

1 Temperature Change of an Ideal Gas

The enthalpy $H \equiv U + pV$ of a certain gas was determined over a range in temperature while pressure was kept constant at the value p_0 and the results are summarized in the expression:

$$H = aT + bT^3$$

where a and b are experimentally determined constants. Consider the process when the gas is heated from temperature T_1 to temperature T_2 , both values within the range of validity of the expression above, while the pressure was kept constant at the value p_0 used in the experiments described above. You may assume that the equation of state for this gas is given by the ideal gas law $pV = Nk_B T$, and that the internal energy of the gas is a function of T only, i.e.

$$\left(\frac{\partial U}{\partial V}\right)_T = 0. \quad (1)$$

Note that this property is only true for an ideal gas!

- Derive an expression for the *change* in constant pressure heat capacity, ΔC_p .
- Derive an expression for the *change* in constant volume heat capacity, ΔC_V .
- Derive an expression for the internal energy change, ΔU .
- Derive an expression for the entropy change, ΔS .

2 Isothermal/Adiabatic Compressibility

The isothermal compressibility is defined as

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \quad (2)$$

K_T is be found by measuring the fractional change in volume when the the pressure is slightly changed with the temperature held constant. In contrast, the adiabatic compressibility is defined as

$$K_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_S \quad (3)$$

and is measured by making a slight change in pressure without allowing for any heat transfer. This is the compressibility, for instance, that would directly affect the speed of sound. Show that

$$\frac{K_T}{K_S} = \frac{C_p}{C_V} \quad (4)$$

Where the heat capacities at constant pressure and volume are given by

$$C_p = T \left(\frac{\partial S}{\partial T}\right)_p \quad (5)$$

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V \quad (6)$$

3 Helmholtz Free Energy of a Van Der Waals Gas

The Helmholtz free energy of a van der Waals gas can be written as:

$$F = -NkT \left\{ 1 + \ln \left[\frac{(V - Nb)T^{\frac{3}{2}}}{N} \right] \right\} - \frac{aN^2}{V}$$

Where a and b are constants. Derive the equation of state (relationship between p , T , and V) for this Helmholtz free energy and sketch (or plot) the pressure as a function of volume at fixed temperature.

4 Ideal gas internal energy

Optional and not graded In this problem, you will prove that the internal energy of an ideal gas depends only on volume, based solely on the ideal gas equation:

$$pV = Nk_B T \quad (7)$$

and of course your knowledge of thermodynamics. It's a pretty tricky proof, so I'll step you through it.

(a) To begin with, use the Helmholtz free energy $F = U - TS$ to show that

$$\left(\frac{\partial U}{\partial V} \right)_T = -p + T \left(\frac{\partial S}{\partial V} \right)_T \quad (8)$$

for *any* material.

(b) Now show that for any material

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V. \quad (9)$$

(c) Finally, show that for an ideal gas

$$\left(\frac{\partial U}{\partial V} \right)_T = 0. \quad (10)$$