

F 320 – Termodinâmica – Lista 5

01. [P.8.3, Adkins] A perfect gas flows adiabatically through a horizontal tube of varying cross-sectional area. If viscous effects are negligible and the flow is streamlined, show that the velocity of flow  $\mathcal{V}$  and the temperature  $T$  of the gas vary along the tube according to the relationship

$$\mathcal{V}^2 + \frac{2\gamma}{\gamma - 1} \frac{RT}{M} = \text{constant},$$

where  $R$  is the molar gas constant,  $M$  the molar mass and  $\gamma$  the ratio of the principal heat capacities which are assumed constant.

02. [P.8.5, Adkins] In a certain compressor a perfect gas at room temperature  $T_0$  and atmospheric pressure  $p_0$  is compressed adiabatically and is then passed through water-cooled tubes until it eventually emerges at pressure  $p_1$  and temperature  $T_0$ . Find an expression for the work required for this process, compared with that which would be needed for a reversible isothermal compression leading to the same result and show that the ratio is not less than unity. Examine also the changes of entropy occurring in the two processes.

Note that if  $a > 1$  and  $x > 0$ , then  $a^x > 1 + x \ln a$ .

03. [P.8.6, Adkins] If the coldest available reservoir is a lake at  $10^\circ\text{C}$ , what is the maximum amount of useful work which may be obtained from  $1 \times 10^3 \text{ m}^3$  of a perfect gas which is initially at  $100^\circ\text{C}$  and 10 atm pressure and for which  $\gamma = 1.5$ ?

P.04. [P.8.11, Adkins] Show that for a gas obeying van der Waals' equation, we have  $T(v-b)^{R/c_v} = \text{const.}$  in a reversible adiabatic expansion provided that  $c_v$  is independent of temperature.

05. [P.9.3, Zemansky] Using the Dieterici equation of state,

$$p = \frac{RT}{v-b} e^{-a/RTv},$$

show that

$$p_c = \frac{a}{4e^2b^2}, \quad v_c = 2b, \quad T_c = \frac{a}{4Rb}.$$

06. [P.8.14, Adkins] The heat capacity of hydrogen at constant volume between 100 and 150 K is adequately described by the equation

$$c_v/R = 1 + 7 \times 10^{-3}T,$$

where  $R$  is the molar gas constant and  $T$  the temperature in Kelvin. If some hydrogen is to be cooled from 150 to 100 K by a reversible adiabatic expansion, by what factor must its volume be increased?

07. [P.9.5, Zemansky] If  $p$ ,  $v$ , and  $T$  are the pressure, molar volume, and temperature of a gas and  $p_c$ ,  $v_c$ , and  $T_c$  are the critical pressure, critical molar volume, and critical temperature, then the reduced pressure  $p_R$ , the reduced molar volume  $v_R$ , and the reduced temperature  $T_R$  are defined as  $p_R = p/p_c$ ,  $v_R = v/v_c$ , and  $T_R = T/T_c$ .

(a) Show that, in terms of reduced quantities, the van der Waals equation becomes

$$\left(p_R + \frac{3}{v_R^2}\right) \left(v_R - \frac{1}{3}\right) = \frac{8}{3}T_R.$$

When the van der Waals equation is in this form, the material constants  $a$  and  $b$  do not appear explicitly. Thus, all gases that obey the van der Waals equation may be considered in the same state when the values of  $p_R$ ,  $v_R$ , and  $T_R$  are the same (i.e., each gas is measured in units of its particular values of  $p_c$ ,  $v_c$ , and  $T_c$ ). This is the principle of corresponding states, which is a principle of universal similarity established first by van der Waals.

(b) Plot three curves for  $p_R$  as a function of  $v_R$ , one for  $T = T_c/2$ , one for  $T = T_c$ , and one for  $T = 2T_c$ . What happens physically when the equation indicates three allowed values of  $v_R$  for a single  $p_R$  and  $T$ ?

08. [P.9.6, Lemons] A diesel engine requires no spark plug. Rather, its fuel ignites spontaneously when sprayed into the highly compressed air of an engine piston. Suppose that initially the air within a diesel engine piston is at 1 atm and that the engine piston adiabatically compresses the air by a factor of 15. This factor, by which the piston volume is decreased, is called the compression ratio. The ratio of specific heats for air  $C_p/C_V = \gamma = 7/5$ . Find the pressure of the completely compressed air.

P.09. [P.9.7, Lemons] Suppose  $n$  moles of ideal gas for which  $E = C_V T$  is the working fluid of a Carnot cycle operating between reservoirs with temperatures  $T_C$  and  $T_H > T_C$ , as illustrated in Figure 9.2. The subscripts 1, 2, 3, and 4 denote the states at which adiabats and isotherms intersect. Thus,  $T_H = T_1 = T_2$ ,  $T_C = T_3 = T_4$ ,  $S_2 = S_3$ , and  $S_4 = S_1$ . Also  $\gamma = C_P/C_V$ . Determine the following in terms of  $n$ ,  $T_H$ ,  $T_C$ ,  $V_1$ ,  $V_2$ ,  $V_3$ ,  $V_4$ , and  $C_V$ .

- The work  $W_{1 \rightarrow 2}$  done by the ideal gas during the isothermal process  $1 \rightarrow 2$ .
- The heat  $Q_H$  absorbed by the ideal gas during the isothermal process  $1 \rightarrow 2$ .
- The work  $W_{2 \rightarrow 3}$  done by the ideal gas during the adiabatic process  $2 \rightarrow 3$ .
- The total work  $W$  done by the ideal gas in one cycle.
- The efficiency  $W/Q_H$  of the cycle implied by the answers to parts (b) and (d). Show that this efficiency is consistent with the efficiency  $1 - T_C/T_H$  of a Carnot cycle.

P.10. [P.6.13, Sears] Show that the difference between the isothermal and adiabatic compressibilities is  $\kappa_T - \kappa_S = T\beta^2 v/c_p$ .

11. [P.8.16, Adkins] An elastic filament is such that when stretched by a force  $f$  at a temperature  $T$ , the extension  $x$  is given by the equation

$$\mu x = \alpha t + f,$$

where  $\mu = \mu_0(1 + \beta t)$  and  $t = T - T_0$ , with  $T_0$ ,  $\alpha$ ,  $\beta$ , and  $\mu_0$  being positive constants. When the filament is maintained at constant length and heated, its heat capacity is found to be proportional to temperature,  $C_x = AT$ . Show that:

- $A$  is independent of  $x$ .
- If the entropy is  $S_0$  when  $t = 0$  and  $x = 0$ , then  $S = S_0 + \alpha x - \mu_0 \beta x^2/2 + At$ .
- If the filament is heated under no tension, the thermal capacity is

$$C_{f=0} = \left( A + \frac{\mu_0^0 \alpha^2}{\mu^3} \right) T.$$

- For small extensions under adiabatic conditions, the filament cools and the appropriate spring constant is  $\mu + \mu_0^2 \alpha^2 / (\mu^2 A)$ .
- When the adiabatic extension is increased so that  $x > \alpha / (\beta \mu_0)$ , the filament starts to get warmer.

12. [P.8.17, Adkins] Show that, if a wire under tension suffers an adiabatic fractional increase in length of  $\Delta x$ , then the increase in temperature is given to first order by

$$\Delta T = -\frac{T}{C_L} \left( \alpha_0 Y - \sigma \frac{d(\ln Y)}{dT} \right) \Delta x,$$

where  $C_L$  is the heat capacity per unit volume of the wire at constant length,  $\sigma$  the stress (the tensional force per unit cross-sectional area),  $Y$  the Young modulus (assumed independent of  $\sigma$ ) and  $\alpha_0$  the linear expansivity at zero tension.

13. [P.10.1, Lemons] Find the four Maxwell-type relations among first-order partial derivatives of rubber band variables  $T$ ,  $S$ ,  $f$ , and  $L$  implied by the fundamental constraint  $dU = TdS + fdL$ . Generate these with the reciprocity, reciprocal, and chain rules or from an appropriate transformation of the Maxwell relations for a fluid.

14. [P.10.4, Lemons] The surface tension of water  $\gamma = 0.073$  N/m when  $T = 298$  K. How much reversible work is required to spread a 3.0 mm-radius spherical drop of water into a circular sheet that is 50 cm in diameter? Note: A sheet has two surfaces.

P.15. [P.10.5, 10.6, 10.7, Lemons]

(a) Show that the characterizing energy for a surface

$$U(S, A) = cAT_c \exp\left(\frac{S}{cA}\right)$$

is consistent with the equations of state:  $U = cAT$  and  $\gamma = cT [1 - \ln(T_c/T)]$ .

(b) The Eötvös equation of state for surface tension is

$$\gamma(T) = \gamma_0(1 - T/T_c),$$

where  $T \leq T_c$ . Considering that  $U = U(S, A)$  and  $\gamma = \gamma(T)$ , show that:

(i) the internal energy  $U = \gamma_0 A$  and (ii) the entropy  $S = \gamma_0 A/T_c$ .

(c) The Ferguson equation of state for surface tension is  $\gamma(T) = \gamma_0(1 - T/T_c)^n$ , where  $n \geq 1$ , i.e., it is a generalization of the Eötvös equation.

Find: (i) the function  $U(A, T)$  and (ii) the function  $S(A, T)$ .

16. [P.8.18, Sears] Show that when a charge  $\Delta Z$  flows reversibly through a voltaic cell of emf  $\mathcal{E}$  at constant temperature and pressure, (a)  $\Delta G = \mathcal{E}\Delta Z$ , and (b)  $\Delta H = \Delta Z d(\mathcal{E}/T)/d(1/T)$ .

17. [P.8.23, Adkins] The temperature of a long metal rod of diameter 2 mm is maintained at  $1000^\circ\text{C}$ . It is surrounded by two coaxial cylindrical radiation shields of diameter 4 mm and 6 mm, and of negligible thickness. If the entire space is evacuated and all radiating surfaces are black, calculate the temperature of the outer shield when equilibrium has been established assuming that the energy incident from the surroundings is negligible.

18. [P.8.25, Adkins] A large storage vessel for liquid oxygen may be considered as a perfectly evacuated spherical Dewar vessel of inner radius 1 m, and outer radius 1.2 m. Treating the walls of the vessel as perfectly black, calculate the rate of loss of oxygen due to radiation.

How would the rate of loss be changed if a spherical copper radiation shield were interposed midway between the inner and outer walls?

Reflectivity of copper is 0.98 and may be taken as independent of wavelength and temperature. Temperature of the surroundings is 300 K. Normal boiling point of liquid oxygen is 90 K. Latent heat of oxygen is  $2.4 \times 10^5 \text{ J kg}^{-1}$ .

19. [P.8.26, Adkins] Heat is generated electrically in a long wire at the rate of 10 W/m. The wire, which is 2 mm in diameter, can only lose heat by radiation to a thin walled coaxial tube, 30 mm in diameter. This, in turn, is covered with a layer of a bad conductor 70 mm thick, the outside of which is maintained at a temperature of  $20^\circ\text{C}$  by cooling water. If the thermal conductivity of the bad conductor is  $5.0 \times 10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$ , what will be the temperature of the wire when conditions are steady?

The surfaces of the wire and tube may be regarded as black.

20. [P.8.28, Adkins] Show that the entropy density of equilibrium radiation is  $4AT^3/3$ , where  $A$  is the constant related to the total energy density  $u = AT^4$ .

Consider that  $n$  identical containers of volume  $V$  and of negligible heat capacities are initially filled with radiation characteristic of temperatures  $T_1, T_2, \dots, T_n$ . Show that if no work or heat is available from other sources, then by operating reversible heat engines between the containers

(a) the maximum work which may be extracted is

$$W = AV \left[ \sum_{i=1}^n T_i^4 - n^{-1/3} \left( \sum_i T_i^3 \right)^{4/3} \right],$$

(b) the highest temperature  $T$  to which the radiation in any one of the containers may be raised is given by

$$\left( \sum_i T_i^3 - T^3 \right)^4 = (n-1) (T_i^4 - T^4)^3.$$

P.21. [P.9.11, 9.12, 9.13, Lemons]

(a) Show that the energy equation of state for cavity radiation  $u = aT^4$ , where  $a$  is a constant, follows directly from the pressure equation of state,  $p = U/3V$ , the fundamental constraint  $dU = TdS - pdV$ , and the condition  $(\partial/\partial V)(U/V)_T = 0$ .

(b) Show that the characterizing function  $U(S, V)$  for cavity radiation is given by  $U(S, V) = (3S/4)^{4/3}/(aV)^{1/3}$ .

(c) Show that its two equations of state  $p = U/3V$  and  $u = aT^4$  follow from appropriate derivatives of this function.

(d) Show that when a region filled with cavity radiation quasistatically and adiabatically expands or contracts, the quantities  $TV^{1/3}$  and  $pV^{4/3}$  remain constant.

P.22. [P.9.14, Lemons] Cavity radiation, described by equations of state  $p = U/3V$  and  $u = aT^4$  is the working fluid of a Carnot cycle operating between reservoirs with temperatures  $T_C$  and  $T_H > T_C$ , as illustrated in Figure 9.2. The subscripts 1, 2, 3, and 4 denote the states at which adiabats and isotherms intersect. Thus  $T_H = T_1 = T_2$ ,  $T_C = T_3 = T_4$ ,  $S_2 = S_3$ , and  $S_4 = S_1$ . Determine the following in terms of  $T_H$ ,  $T_C$ ,  $V_1$ ,  $V_2$ ,  $V_3$ , and  $V_4$ .

- (a) The work  $W_{1 \rightarrow 2}$  done by the cavity radiation during the isothermal expansion  $1 \rightarrow 2$ .
- (b) The heat  $Q_H$  absorbed by the cavity radiation during the isothermal expansion  $1 \rightarrow 2$ .
- (c) The work  $W_{2 \rightarrow 3}$  done by the cavity radiation during the adiabatic process  $2 \rightarrow 3$ .
- (d) The total work  $W$  done by the cavity radiation during one cycle.
- (e) The efficiency  $W/Q_H$  of the cycle implied by answers to parts (b) and (d). Show that this efficiency is consistent with the efficiency  $1 - T_C/T_H$  of a Carnot cycle.

23. [P.9.15 and P.9.16, Lemons] The sun may be considered a sphere of ideal gas composed of neutral molecules, electrons, and ions with a superimposed sphere of equilibrium cavity radiation. The gas density and temperature vary from the center to the surface of the sphere. Find the ideal gas pressure and the pressure of the cavity radiation at the following places within the sun; express these pressures in atmospheres; and form the ratio of ideal gas pressure to cavity radiation pressure.

- (a) The solar center at which the mole number density of solar gas (neutral molecules, electrons, and ions) is  $8.3 \times 10^7$  moles/m<sup>3</sup> and the temperature  $1.5 \times 10^7$  K.
- (b) The photosphere - that is, the visible solar surface - at which the mole number of solar gas is 0.17 moles/m<sup>3</sup> and the temperature is 5800 K.
- (c) The solar flux originates at the solar photosphere, spreads uniformly in all directions, and eventually strikes the earth. Calculate the solar constant, that is, the magnitude of the solar flux at the earth in W/m<sup>2</sup>. Recall that the flux of cavity radiation is  $c/4$  times the cavity radiation energy density  $u$ . Use the data from previous items and the facts that the solar radius  $R_S = 6.96 \times 10^8$  m and the mean sun-earth distance is  $R_{SE} = 1.50 \times 10^{11}$  m.

P.24. [P.8.21, Sears] Show that the heat added during an isothermal expansion of black-body radiation is four times larger than that expected for the heat added during the expansion of an ideal gas of photons obeying the same equation of state. The factor of four arises because the number of photons is not conserved but increases proportionally to the volume during an isothermal expansion.

25. [P.8.22, Sears] The walls of an evacuated insulated enclosure are in equilibrium with the radiant energy enclosed. The volume of the enclosure is changed suddenly from 100 to 50 cm<sup>3</sup>. If the initial temperature of the walls is 300 K, compute

- (a) the final temperature of the walls,
- (b) the initial and final pressure exerted on the walls by the radiant energy, and
- (c) the change of entropy of the radiant energy.

26. [P.8.27, Adkins] A paramagnetic ideal gas obeys Curie law  $\chi_m = a/T$ , where  $\chi_m$  is the susceptibility and  $a$  is a constant. A volume  $V_0$  of the gas is placed in a magnetic field of flux density  $H_0$ , which is then reduced adiabatically to zero. How must the volume be changed as a function of field if the temperature of the gas is to remain constant?

P.27. [P.10.2 and 10.3, Lemons]

- (a) Find the four Maxwell-type relations among first-order partial derivatives of the paramagnetic material variables  $T$ ,  $S$ ,  $H$ , and  $m$  implied by the fundamental constraint  $dU = TdS + \mu_0 H dm$ . Generate these with the reciprocity, reciprocal, and chain rules.
- (b) Show that the energy  $U$  of a paramagnetic material that obeys Curie law is a function of temperature  $T$  alone. Work only from what we know about paramagnetic materials.

P.28. [P.9.1, Adkins] A perfect gas has constant principal heat capacities and is initially at a pressure  $p_1$  and a temperature  $T_1$ . Find its final temperature when it undergoes an expansion to a pressure  $p_2$ :

- (a) without change of entropy,
- (b) without change of internal energy,
- (c) without change of enthalpy. How would such expansions be achieved?

29. [P.9.3, Adkins] One mole of hydrogen occupies a volume of  $0.1 \text{ m}^3$  and is at 300 K. One mole of argon also occupies a volume of  $0.1 \text{ m}^3$  but is at 400 K. While isolated from their surroundings, each undergoes a free expansion, the hydrogen to five times and the argon to eight times its initial volume. The two masses are then placed in thermal contact with each other and reach thermal equilibrium. What is the total change in entropy?

For hydrogen,  $c_v = 10 \text{ kJ/ K kg}$ . Argon has a relative atomic mass of 40 and  $c_v = 0.31 \text{ kJ/ K kg}$ .

30. [P.9.2 and P.9.4, Adkins]

(a) Two vessels A and B have equal volumes and negligible thermal capacities. They are thermally insulated from one another and from the surroundings, but are connected by a narrow capillary fitted with a tap. Initially, A contains a perfect gas at a pressure  $p_0$  and temperature  $T_0$  and B is evacuated. The tap is opened, and gas flows from A to B until the pressures becomes equal. What is the final pressure, and what are the final temperatures of A and B?

(b) One mole of a gas whose equation of state is  $p(v - b) = RT$  undergoes a free expansion from a volume  $2b$  to a volume  $4b$ . Calculate the change in entropy and the change in temperature.

31. [P.9.9, Adkins] Show that when a Dieterici gas suffers a Joule-Kelvin expansion in which the pressure drop is small, then there is no change of temperature when

$$b = v \left( 1 - \frac{RTb}{2a} \right).$$

P.32. [P.10.21 and P.11.2, Zemansky]

(a) A measure of the result of an adiabatic Joule free expansion is provided by the Joule coefficient  $\eta = (\partial T/\partial V)_U$ . Show that

$$\eta = -\frac{1}{C_V} \left( \frac{\beta T}{\kappa} - p \right).$$

(b) A measure of the result of the Joule-Thomson expansion (adiabatic throttling process or isenthalpic expansion) is provided by the Joule-Thomson coefficient  $\mu = (\partial T/\partial p)_H$ . Show that

$$\mu = \frac{V}{C_p} (\beta T - 1).$$

(c) The Joule-Thomson coefficient  $\mu$  is a measure of the temperature change during a throttling process. A similar measure of the temperature change produced by an isentropic change of pressure is provided by the coefficient  $\mu_S = (\partial T/\partial p)_S$ .

Prove that  $\mu_S - \mu = V/C_p$ .

33. [P.11.1, Zemansky]

(a) Show that in a Joule-Thomson expansion, no temperature change occurs if  $(\partial v/\partial T)_p = v/T$ .

(b) Show that

$$\mu c_p = T \left( \frac{\partial v}{\partial T} \right)_p - v.$$

In the region of moderate pressures, the equation of state of 1 mol of gas may be written  $pv = RT + B'p + C'p^2$ , where the second and third virial coefficients  $B'$  and  $C'$  are functions of  $T$  only.

(c) Show that, as the pressure approaches zero,

$$\mu c_p \rightarrow T \frac{dB'}{dT} - B'.$$

(d) Show that the equation of the inversion curve is

$$p = -\frac{B' - T(dB'/dT)}{C' - T(dC'/dT)}.$$

P.34. [P.6.20, Sears] One kilomole of an ideal gas undergoes a throttling process from a pressure of 4 atm to 1 atm. The initial temperature of the gas is 50°C.

(a) How much work could have been done by the ideal gas had it undergone a reversible process to the same final state at constant temperature?

(b) How much does the entropy of the universe increase as a result of the throttling process?

35. [P.6.28, Sears] Compute  $\eta$  and  $\mu$  for a gas whose equation of state is given by (a)  $p(v - b) = RT$  and (b)  $(p + b)v = RT$ , where  $b$  is a constant. Assume that  $c_p$  and  $c_v$  are constants.

36. [P.6.31, P.6.32, P.6.34, Sears]

(a) For a van der Waals gas, determine  $\mu$  and the inversion temperature which is related to the condition  $\mu = 0$ . See Eqs. (6.59) and (6.60), Sears.

(b) Assuming that helium is a van der Waals gas, calculate the pressure so that the inversion temperature of helium is 20 K. See Table 6-1 from Sears for data.

(c) Calculate the minimum inversion temperature of helium.

37. [P.6.29 and P.6.33, Sears]

(a) Assuming that helium obeys the van der Waals equation of state, determine the change in temperature when one kilomole of helium gas undergoes a Joule expansion at 20 K to atmospheric pressure. The initial volume of the helium is 0.12 m<sup>3</sup>.

(b) The helium gas undergoes a throttling process. Calculate the Joule-Thomson coefficient at (i) 20 K and (ii) 150 K. For each process calculate the change of the temperature of the helium if the final pressure is 1 atm, assuming that  $\mu$  is independent of  $p$  and  $T$ . See Tables 2-1 and 9-1 from Sears for data.

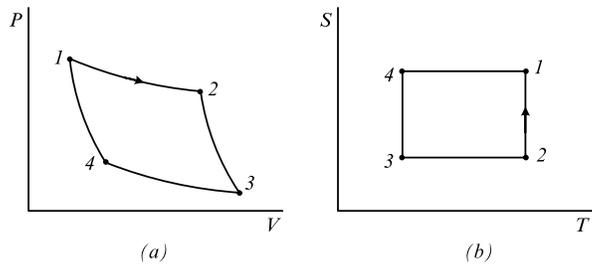


FIGURE 9.2 State variable diagrams for Carnot cycle. (Used in Problems

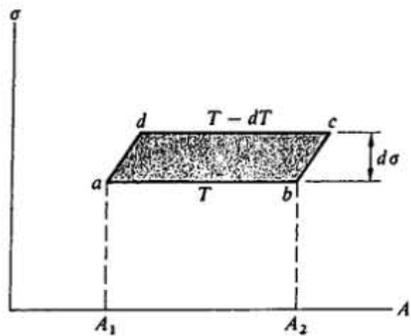


Figure 8-12