure were made adiabatically?

For water at 15°C, the cubic expansivity is $1.5 \times 10^{-4} \text{ K}^{-1}$ and the compressibility is $4.9 \times 10^{-12} \text{ Pa}$.

13. [P.8.18, Lemons] Suppose a block of an incompressible solid (that is, with constant V) is subjected to an adiabatic reversible increase of pressure from p_i to p_f . Show that the ratio of its final temperature T_f to its initial temperature T_i is given by

$$T_f = T_i \exp [V\beta_p(p_f - p_i)/C_p].$$

P.14. [P.10.9, Zemansky] The pressure on 500 g of copper is increased reversibly and isothermally from 0 to 5000 atm at 298 K. Take the density $\rho = 8.96 \times 10^3 \text{ kg/m}^3$, volume expansivity $\beta = 49.5 \times 10^{-6} \text{ K}^{-1}$, isothermal compressibility $\kappa = 6.18 \times 10^{-12} \text{ Pa}^{-1}$, and specific heat $C_p = 385 \text{ J/kg K}$ to be constant.

- (a) How much heat is transferred during the compression?
- (b) How much work is done during the compression?
- (c) Determine the change of internal energy.
- (d) What would have been the rise of temperature if the copper had been subjected to a reversible adiabatic compression?

15. [P.11.2 and P.11.4, Lemons]

(a) Show that a room-temperature elastic solid is stable by showing that its equations of state observe $(\partial p/\partial V)_T < 0$, $(\partial p/\partial V)_S < 0$, and $C_P > 0$.

Note: $C_V > 0$ is part of the model definition.

(b) Show that $(\partial p/\partial V)_S < 0$ and $C_P > 0$ follow from the conditions $(\partial p/\partial V)_T < 0$ and $C_V > 0$ for any fluid.

16. [P.7.4, Adkins] The free energy of a Debye solid may be written in the form

$$F(T, V) = U_0(V) + Tf(\Theta/T),$$

where $U_0(V)$ is the internal energy at absolute zero for the solid with volume V and Θ is the Debye temperature, a function of the volume only. Obtain an expression for the pressure and show that the cubic expansivity β is related to the isothermal compressibility κ by the formula

$$\beta = \frac{\kappa\gamma C_v}{V}, \quad \text{with} \quad \gamma = -\frac{d(\ln \Theta)}{d(\ln V)}.$$

17. [P.7.4, Sears] Use Helmholtz function derived in problem 01 with C_p and C_V constants and calculate:

- (a) the equation of state,
- (b) the energy equation,
- (c) the Gibbs function, and
- (d) the enthalpy of an ideal gas.

P.18. [P.7.6, Sears] The specific Gibbs function of a gas is given by

$$g = RT \ln(p/p_0) - Ap,$$

where A is a function of T only.

- (a) Derive expressions for the equation of state of the gas and its specific entropy.
- (b) Derive expressions for the other thermodynamic potentials.
- (c) Derive expressions for c_p and c_v .
- (d) Derive expressions for the isothermal compressibility and the expansivity.

19. [P.7.15, Sears] Show that the internal energy of a system at constant entropy and volume must decrease in any spontaneous process.

20. [P.7.16, Sears] If the Gibbs function of a system must decrease during any spontaneous processes in which the temperature and pressure remain constant, show that the entropy of an isolated system must increase during a spontaneous process.

Hint: Show that $\Delta G_{T,p}$ must increase for any process that includes a stage in which ΔS_U decreases.

21. [P.7.17, Sears] By the same method as used in the problem 20, show that if the Gibbs function of a system must decrease during any spontaneous process in which the temperature and pressure remain constant,

(a) the Helmholtz function must also decrease in any spontaneous process at constant volume and temperature; and

(b) the enthalpy must decrease in any spontaneous process at constant pressure and entropy.

P.22. [P.7.11, Sears] The work necessary to stretch a wire is given by $dW = fdL$.

(a) Derive expressions for the differentials of the thermodynamic potentials.

(b) Derive the four Maxwell relations for this system.

(c) Derive the TdS equations.

23. [P.7.1, Adkins] A piece of rubber is subject to work by hydrostatic pressure and by a tensional force.

(a) Construct the expression for dU .

(b) Generate the potentials which have as proper variables: (S, V, f) , (S, p, f) , (T, p, f) .

(c) Derive the Maxwell relations

$$\left(\frac{\partial T}{\partial V}\right)_{L,S} = -\left(\frac{\partial p}{\partial S}\right)_{V,L}, \quad \left(\frac{\partial S}{\partial L}\right)_{T,p} = -\left(\frac{\partial f}{\partial T}\right)_{p,L}, \quad \left(\frac{\partial S}{\partial f}\right)_{p,L} = -\left(\frac{\partial L}{\partial T}\right)_{S,p}.$$

P.24. [P.7.13, Sears] The work dW in a reversible process undergone by a paramagnetic gas is given by $dW = -pdV + \mu_0 H dm$.

(a) Write expressions for dU , dH , dF , and dG for this system.

(b) Use the expressions of part (a) to derive Maxwell relations for this system.

(c) Write the TdS equations for a paramagnetic gas.

25. [P.7.5, Adkins] A system consists of a film of a paramagnetic liquid thermally isolated from its surroundings and held at constant tension in a constant magnetic field. Find the potential function that must be minimum at equilibrium.

26. [P.10.15, Zemansky] Show that the differentials of the three thermodynamic potentials U , H , and F may be written

$$dU = (C_p - pV\beta)dT + V(\kappa p - \beta T)dp,$$

$$dH = C_p dT + V(1 - \beta T)dp,$$

$$dF = -(pV\beta + S)dT + pV\kappa dp.$$

P.27. [P.10.16, Zemansky] (a) Show that

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V.$$

(b) Prove that C_v of an ideal gas is a function of T only.

(c) In the case of a gas obeying the equation of state

$$pV = RT\left(1 + \frac{B}{V}\right),$$

where B is a function of T only, show that

$$C_V = -\frac{RT}{V} \frac{d^2}{dT^2}(BT) + c_0,$$

where c_0 is the value at very large volumes.