

1. (i) A system initially with volume 10 liters and temperature $T = 0^\circ\text{C}$ is compressed adiabatically to a state with volume 5 liters and temperature $T = 100^\circ\text{C}$. In this process, 1000 J of work is done on the system. By how much does the internal energy of the system change in this process? (ii) Instead, we start from the same initial state as above, and end at the same final state as above, by going through the following two steps. Step 1: the system is first heated isochorically (constant volume) to the final temperature $T = 100^\circ\text{C}$. Step 2: the system is then compressed isothermally (constant temperature) to the final volume of 5 liters. In the first step, 800 J of heat had to be added to the system. In the second step, 1900 J of heat flowed out of the system. Compute the energy changes and amounts of work done in each of these two steps. (iii) Can this system be regarded as an ideal gas? Why or why not?

Solution: (i) $\Delta U = \Delta Q - \Delta W = 1000$ J. (ii) Step 1: $\Delta W = 0$ as the volume remains constant; $\Delta Q = 800$ J; $\Delta U = \Delta Q - \Delta W = 800$ J. Step 2: $\Delta Q = -1900$ J; 1000 J = 800 J + $\Delta U \Rightarrow \Delta U = 200$ J; $\Delta W = \Delta U - \Delta Q = -1900$ J - 200 J = -2100 J. (iii) No, the system is not an ideal gas. The internal energy of the system changes under the isothermal process in Step 2, while for an ideal gas its internal energy should depend on temperature only.

2. The temperature of an ideal gas at initial pressure P_1 and volume V_1 is increased isochorically until the pressure has doubled. The gas is then expanded isothermally (constant temperature) until the pressure drops to its original value. Then it is compressed isobarically (constant pressure) until the volume returns to its initial value. (i) Sketch these processes in the $P - V$ plane and the $P - T$ plane. (ii) Compute the work done in each process, and the net work done in the cycle, if $n = 2$ kilomoles, $P_1 = 10^5$ Pa, and $V_1 = 2$ m³.

Solution: (i) The $P - V$ and $P - T$ diagrams are shown in Fig. 1. (ii) Step 1: Use the equation of state of the ideal gas to obtain $P_1 V_1 = nRT_1$; $\Delta W_1 = 0$; remains constant; $P_2 = 2P_1$ and so $2P_1 V_1 = T_2 nR$. Step 2: $\Delta W_2 = \int_{V_1}^{V_2} P_2 dV = \int_{V_1}^{V_2} \frac{nRT_2}{V} dV = 2P_1 V_1 \ln 2$. Step 3: $\Delta W_3 = \int_{V_2}^{V_1} P_1 dV = P_1(V_1 - V_2) = -V_1 P_1$. Step 1 + Step 2 + Step 3: $\Delta W = \Delta W_1 + \Delta W_2 + \Delta W_3 = P_1 V_1 (2 \ln 2 - 1) = 7.73 \times 10^4$ J.

3. A hypothetical substance has expansivity $\beta = aT^3/v$ and isothermal compressibility $\kappa = b/v$, where a and b are constants. Find the equation of state (including the unknown constant of integration).

Solution Express the volume as a function of T and P . Relate the partial derivatives to the thermodynamic coefficients to obtain $dv = \beta v dT - \kappa v dP = aT^3 dT - b dP$. The equation of state is then $v - v_0 = a(T^4 - T_0^4)/4 - b(P - P_0)$.

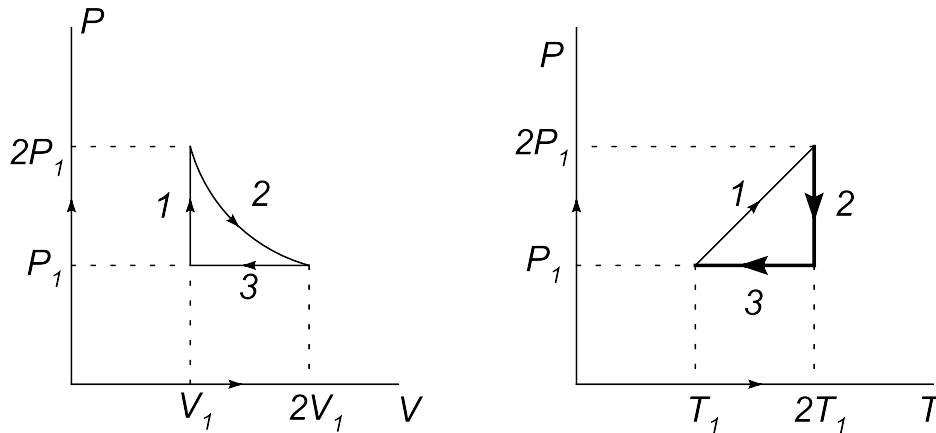


Figure 1: $P - V$ diagram (left) and $P - T$ diagram (right).

4. For stainless steel, the coefficient of linear thermal expansion is $\alpha = 17.3 \times 10^{-6}/K$ at 20°C , and the bulk modulus is about 1.6×10^{11} Pa. What pressure ΔP is needed to keep stainless steel from expanding, when heated from 20°C to 25°C . Assume that the coefficients are constant over this temperature range. Consider the pressure needed on a little steel nugget, to prevent its volume from expanding in any direction. [Hints: This question is about expansion in any direction, not just one linear direction: be careful about factors of 3. The isothermal compressibility is the inverse of the bulk modulus.]

Solution: The coefficient of volume thermal expansion $\beta = 3\alpha = 5 \times 10^{-5} \text{ K}^{-1}$, and the isothermal compressibility $\kappa = 1/(\text{bulk modulus}) = 6.25 \times 10^{-12} \text{ Pa}^{-1}$. Express the volume as a function of T and P . Relate the partial derivatives to the thermodynamic coefficients to obtain $dv = \beta v dT - \kappa v dP$. For constant volume, this leads to $\beta \Delta T = \kappa \Delta P$, hence $\Delta P = \beta \Delta T / \kappa = 4.15 \times 10^7$ Pa.

5. The pressure on 100 g of nickel is increased quasistatically and isothermally from zero pressure to 500 atm. Calculate the work done on the material, assuming that the density and isothermal compressibility remain constant at the values of $8.90 \times 10^3 \text{ kg m}^{-3}$ and $6.75 \times 10^{-11} \text{ Pa}^{-1}$.

Solution: The volume of 100 g of nickel is $0.10 \text{ kg} / (8.90 \times 10^3 \text{ kg m}^{-3}) = 1.12 \times 10^{-5} \text{ m}^3$. $P_2 = 500 \text{ atm} = 5 \times 1.01 \times 10^7 \text{ Pa} = 5.05 \times 10^7 \text{ Pa}$. You can compute the work done on the material from $dW = -PdV = -P \left[\left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP \right] = -PV\beta dT + PV\kappa dP$. For $dT = 0$, $W = V\kappa \int P dP = \frac{1}{2} V \kappa P^2 \Big|_{P_1}^{P_2} = 9.7 \times 10^{-2} \text{ J}$.