Thermodynamics. Problems. Sheet 1.

Solutions of the problems.

1. Classify each property as extensive or intensive: a) temperature; b) mass; c) density; d) electric field intensity; e) coefficient of thermal expansion; f) refractive index.

   Mass is extensive; the rest, intensive.

   Note: Density is the ratio of two extensive quantities, therefore a 'specific' variable.

2. Identify whether the following systems are open, closed, or isolated: a) coffee in a high-quality thermos; b) gasoline in the tank of a running car; c) mercury in a mercury thermometer; d) a plant in a greenhouse.

   a) isolated; b) open; c) closed; d) open.

   Note: It is important to define the system by defining the boundaries of the system. Note also that in the real world no system can be perfectly isolated; therefore, the classification of a system would depend on the "observation time".

3. A constant-volume gas thermometer is placed in contact with a system of unknown temperature and then in contact with water at its triple point (273.16 K). The mercury column reaches a height of -10.7 and -15.5 cm respectively. What is the system temperature? The barometric pressure is 0.980 bar, and the thermometer contains hydrogen. The density of mercury is 13.546 g cm^{-3}.

   We assume the gas to behave as an ideal gas (since no more information is available). Under this assumption, and since the gas volume V and the number of moles N are constant in the gas thermometer, then, after applying the ideal gas law $PV = NRT$, we have that P/T = constant. Hence, the unknown temperature T is given by

   $$T = T_{TP} \cdot P/P_{TP}$$

   where subscript 'TP' stands for 'triple point'. The pressures are the sum of the barometric pressure P_a plus the mercury column pressure; so:

   $$P = P_a + \rho g h$$

   $$P_{TP} = P_a + \rho g h_{TP}$$

   where

$$P_a = 0.980 \text{ bar} = 98000 \text{ Pa}$$

$$\rho = 13.546 \text{ g/cm}^3 = 13546 \text{ kg/m}^3$$

$$g = 9.8 \text{ m/s}^2,$$

$$h = \text{-10.7 cm} = \text{-0.107 m,}$$

$$h_{TP} = \text{-15.5 cm} = 0.155 \text{ m}$$

After substituting,

$$T(K) = T_{TP} \frac{P_a + \rho g h}{P_a + \rho g h_{TP}}$$

$$T(K) = 273.16 \frac{98000 + 13546 * 9.8 * (-0.107)}{98000 + 13546 * 9.8 * (-0.155)} = 273.16 \frac{8.380 \cdot 10^4}{7.742 \cdot 10^4}$$
$$= 296.2 \ K$$

Note: The standard acceleration of gravity is 9.80665 m/s^2, and here we have taken 9.8, as value, an underestimate of less than 1 part in 1000. Yet, gravity on Earth can vary within ~1%. Therefore, depending on the accuracy required, one might have to consider the local value of the acceleration of gravity.

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4. The Maxwellian distribution function of velocities of particles of a gas in equilibrium at a temperature T (constant), moving in one direction (x), has the form:

$$f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_x^2/(2k_B T)}$$

where m is the mass of a single particle, T is the absolute temperature, and k_B Boltzmann's constant. Use this to prove that the distribution function of *speeds* v of the particles (v being the modulus of the velocity vector) is:

$$f(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 e^{-mv^2/(2k_B T)}$$

Here, $f(v)dv$ is the probability of finding a particle with speed between v and $v + dv$.

Although the problem statement uses the same symbol for different functions, it is obvious that different things are meant.

Now, let us introduce another probability density function $g(\vec{v})$, such that $g(\vec{v})d^3v$ expresses the probability of finding a particle with velocity (vector) lying between $\vec{v}$ and $\vec{v} + \vec{dv}$, where $\vec{dv} = (dv_x, dv_y, dv_z)$ and $d^3v = dv_x dv_y dv_z$. This volume element in (v_x, v_y, v_z) space is expressed in Cartesian coordinates, but it could be written in other coordinate systems (e.g. spherical, as used later below).

Because the components of a particle's velocity are uncorrelated to one another (independent), the probability that the (x, y, z) components of its $\vec{v}$ will lie between (v_x, v_y, v_z) and $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$ is the product of the individual probabilities for each event. This can be expressed in Cartesian coordinates as

$$g(v_x, v_y, v_z)dv_x dv_y dv_z = f(v_x)dv_x \cdot f(v_y)dv_y \cdot f(v_z)dv_z$$

Therefore,

$$g(\vec{v}) = g(v_x, v_y, v_z) = f(v_x)f(v_y)f(v_z)$$

and, more explicitly,

$$g(\vec{v}) = g(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/(2k_B T)}$$

(Incidentally, note that we can easily integrate g over v_y and v_z to obtain $f(v_x)$.)

In this expression, $g(\vec{v})$ depends only on v, but its units are 1 over cube of speed. Therefore, to compute a probability it needs to be multiplied by a volume element (in velocity space, i.e., $d^3 v = dv_x dv_y dv_z$), not by dv. Regardless, we can express it as:

$$g(\vec{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/(2k_B T)}$$

Now, recalling from the problem statement that "$f(v)dv$ is the probability of finding a particle with speed between v and $v + dv$", to get $f(v)$ we can integrate $g(\vec{v})$ over a sphere of radius v centered around the origin ($\vec{v} = 0$).

$$f(v)dv = \iint_{\text{sphere } v} g(\vec{v}) \, d^3 v$$

Let us express the volume differential in this integral, $d^3 v$, in spherical coordinates ($d^3 v = (vd\theta)(v\sin\theta \, d\varphi)dv$), and let us integrate the polar (θ) and azimuthal (φ) angles (see figure):

$$f(v)dv = \iint_{\text{sphere } v} g(\vec{v}) \cdot (vd\theta)(v\sin\theta \, d\varphi)dv$$

$$= \left(\int_0^\pi \sin\theta \, d\theta\right)\left(\int_0^{2\pi} d\varphi\right)g(\vec{v})v^2 dv$$

Since

$$\int_0^\pi \sin\theta \, d\theta = (-\cos\pi) - (-\cos 0) = 2$$

$$\int_0^{2\pi} d\varphi = 2\pi$$

we finally get

$$f(v) = 4\pi v^2\, g(\vec{v})$$

where we have crossed out dv from both sides.

Finally, we can substitute the last expression above for $g(\vec{v})$:

$$f(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 e^{-mv^2/(2k_B T)}$$

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5. Starting with the suitable Maxwellian distribution function (see problem 4), show that:

5a. $< v >= \left(\frac{8k_B T}{\pi m}\right)^{1/2}$ (average gas particle speed)

5b. $< v^2 >^{1/2} = \left(\frac{3k_B T}{\pi m}\right)^{1/2}$ (root mean square of particle speeds)

5c. $< v_z >= 0$

5a.

To compute the average of the speed (modulus of the velocity vector), we need to solve $< v >= \int_0^\infty v\, f(v)\, dv$, where $f(v)$ is the distribution function for the speed:

$$f(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 e^{-mv^2/2k_B T}$$

Substituting and getting the constants out of the integral, leads to:

$$< v >= \int_0^\infty v\, f(v)\, dv = \int_0^\infty \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^3 e^{-mv^2/2k_B T}\, dv$$

$$= 4\pi \left(\frac{1}{\pi a^2}\right)^{3/2} \int_0^\infty v^3 e^{-v^2/a^2}\, dv$$

where, for convenience, we have defined a constant $a \equiv (2k_B T/m)^{1/2}$ (which, incidentally, has units of speed). Here we resort to a handbook of solved integrals and find that we can apply the following with $n = 1$:

$$\int_0^\infty x^{2n+1} e^{-x^2/a^2}\, dx = \frac{n!}{2} a^{2n+2}$$

Therefore,

$$\int_0^\infty v^3 e^{-v^2/a^2}\, dv = \frac{1}{2} a^4$$

and $< v >$ becomes

$$< v >= 4\pi \left(\frac{1}{\pi a^2}\right)^{3/2} \frac{1}{2} a^4 = \frac{2a}{\pi^{1/2}}$$

Substituting the definition of a back into this expression, we get the expression we wanted to prove (see above).

Note: The average value of the speeds is not a quantity which shows up much. The rms (root mean square) in the next problem (5b) is much more relevant.

5b.

For this problem, we proceed similarly as in 5a, to compute

$$< v^2 >^{1/2} = \left[\int_0^\infty v^2 f(v) \, dv\right]^{1/2}$$

First, we square it so we are computing the average of v^2.

$$< v^2 > = \int_0^\infty v^2 f(v) \, dv = \int_0^\infty \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^4 e^{-mv^2/2k_B T} \, dv$$

After using the definition of $a \equiv (2k_B T/m)^{1/2}$, we can write the integral as:

$$< v^2 > = 4\pi \left(\frac{1}{\pi a^2}\right)^{3/2} \int_0^\infty v^4 e^{-v^2/a^2} \, dv$$

To solve this integral we go to a handbook of solved integrals, where we find the appropriate integral; for example,

$$\int_0^\infty x^{2n} e^{-bx^2} \, dx = \frac{(2n-1)!!}{b^n 2^{n+1}} \left(\frac{\pi}{b}\right)^{1/2}$$

We take $x = v$, $n = 2$, and $b = a^{-2}$, and find that

$$\int_0^\infty v^4 e^{-v^2/a^2} \, dv = \frac{3a^5 \pi^{1/2}}{2^3}$$

where we used: 3!!=1·3=3. Inserting this result in the expression for $< v^2 >$ above leads to:

$$< v^2 > = 4\pi \left(\frac{1}{\pi a^2}\right)^{3/2} \frac{3a^5 \pi^{1/2}}{2^3} = \frac{3}{2} a^2$$

Finally, we substitute the definition of a (see earlier above) and take the square root:

$$< v^2 >^{1/2} = \left(\frac{3k_B T}{m}\right)^{1/2}$$

Note: If we already had the value of $< v_x^2 >$, which is $k_B T / m$ (obtained by integrating $v_x^2 f(v_x) dv_x$, also given in class), we could use that result to compute $< v^2 >^{1/2}$ directly:

$$< v^2 >^{\frac{1}{2}} = \left(< v_x^2 > + < v_y^2 > + < v_z^2 >\right)^{\frac{1}{2}}$$

$$= (3 < v_x^2 >)^{1/2} = \left(\frac{3k_B T}{m}\right)^{1/2}$$

5c.

To show that $< v_z >= 0$, we need to write that

$$< v_z >= \int_{-\infty}^{\infty} v_z f(v_z) dv_z$$

where

$$f(v_z) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_z^2/2k_B T}$$

Since the integrand of the integral changes sign at $v_z = 0$ and its absolute value is symmetric with respect to the $v_z = 0$ point, then we have that:

$$\int_{-\infty}^{0} v_z f(v_z) dv_z = - \int_{0}^{\infty} v_z f(v_z) dv_z \quad (< 0)$$

$$< v_z >= \int_{-\infty}^{0} v_z f(v_z) dv_z + \int_{0}^{\infty} v_z f(v_z) dv_z$$

$$= - \int_{0}^{\infty} v_z f(v_z) dv_z + \int_{0}^{\infty} v_z f(v_z) dv_z = 0$$

Note: This mathematical result is logical and expected based on purely physical arguments: The probability density at a particular speed is exactly the same as for minus that speed. (As many atoms move in one direction as in the other.) Therefore, the average of any component of the speed must be zero, reflecting that the gas as a whole is at rest.

6. Show mathematically that the combination of Boyle's and Charles' laws, lead to $PV = kNT$, where k is a constant. (P = pressure; V = volume; N = moles; T = absolute temperature.)

Boyle's law states: $PV = f(T, N)$

Charles' law states: $V/T = g(P, N)$

For these two expressions to hold true at the same time, it should be possible to separate the dependences of f and g on their variables like this:

$$PV = k(T) \cdot l(N)$$

$$V/T = h(P) \cdot j(N)$$

We choose one expression and transform it so that the LHS looks like in the other. For example, we can take the first expression and we multiply it times $1/(PT)$, to get:

$$\frac{V}{T} = \frac{l(N)}{P} \cdot \frac{k(T)}{T}$$

By comparing this to Charles' law, we conclude that

$$\frac{k(T)}{T} = 1$$

(Also, that $h(P) = 1/P$, and $l(N) = j(N)$. But we will not have to use these. Also note that if we had not factored out f into $k(T) \cdot l(N)$, we would arrive at this conclusion at the time of comparing the RHS of the expression for V/T with Charles' law.)

Therefore,

$$\frac{V}{T} = \frac{l(N)}{P}$$

Hence,

$$\frac{PV}{T} = l(N)$$

Un-hinted by the problem statement, to do further progress we actually need Physics: We need to recognize that V and N are extensive variables, thus proportional to each other (while P and T are intensive). With that we can conclude that

$$\frac{PV}{T} = kN$$

where k is a constant.

Note: Avogadro states that "*The same volume of different gases at the same pressure contain the same number of particles*". Since N is proportional to the number of

particles (as by N we mean the number of moles), Avogadro is saying that k in the above expression is *independent of the gas composition* (so long as it behaves as an ideal gas).

Note also we could have done this exercise by starting by Charles' law instead of Boyle's law. We'd do that by multiplying Charles' law by PT to get

$$PV = PT\, h(P) \cdot j(N)$$

By comparing to Boyle's law, we conclude that $P\, h(P) = 1$; namely, that, $h(P) = 1/P$.

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Another solution of this problem, by student David Diestre:

Take Charles' and solve for V and substitute into Boyle's law (or take Boyle's law, and solve for V. Then substitute into Charles' law.). We get:

$$PT = \frac{f(T,N)}{g(P,N)}$$

Since the two laws are the same equation of state, when substituting V we must get and identical expression of the kind: $1 = 1$. To get that, first, the dependences on the RHS must admit separation of variables (as expressed earlier in the problem), so that the dependence with N can "go away". And second, f must be linear with T and g must be inversely proportional to P. in other words, we must have that:

$$f(T,N) = T\, l(N)$$

$$g(P,N) = \frac{1}{P}\, l(N)$$

Therefore, substituting any of them above, yields

$$\frac{PV}{T} = l(N)$$

From this point, the problem continues as in the earlier solution.

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7. Show that the van der Waals equation of state is a cubic function of V. Discuss whether all the terms scale the same way with the extension (size) of the system.

Let us write the vdW equation:

$$P = \frac{NRT}{V - Nb} - a\left(\frac{N}{V}\right)^2$$

We need to get the volume out of the denominators, in order to get a polynomial of order 3 in V. Therefore, let us multiply the left and right sides by $V^2(V - Nb)$. At the same time let us divide by P:

$$V^2(V - Nb) = V^2 \frac{NRT}{P} - a\frac{N^2}{P}(V - Nb)$$

Grouping all terms at the left side into V power terms, we get the following equation:

$$V^3 - \left(Nb + \frac{NRT}{P}\right)V^2 + a\frac{N^2}{P}V - ab\frac{N^3}{P} = 0$$

The left-hand side is a cubic polynomial (or polynomial of degree 3).

Discussion: Each term scales as the cube of the size of the system, being proportional to V^3, NV^2, N^2V, and N^3 respectively. If we divided this equation by N^3, we would obtain a cubic equation for the molar volume $v \equiv V/N$:

$$v^3 - \left(b + \frac{RT}{P}\right)v^2 + \frac{a}{P}v - \frac{ab}{P} = 0$$

Additional comments: The solutions of this equations are the roots of the cubic polynomial. Since all the coefficients are real, there is at least one real root. (This is because for large absolute value of V the polynomial is dominated by the cubit term, and therefore, the polynomial must "cross" the abscissae axis at least at one point in varying from the variable V being negative to positive. Physically, V cannot be negative; therefore, the positiveness of at least one root must imply some constraint on the coefficients; which we will not develop.) Below the critical point there are three real solutions, and above it there is only one (the other two being imaginary).

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8. Find the expression for the second virial coefficient for a van der Waals gas.

The virial is the expansion of the pressure $P(v,T)$ in powers of the inverse of the molar volume $v = V/N$ (see class notes):

$$P(v,T) = \frac{RT}{v}\left(1 + A_2(T)\frac{1}{v} + A_3(T)\frac{1}{v^2} + \cdots\right)$$

So,

$$\frac{Pv}{RT} = 1 + A_2(T)\frac{1}{v} + A_3(T)\frac{1}{v^2} + \cdots$$

To express the van der Waals equation of state in the virial form, we start with the van der Waals equation:

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

Therefore,

$$\frac{Pv}{RT} = \frac{v}{v - b} - \frac{a}{vRT}$$

Let us expand the right-hand side as a Taylor series of powers of $1/v$. The right addend is already a term proportional to $1/v$. Therefore, we need to expand the left addend as a Taylor series. Note that b is akin to the volume occupied by a single molecule, whereas v is the volume occupied by a mole of gas molecules. Therefore, far from the critical volume, $v \gg b$, or $b/v \ll 1$. The left addend can be written as;

$$\frac{v}{v - b} = \frac{1}{1 - b/v}$$

We can expand this as Taylor series, to the first order,

$$\frac{v}{v - b} = \frac{1}{1 - b/v} \approx 1 + \frac{b}{v}$$

Therefore, to first order,

$$\frac{Pv}{RT} = \frac{v}{v - b} - \frac{a}{vRT} \approx 1 + \frac{b}{v} - \frac{a}{vRT} = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{v}$$

where, the second virial coefficient equals:

$$A_2(T) = b - \frac{a}{RT}$$

9. Find the Boyle temperature of a van der Waals gas.

We start with the second virial coefficient for a van der Waals gas (see the previous problem), and equate to zero and solve for $A_2 = 0$ when $T = T_B$:

$$A_2(T_B) = b - \frac{a}{RT_B} = 0$$

Therefore, the Boyle temperature of a van der Waals gas is:

$$T_B = \frac{a}{Rb}$$