

Problem 1. Nitrogen gas

Two moles of nitrogen (N_2) are in a 6-L container at a pressure of 5 bar.

Try not to look up numbers. Rather try to remember a few numbers and ratios, and put them in context, like I did in lecture. A summary of the constants you will need in this course is given in an [Appendix](#). Read this appendix as you work through this problem.

Here are some things to consider: the Nitrogen atom has seven protons and seven neutrons, and the N_2 molecule contains two nitrogen atoms. In part (b) it is useful to know that the binding energy of an electron in the hydrogen atom is 13.6 eV, which is known as the Rydberg constant. The Bohr model of hydrogen relates the binding energy (BE) of an electron in hydrogen to the Bohr radius $a_0 \simeq 0.53 \text{ \AA}$

$$|\text{BE}| = \frac{\hbar^2}{2m_e a_0^2} = 13.6 \text{ eV} \quad (1)$$

A quick reminder about what you will need about the Bohr model is given in the appendix. You will also need the ratio of the proton to electron mass, m_p/m_e , which was given in lecture.

- Find the average kinetic energy of one molecule of the gas in electron volts and the root-mean-square velocity in m/s . I find that the energy and rms velocity are, 0.04 eV and 400 m/s. Is the kinetic energy $\frac{1}{2}mv^2$?
- The bond length of N_2 (i.e. the distance between the N atoms) is $r_0 \simeq 2a_0 \simeq 1 \text{ \AA} = 0.1 \text{ nm}$. Determine the moment of inertia, and use the equipartition theorem to determine the root-mean-squared angular momentum of the molecule in units of \hbar in terms of the mass of a nitrogen atom m_N , the bond length r_0 , the temperature, and fundamental constants, i.e. find¹

$$\frac{L_{\text{rms}}}{\hbar} \equiv \frac{\sqrt{\langle \vec{L}^2 \rangle}}{\hbar}. \quad (2)$$

Evaluate the result numerically. The rotations of the molecule can be considered as classical when the angular momentum is large compared to \hbar , otherwise the angular motion is quantized. If the corrections to the classical description are of order $\sim \hbar/L$, how good is the classical description of the motion here? What is parametric dependence of L_{rms} on temperature²? Will the classical approximation get worse or better as the temperature increases?

¹*Hint:* Recall that the rotational kinetic energy

$$\frac{1}{2}I\vec{\omega}^2 = \frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_y^2 = \frac{L_x^2}{2I} + \frac{L_y^2}{2I} = \frac{\vec{L}^2}{2I}$$

has two degrees of freedom, while the translational kinetic energy has three. Technically this is because rotational kinetic energy (or Hamiltonian) has two quadratic forms, $\frac{1}{2}I\omega_x^2$ and $\frac{1}{2}I\omega_y^2$. You should find about $L_{\text{rms}} \simeq 8\hbar$.

²i.e. does it grow exponentially with temperature or as a power, and if a power, then what power?

Speed of Nitrogen Gas: N_2 diatomic nitrogen

$$PV = N k_B T$$

• So

$$k_B T = \frac{PV}{N} = \frac{(5 \times 10^5 \text{ N/m}^2)(6 \times (0.1 \text{ m})^3)}{2 \times 6 \times 10^{23}}$$

$$= 2.5 \times 10^{-21} \text{ J}$$

$$k_B = \frac{1.44}{273} \frac{\text{eV}}{\text{K}}$$

$$\approx 0.016 \text{ eV}$$

$$T = 180^\circ \text{K}$$

• So the molecule has five degrees of freedom

$$E = \frac{5}{2} k_B T \approx 0.040 \text{ eV}$$

• The translational motion is 3-degrees of freedom

$$\left\langle \frac{1}{2} m v^2 \right\rangle = 3 \times \frac{1}{2} k_B T$$

So

$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3 k_B T}{m}}$$

$$V_{\text{rms}} = \left(\frac{3 k_B N_A T}{m N_A} \right)^{1/2}$$

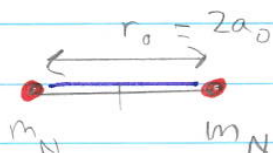
Now $k_B N_A = 8.32 \frac{\text{J}}{\text{K}}$ $T = 180^\circ \text{K}$

So $m N_A = \text{molar mass} \approx 28 \text{g} = 2 \times 14 \text{g}$

$$V_{\text{rms}} = \left(\frac{3 \cdot 8.32 \frac{\text{J}}{\text{K}} \cdot 180^\circ \text{K}}{28 \text{g}} \right)^{1/2}$$

$$\approx 400 \text{m/s}$$

b) The moment of inertia is



• So

$$I = m_N a_0^2 + m_N a_0^2 = 2m_N a_0^2$$

• Then using the equipartition theorem

$$\langle \varepsilon_{\text{rot}} \rangle = \left\langle \frac{1}{2} I (\omega_x^2 + \omega_y^2) \right\rangle = \left\langle \frac{L_x^2}{2I} + \frac{L_y^2}{2I} \right\rangle = 2 \left(\frac{1}{2} k_B T \right)$$

• So $\langle \vec{L}^2 \rangle$ is

$$\langle L^2 \rangle = 2 I k_B T$$

And

$$\frac{\langle L^2 \rangle}{\hbar^2} = 2 \left(\frac{2m_N a_0^2}{\hbar^2} \right) k_B T$$

• So now we estimate

$$\frac{\hbar^2}{2m_N a_0^2} = \frac{1}{14.2000} \left(\frac{\hbar^2}{2m_e a^2} \right) = \frac{13.6 \text{ eV}}{14.2000} = 0.0005 \text{ eV}$$

$$\approx 0.5 \text{ meV}$$

While

$$k_B T = \frac{1/40 \text{ eV}}{300^\circ \text{K}} \cdot 180^\circ \text{K} = 15 \text{ meV}$$

So

$$\frac{\langle L^2 \rangle}{\hbar^2} = 2 \cdot \frac{(15 \text{ meV})}{0.5 \text{ meV}} \approx 60$$

So

$$\frac{L_{\text{rms}}}{\hbar} \approx \sqrt{60} \approx 7.8$$

Problem 2. Partial Derivatives

Consider a particle whose height z is a function of x, y

$$z = z_1(x, y) = x^2 + 2y^2 \quad (3)$$

Now assume $x = r \cos \theta$ and $y = r \sin \theta$. Expressed in terms of x and r the height reads (work this out!)

$$z = z_2(x, r) = 2r^2 - x^2 \quad (4)$$

The functions $z_1(x, y)$ and $z_2(x, r)$ return the same *value* (at corresponding arguments)

$$z = z_1(x, y) = z_2(x, r) \quad (5)$$

but they have different *functional forms*. A mathematician would say (correctly) that they are different functions, i.e. different maps from $\mathbb{R}^2 \rightarrow \mathbb{R}$. The first map z_1 adds the square of the first argument to twice the square of the second argument, while the second map z_2 takes twice the square of the second argument and subtracts the square of the first. For a mathematician the functional form is paramount, and the mere name of the arguments makes no difference, $z_2(a, b) = 2b^2 - a^2$. Having two different symbols, z_1 and z_2 , for the same physical quantity would lead to an explosion of symbols and is not practical. So, physicists keep track of the function we are working with by indicating the arguments of the function:

$$z(x, y) \equiv z_1(x, y) \quad z(x, r) \equiv z_2(x, r) \quad (6)$$

This sneakily uses the *same* symbol z for two *different* functions and it is not clear at all what $z(a, b)$ means, but clear enough that $z(x_2, r_2) = 2r_2^2 - x_2^2$.

When one takes derivatives one needs to be clearer

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{\partial z_1}{\partial x} = 2x \quad \left(\frac{\partial z}{\partial x}\right)_r = \frac{\partial z_2}{\partial x} = -2x \quad (7)$$

Compute the following³

$$\left(\frac{\partial z}{\partial x}\right)_y, \left(\frac{\partial z}{\partial x}\right)_r, \left(\frac{\partial z}{\partial x}\right)_\theta, \left(\frac{\partial z}{\partial y}\right)_x, \left(\frac{\partial z}{\partial y}\right)_r, \left(\frac{\partial z}{\partial y}\right)_\theta, \frac{\partial z}{\partial x \partial \theta}$$

³Answers: $2x, -2x, 2x(1 + 2 \tan^2 \theta), 4y, 2y, 2y(2 + \cot^2 \theta), 8x \sec^2(\theta) \tan(\theta)$

Solution:

Straight forward algebra shows

$$z(x, y) = x^2 + 2y^2 \quad (8)$$

$$z(x, r) = 2(x^2 + y^2) - x^2 \quad (9)$$

$$= 2r^2 - x^2 \quad (10)$$

$$z(x, \theta) = x^2 + 2r^2 \sin^2 \theta = x^2 + 2 \frac{x^2}{\cos^2 \theta} \sin^2 \theta \quad (11)$$

$$= x^2 (1 + 2 \tan^2 \theta) \quad (12)$$

$$z(y, r) = (x^2 + y^2) + y^2 \quad (13)$$

$$= r^2 + y^2 \quad (14)$$

$$z(y, \theta) = r^2 \cos^2 \theta + 2y^2 \quad (15)$$

$$= \frac{y^2}{\sin^2 \theta} \cos^2 \theta + 2y^2 \quad (16)$$

$$= y^2 (2 + \cot^2 \theta) \quad (17)$$

$$(18)$$

Then straightforward differentiation of the *right* function (out of the five functions written here) gives the answers quoted. For example

$$\frac{\partial z}{\partial x \partial \theta} = \frac{\partial z(x, \theta)}{\partial x \partial \theta} = \frac{\partial}{\partial \theta} 2x(1 + 2 \tan^2 \theta) = 8x \sec^2 \theta \tan \theta \quad (19)$$

Problem 3. A classical solid

A solid consists of an array of atoms in a crystal structure shown below. In a simple model (used by Einstein at the advent of quantum mechanics) each atom is assumed to oscillate independently of every other atom ⁴.

In one dimension a “solid” of N atoms consists of N independent harmonic oscillators. The Hamiltonian⁵ of each oscillator is

$$H(x, p) = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \quad (20)$$

where m is the mass of the atom. Here we have written the Hamiltonian in the “mature” way writing noting that

$$\frac{p^2}{2m} = \frac{1}{2}mv^2 \quad \text{and} \quad \frac{1}{2}m\omega_0^2 x^2 = \frac{1}{2}k_0 x^2 \quad (21)$$

where $\omega_0 = \sqrt{k_0/m}$ is the natural oscillation frequency of the oscillator. In two dimensions each atom can oscillate in the x direction and the y direction. Thus, the solid of N atoms consists of $2N$ independent oscillators. The Hamiltonian (or energy as a function of x, y, p_x, p_y) of each atom is a sum of two harmonic oscillators:

$$H(x, y, p_x, p_y) = H_x + H_y \quad (22)$$

$$= \left(\frac{p_x^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \right) + \left(\frac{p_y^2}{2m} + \frac{1}{2}m\omega_0^2 y^2 \right) \quad (23)$$

Finally in three dimensions (shown below) the solid of N atoms consists of $3N$ independent oscillators as shown below, and each atom can oscillate in the x , y , or z directions. The Hamiltonian of each atom shown in Fig. 1 consists of three harmonic oscillators:

$$H = H_x + H_y + H_z \quad (24)$$

$$= \left(\frac{p_x^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \right) + \left(\frac{p_y^2}{2m} + \frac{1}{2}m\omega_0^2 y^2 \right) + \left(\frac{p_z^2}{2m} + \frac{1}{2}m\omega_0^2 z^2 \right) \quad (25)$$

The total Hamiltonian is a sum of the Hamiltonians of each atom.

- (a) By appealing to the equi-partition theorem for a classical harmonic oscillator, determine the energy of the solid in a classical approximation. Determine the specific heat C_V^{lmol} for one mole of substance in this case. You should find $C_V^{\text{lmol}} \simeq 25 \text{ J/mol}$, known as the Dulong and Petit rule. The specific heat of a variety of solids is shown on the next page. What does the simple model get right and wrong?

A Differential Scanning Calorimeter (DSC) is a device used to measure the specific heat of solids accurately and quickly and costs $\sim \$10 \text{ K}$. A schematic of a DSC is shown below and consists of a reference material with known specific heat, C_p^{ref} . A computer supplies heat to a

⁴In reality the motions of the atoms are coupled to each other, and the oscillation pattern of the solid, may be found by breaking it up into normal modes.

⁵The Hamiltonian is as a function of position and momentum returning the energy of the particle (i.e. a specific map $\mathbb{R}^2 \rightarrow \mathbb{R}$).

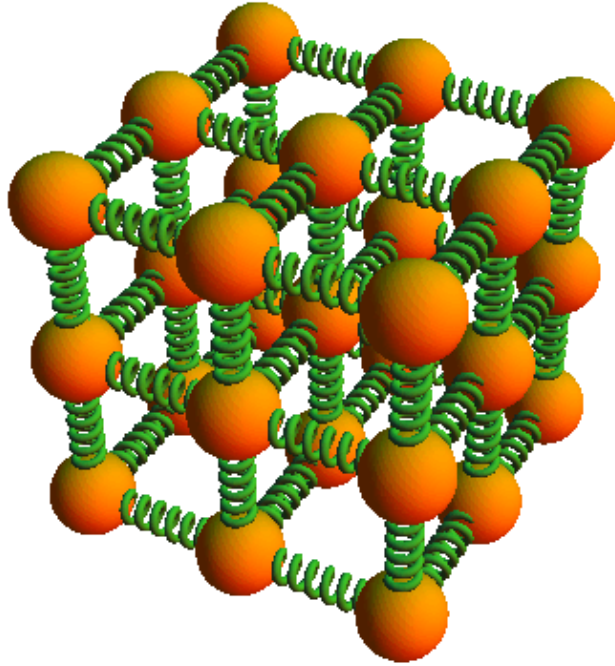


Figure 1:

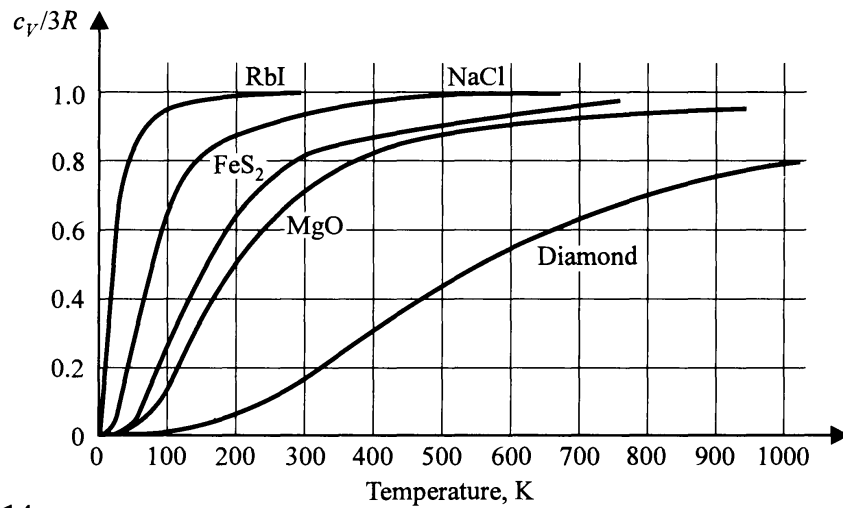


Figure 2: Specific heats of various solids

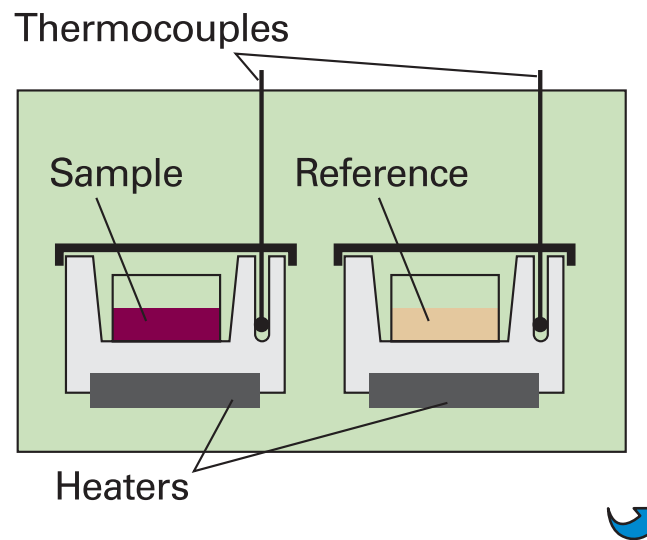


Fig. 2.15 A differential scanning calorimeter. The sample and a reference material are heated in separate but identical metal heat sinks. The output is the difference in power needed to maintain the heat sinks at equal temperatures as the temperature rises.

Figure 3: A differential scanning calorimeter

reference material (typically by delivering power to a resistive heating element $P = I^2 R$) so that the temperature of the reference material rises at a constant rate. Then, the computer adjusts the power delivered to sample so that the temperature of the sample equals the temperature of the reference at all times. By knowing the power delivered to the reference and the sample, and the specific heat of the reference, the specific heat of the sample can be determined.

- (b) Assume that the reference and sample are NaCl and Diamond respectively. Using Fig. 2, estimate the ratio of currents delivered to the reference and sample at a temperature of 300 °K, $I^{\text{ref}}/I^{\text{sample}}$. Assume that $C_p \simeq C_V$ which is a good approximation for solids and many liquids, and that the sample and reference materials have the same number of moles⁶.

⁶Answer: ~ 2

Solution:

(a) We have N atoms. Each atom has 3 harmonic oscillator (x, y, z) . Then each oscillator has two quadratic forms

$$\frac{1}{2}m\omega_0^2x^2 \quad \frac{p^2}{2m} \quad (26)$$

i.e. two degrees of freedom. Thus there are six times N quadratic forms in the classical energy leaving

$$U = 6N \times \frac{1}{2}kT = 3NkT \quad (27)$$

For one mole $N = N_A$ and $N_Ak_B = R$

$$U^{1\text{ mol}} = 3RT \quad (28)$$

The specific heat is

$$C_V^{1\text{ mol}} = \left(\frac{\partial U^{1\text{ mol}}}{\partial T} \right)_V = 3R \simeq 25 \text{ J}. \quad (29)$$

Looking at the curves. They approach the $3R$ at high temperatures, but at low temperatures the classical prediction does not seem to work.

(b) The sample and the reference have the same rate of change in temperature $dT_{\text{ref}}/dt = dT_{\text{sample}}/dt = dT/dt$. The heat that is supplied to each is determined by the specific heat and dT :

$$I_{\text{ref}}^2 R = \frac{dQ_{\text{ref}}}{dt} = C_{\text{ref}} \frac{dT}{dt} \quad (30)$$

$$I_{\text{samp}}^2 R = \frac{dQ_{\text{samp}}}{dt} = C_{\text{samp}} \frac{dT}{dt} \quad (31)$$

So

$$\frac{I_{\text{ref}}}{I_{\text{samp}}} = \sqrt{\frac{C_{\text{ref}}}{C_{\text{samp}}}} \simeq \sqrt{\frac{0.9}{0.18}} \simeq 2.2 \quad (32)$$

Problem 4. The generating function trick

Consider integrals of the form

$$I_n = \int_0^\infty e^{-x} x^n dx \quad (33)$$

We will evaluate this by exploiting a simple trick, which occurs throughout statistical mechanics. I will call this the generating function trick. Generalize the integral by inserting a parameter β

$$I_n(\beta) = \int_0^\infty e^{-\beta x} x^n dx \quad (34)$$

(a) Without doing any integrals, show that

$$I_1(\beta) = -\frac{\partial I_0(\beta)}{\partial \beta} \quad (35)$$

Show more generally that

$$I_n(\beta) = \left(-\frac{\partial}{\partial \beta}\right)^n I_0(\beta) \quad (36)$$

We say that $I_0(\beta)$ “generates” the other integrals by differentiation.

(b) Compute $I_0(\beta)$ and show that

$$I_n(\beta) = \frac{1}{\beta} \left(\frac{n!}{\beta^n}\right) \quad (37)$$

Setting $\beta = 1$, we have established that

$$\boxed{I_n = \int_0^\infty e^{-x} x^n dx = n!} \quad (38)$$

(a) We only need to differentiate under the integral

$$-\frac{\partial}{\partial \beta} \int_0^\infty dx e^{-\beta x} = \int_0^\infty dx \left(-\frac{\partial e^{-\beta x}}{\partial \beta}\right) = \int_0^\infty dx e^{-\beta x} x = I_1 \quad (39)$$

So

$$I_1(\beta) = -\frac{\partial I_0(\beta)}{\partial \beta} \quad (40)$$

The trick repeats itself

$$\left(-\frac{\partial}{\partial \beta}\right)^n e^{-\beta x} = e^{-\beta x} x^n \quad (41)$$

So

$$I_n(\beta) = \left(-\frac{\partial}{\partial \beta}\right)^n I_0(\beta) \quad (42)$$

(b) We have

$$I_0 = \int_0^\infty e^{-\beta x} n \, dx = \frac{1}{\beta} \quad (43)$$

Differentiating once

$$I_1 = \left(-\frac{\partial}{\partial \beta} \right) \frac{1}{\beta} = \frac{1}{\beta^2} \quad (44)$$

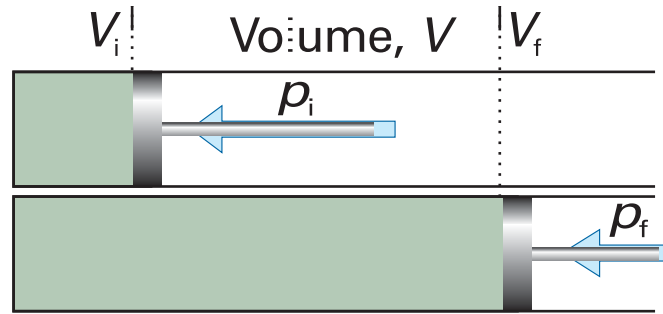
Differentiating 2 times give

$$I_2 = \left(-\frac{\partial}{\partial \beta} \right)^2 \frac{1}{\beta} = \frac{1}{\beta} \frac{2}{\beta^2} \quad (45)$$

The process repeats leading to the answers quoted in the text.

Problem 5. Adiabatic Expansion

(Optional) Optional problems should *not* be turned in. In an adiabatic expansion of an ideal gas with constant specific heat C_V , the gas in a cylinder exchanges no heat with its environment. This is often a very good idealization when the motion is relatively rapid. Consider the adiabatic expansion from initial volume V_i to final volume V_f .



The temperature changes from T_i to T_f and the pressure changes from p_i to p_f . Use the first law, and properties of specific heats to show that

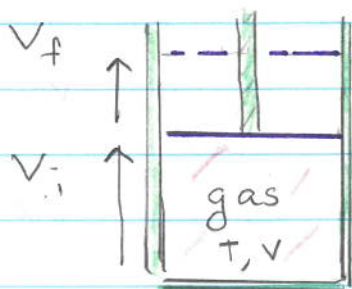
$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \quad \text{and} \quad p_i V_i^{\gamma} = p_f V_f^{\gamma} \quad (46)$$

Here $\gamma = C_p/C_v$. If you get stuck you may look in the lecture notes.

Adiabatic Expansion of Ideal Gas @ Constant C_v

- We will consider a ^{ideal} gas with constant specific heat $C_v = \text{const}$, and, $C_p = C_v + Nk_B$, is also constant.
- In an adiabatic expansion we do not allow heat to flow into the cylinder, $dQ = 0$.
- Adiabatic expansions are much more common in practice since if the expansion is relatively quick, there isn't time for heat exchange.

Temperature drops as gas expands



← thermally insulated walls, or just do the expansion fast enough (but not too fast) that no heat can be exchanged

$$dQ = 0$$

$$dU = dW \quad (1)$$

$$\text{Use } dW = p dV$$

$$C_v dT = -p dV$$

(2) use ideal gas $dU = C_v dT + \left(\frac{\partial U}{\partial V} \right)_T dV$
relation; ↑
ideal gas

$$C_v dT = - \frac{Nk_B T}{V} dV \quad (3) \quad \text{Use ideal gas EOS.}$$

- So we can integrate this assuming constant specific heat

$$\frac{dT}{T} = - \frac{Nk_B}{C_V} \frac{dV}{V}$$

$$C_P = C_V + Nk_B$$

$$\gamma \equiv \frac{C_P}{C_V} = 1 + \frac{Nk_B}{C_V}$$

$$\frac{dT}{T} = - (\gamma - 1) \frac{dV}{V}$$

- Integrating both sides $\ln \frac{T_f}{T_i} = - (\gamma - 1) \ln \frac{V_f}{V_i}$ or

$$\boxed{T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}} \quad \text{or} \quad TV^{\gamma-1} = \text{const}$$

So since $pV \propto T$ we find

$$\boxed{p_i V_i^{\gamma} = p_f V_f^{\gamma}} \quad \text{or} \quad pV^{\gamma} = \text{const}$$

Problem 6. Energy Derivatives

(Optional) The volume expansion coefficient is β_p describes how much a substance expands upon heating at constant pressure.

$$\beta_p \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (47)$$

Strictly β_p is the percent change in volume dV/V per dT . Use the First Law to show that

$$\left(\frac{\partial U}{\partial V} \right)_T = \frac{C_p - C_v}{V\beta_p} - p \quad (48)$$

Is the result consistent for an ideal gas? Explain why or why not.

Solution:

$$dU = \delta Q - \delta W_{\text{out}} \quad (49)$$

We use

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad (50)$$

$$= C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad (51)$$

and

$$\delta W_{\text{out}} = p dV \quad (52)$$

So generally we have

$$C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV = \delta Q - p dV \quad (53)$$

This is true for any path in the (T, V) plane. Now we consider path in the (T, V) plane with fixed pressure. This means that dT and dV are related to each other. For instance, if we are talking an ideal gas then $P = NkT/V$ and

$$dP = 0 = \frac{Nk_B}{V} dT_p - \frac{Nk}{V^2} dV_p \quad (54)$$

I like to put a “subscript p ” to indicate that we are indicating a small change (or a small amount) on a specific path where $P(T, V)$ is constant. Thus

$$C_V dT_p + \left(\frac{\partial U}{\partial V} \right)_T dV_p = \delta Q_p - p dV_p \quad (55)$$

dividing by dT_p we get

$$C_V + \left(\frac{\partial U}{\partial V} \right)_T \frac{dV_p}{dT_p} = \frac{\delta Q_p}{dT_p} - p \frac{dV_p}{dT_p} \quad (56)$$

Then we recognize that

$$\frac{\delta Q_p}{dT_p} = C_p \quad (57)$$

by definition. We recognize that that the derivative of V with respect to T with P held fixed is a partial derivative:

$$\frac{dV_p}{dT_p} = \left(\frac{\partial V}{\partial T} \right)_P = V \beta_p \quad (58)$$

So

$$C_V + \left(\frac{\partial U}{\partial V} \right)_T V \beta_p = C_p - p V \beta_p \quad (59)$$

Solving for the $\partial U / \partial V$ we find the answer quoted in the text.

We note that for an ideal gas with $V = NkT/p$

$$\beta_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{T} \quad (60)$$

We also note that

$$C_p = C_V + Nk_B \quad (61)$$

So

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{Nk_B}{V^{\frac{1}{T}}} - p = 0 \quad (62)$$

as expected for an ideal gas.