

1. A process on an ideal gas is defined by  $P = AT^b$ . (i) Express this process in terms of  $(P, V)$  and  $(V, T)$ . (ii) Calculate compressibility and thermal expansivity in this process. (iii) What is the limitation on  $b$ ? (iv) For which values of  $b$  this process becomes a known process? (v) Find adiabatic values of the two thermodynamic coefficients above.

Solution: (i) Use the equation of state of the ideal gas,  $PV = nRT$ , to obtain:  $P = A\left(\frac{PV}{nR}\right)^b$ . This can be represented in the simplified form  $P^{1-1/b}V = nR/A^{1/b}$ . Alternatively, write  $nRT/V = AT^b$ , which can be simplified to  $T^{b-1}V = nR/A$ . (ii) The compressibility coefficient is given by  $\kappa = -\frac{1}{V} \frac{dV}{dP}$ . Use  $V \propto P^{-(1-1/b)}$ , to find  $\kappa = \left(1 - \frac{1}{b}\right) \frac{P^{-(1-1/b)-1}}{V} = \left(1 - \frac{1}{b}\right) \frac{1}{P}$ . The thermal expansion coefficient is defined by  $\beta = \frac{1}{V} \frac{dV}{dT}$ . Use  $V \propto T^{-(b-1)}$ , to find  $\beta = \frac{1-b}{T}$ . (iii) Since mechanical stability requires  $\kappa_T > 0$ , the condition on  $b$  is  $b > 1$  or  $b < 0$ . (iv) For  $b \rightarrow 0^-$ , the process is isobaric; for  $b \rightarrow 1$ , isochoric; for  $b \rightarrow \pm\infty$  isothermic, and for  $b = \gamma/(\gamma - 1) > 1$  adiabatic. (v) From the latter you can obtain the adiabatic thermodynamic coefficients  $\kappa_S = \frac{1}{\gamma P}$  and  $\beta_S = -\frac{1}{(\gamma-1)T}$ , which can be compared with  $\kappa_T = \frac{1}{P}$  and  $\beta_P = \frac{1}{T}$ . Note that  $\beta_S < 0$  because in the adiabatic process the volume decreases and the temperature increases.

2. A process on an ideal gas is defined by  $P = AT^2$ , with  $A = \text{constant}$ . Calculate the received work and heat upon changing the temperature from  $T_1$  to  $T_2$ . Assume  $C_V = \text{constant}$ .

Solution: Use the equation of state of the ideal gas to express  $P$  in terms of  $V$  as  $P = \frac{(nR)^2}{AV^2}$  and integrate  $W_{12} = \int_1^2 P dV = \int_1^2 \frac{(nR)^2}{AV^2} dV = \frac{(nR)^2}{A} \left(\frac{1}{V_1} - \frac{1}{V_2}\right)$ . Then express  $V$  via  $T$ :  $V = \frac{nRT}{P} = \frac{nR}{AT}$ , and substitute it into the work,  $W_{12} = nR(T_1 - T_2)$ . To calculate the heat, use the first law of thermodynamics in the form  $U_2 - U_1 = Q_{12} - W_{12}$ . Using the internal energy for a perfect gas,  $U = C_V T + \text{constant}$ , and the result for the work obtained above, you straightforwardly find  $Q_{12} = C_V(T_2 - T_1) + W_{12} = (C_V - nR)(T_2 - T_1)$ .

3. System  $A$  is in equilibrium and has  $V_A = 2 \text{ m}^3$  and  $P_A = 0.01 \text{ bar}$ . System  $B$  is in equilibrium, and has  $V_B = 3 \text{ m}^3$  and  $P_B = 0.02 \text{ bar}$ . Systems  $A$  and  $B$  are put in thermal contact with each other, and it is found that they are also in thermal equilibrium with each other. Suppose that the densities of each system are very dilute. Moreover, suppose that the gas in each system happens to be  $\text{N}_2\text{O}$  (nitrous oxide). Throughout in what follows, suppose that the systems remain closed, i.e. they do not leak or exchange gasses. (i) Compute the ratio  $M_A/M_B$  of the masses of the gas in each container. (ii) System  $A$  is kept in contact with system  $B$ . The volume  $V_A$  is slowly changed to  $V'_A = 4 \text{ m}^3$ , and the pressure  $P_A$  is changed to  $P'_A = 0.03 \text{ bar}$ . The volume  $V_B$  is unchanged,  $V'_B = 3 \text{ m}^3$ . What should the new pressure  $P'_B$  be, in order for the systems  $A$  and  $B$  to remain in thermal equilibrium? (iii) Is the temperature of the systems, in their final state of part (ii), hotter or colder than they were in their initial state? Compute the ratio  $T_{\text{final}}/T_{\text{initial}}$ , where the temperatures are measured in Kelvin.

Solution: (i) Use the equation of state of the ideal gas to write  $n_i = \frac{P_i V_i}{RT_i}$ , which implies  $\frac{m_A}{m_B} = \frac{n_A M}{n_B M} = \frac{n_A}{n_B} = \frac{P_A V_A / T_A}{P_B V_B / T_B} = \frac{1}{3}$ . (ii) Use the equation of state of the ideal gas to write  $T_i = \frac{P_i V_i}{n_i R}$ . To be in thermal equilibrium, system A and system B must be at the same temperature:  $T'_A = T'_B$ . Hence,  $\frac{P'_A V'_B}{n_a} = \frac{P'_B V'_B}{n_B}$ , yielding  $P'_B = \frac{P'_A V'_A n_B}{n_A V'_B} = 0.12$  bar. (iii)  $\frac{T_{\text{final}}}{T_{\text{initial}}} = \frac{P'_A V'_A}{P_A V_A} = \frac{P'_B V'_B}{P_B V_B} = 6$ .

4. A tank of volume  $10 \text{ m}^3$  contains nitrous oxide at a pressure  $1000 \text{ Pa}$  and temperature of  $20^\circ \text{ C}$ . Assume that it behaves like an ideal gas. (i) How many kilomoles of  $\text{N}_2\text{O}$  are in the tank? (ii) How many kilograms? (iii) Find the pressure if the temperature is increased to  $50^\circ \text{ C}$ . (iv) At a temperature of  $20^\circ \text{ C}$ , how many kilomoles should be withdrawn from the tank for the pressure to become  $100 \text{ Pa}$ ?

Solution: (i) Use the equation of state of the ideal gas to obtain  $n = \frac{PV}{RT} = 0.0041$  kilomole; (ii)  $m = nM = 0.0041(14 \times 2 + 16) = 0.81$  kg; (iii)  $P = \frac{nRT}{V} = 1102 \text{ Pa}$ ; (iv)  $n'/n = P'/P$ , which implies  $n' = 0.1 n$ , yielding  $\Delta n = 0.9n = 0.0037$  kilomole.

5. A glass bottle of nominal capacity  $250 \text{ cm}^3$  is filled brim full of water at  $20^\circ \text{ C}$ . If the bottle and contents are heated to  $50^\circ \text{ C}$ , how much water spills over? (For water,  $\beta = 0.21 \times 10^{-3} \text{ K}^{-1}$ . Assume that the expansion of the glass is negligible.)

Solution:  $\Delta V = \beta V_0 \Delta T = 1.6 \text{ cm}^3$ .

6. (i) Calculate the heat capacity in the process  $P = AT^b$  of an ideal gas, expressing it as a function of  $T$ . (ii) Analyze different cases of  $b$ .

Solution: (i) Use the first law of thermodynamics,  $dU = \delta Q - PdV$ , to obtain the infinitesimal heat received:  $\delta Q = dU + PdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV$ . Next, use the isochoric heat capacity  $C_V = \left(\frac{\partial U}{\partial T}\right)_V$  and the fact that for the ideal gas  $\left(\frac{\partial U}{\partial V}\right)_T = 0$  to simplify the previous expression to  $\delta Q = C_V dT + PdV$ . After that, express  $dV$  through  $dT$ . To this end, use  $P = AT^b$  and the equation of state of the ideal gas to write  $V = \frac{nR}{A} T^{1-b}$ , which leads to  $dV = \frac{nR}{A} (1-b) T^{-b} dT$ . Since  $P = AT^b$ , it follows that  $\delta Q = C_V dT + nR(1-b)dT$  and hence  $C = \frac{\delta Q}{dT} = C_V + nR(1-b)$ . (ii) For the isobaric process,  $b = 0$ , it follows that  $C = C_P = C_V + nR$  (Mayer's relation). For the isochoric process,  $b = 1$ , it follows that  $C = C_V$ . For the isothermic process,  $b \rightarrow \pm\infty$ , it follows that  $C \rightarrow \mp\infty$ . For the adiabatic process,  $b = \gamma/(\gamma-1)$ , where  $\gamma = C_P/C_V$ , it follows that  $C = C_V - \frac{nR}{\gamma-1} = \frac{C_V(C_P/C_V-1)-nR}{(\gamma-1)} = \frac{C_P-C_V-nR}{\gamma-1}$ , and taking into account Mayer's relation  $C = 0$ .