Selected problems from Schroeder, An introduction to Thermal physics

Problem 1.16. The exponential atmosphere.

(a) Consider a horizontal slab of air whose thickness (height) is dz. If this slab is at rest the pressure holding it up from below must balance both the pressure from above and the weight of the slab. Use this fact to find an expression for dP/dz, the variation of pressure with altitude, in terms of the density of air.

(b) Use the ideal gas law to write the density of air in terms of pressure, temperature, and the average mass m of the air molecules. (The information needed to calculatge m is given in Problem 1.14.) Show, then, that the pressure obeys the differential equation

$$\frac{dP}{dz} = -\frac{mg}{k_B T} P,$$

called the **barometric equation**.

(c) Assuming that the temperature of the atmosphere is independent of height (not a great assumption, but not terrible either), solve the barometric equation to obtain the pressure as a function of height:

$$P(z) = P(0) \exp\left(-\frac{mgz}{k_B T}\right).$$

Show also that the density obeys a similar equation.

Problem 1.21. During a hailstorm, hailstones with an average mass of 2 g and a speed of 15 m/s strike a window pane at a 45° angle. The area of the window is 0.5 m^2 and the hailstones hit it at a rate of 30 per second. What average pressure do they exert on the window? How does this compare to the pressure of the atmosphere?

Problem 1.31a–d. Imagine some helium in a cylinder with an initial volume of 1 liter and an initial pressure of 1 atm. Somehow the helium is made to expand to a final volume of 3 liters, in such a way that its pressure rises in direct proportion to its volume. (Yes, this is odd!)

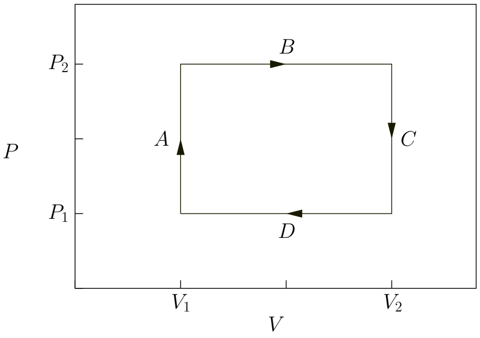
(a) Sketch a graph of pressure vs. volume for this process.

(b) Calculate the work done on the gas during this process, assuming that there are no "other" types of work being done.

(c) Calculate the change in the helium's energy content during this process.

(d) Calculate the amount of heat added to or removed from the helium during this process.

Problem 1.34. An ideal diatomic gas, in a cylinder with a movable piston undergoes the rectangular cyclic process shown below. Assume that the temperature is always such that rotational degrees of freedom are active, but vibrational modes are "frozen out". Also assume that the only type of work done on the gas is quasistatic compression-expansion work.



(a) For each of the four steps A through D, compute the work done on the gas, the heat added to the gas, and the change in the energy content of the gas. Express all answers in terms of P_1, P_2, V_1, and V_2. (Hint: Compute ΔU before Q, using the ideal gas law and the equipartition theorem.)

(b) Describe in words what is physically being done during each of the four steps; for example, during step A, heat is added to the gas (from an external flame of something) while the piston is held fixed.

(c) Compute the net work done on the gas, the net heat added to the gas, and the net change in the energy of the gas during the entire cycle. Are the results as you expected? Explain briefly.

Problem 1.37. In a Diesel engine, atomspheric air is quickly compressed to about 1/20 of its original volume. Estimate the temperature of the air after compression, and explain why a Diesel engine does not require spark plugs.

Problem 1.49. Consider the combustion of one mole of H_2 with 1/2 mole of O_2 under standard conditions, as discussed on p. 35 in the textbook. How much of the heat energy produced comes from a decrease in the internal energy of the system, and how much comes from work done by the collapsing atmosphere? (Treat the volume of the liquid water as negligable.)

Problem 2.17 Use the methods of p. 63–64 to derive a formula, similar to Eq. 2.21, for the multiplicity of an Einstein solid in the "low-temperature" limit, $q \ll N$.

Problem 2.24 For a single *large* two-state paramagnet, the multiplicity function is very sharply peaked about $N_\uparrow = N/2$.

(a) Use Stirling's approximation to estimate the height of the peak in the multiplicity function.

(b) Use the methods of this section to derive a formula for the multiplicity function in the vicinity of the peak, in terms of $x \equiv N_\uparrow - N/2$. Check that your formula agrees with your answer to part (a) when $x = 0$.

(c) How wide is the peak in the multiplicity function?

Problem 2.25 The mathematics of the previous problem can also be applied to a one-dimensional random walk: a journey consisting of N steps, all the same size, each chosen randomly to be either forward or backward. (The usual mental image is that of a drunk stumbling along an alley.)

(a) Where are you *most* likely to find yourself, after the end of a long random walk?

(b) Suppose you take a random walk of 10,000 steps (say each half a meter long). About how far from your starting point would you expect to be at the end?

Problem 2.26 Consider an ideal monatomic gas that lives in a two-dimensional universe ("flatland"), occupying an area A instead of a volume V. By following the same logic as above, find a formula for the multiplicity of the gas, analogous to Eq. 2.40.

Problem 2.32 Find an expression for the entropy of the two-dimensional ideal gas considered in Problem 2.26. Express your result in terms of U, A, and N.

Problem 2.34 Show that during the quasistatic isothermal expansion of a monatomic ideal gas, the change in entropy is related to the heat input Q by the simple formula

$$\Delta S = \frac{Q}{T}.$$

Problem 2.35 According to the Sackur-Tetrode equation, the entropy of a monatomic ideal gas can become *negative* when its temperature (and hence its energy) is sufficiently low. Of course this is absurd, so the Sackur-Tetrode equation must be invalid at very low temperatures. Suppose you start with a sample of helium at room temperature and atmospheric pressure, then lower the temperature holding the density fixed. Pretend that the helium remains a gas and does not liquefy. Below what temperature would the Sackur-Tetrode equation predict that S is negative?

Problem 2.37 Using the same method as in the text, calculate the entropy of mixing for a system of two monatomic ideal gases, A and B, whose relative proportion is arbitrary. Let N be the *total* number of molecules and let x be the fraction of these that are of species B. You should find

$$\Delta S_{\text{mixing}} = -Nk_B[x \ln x + (1-x)\ln(1-x)].$$

Problem 3.5 Starting with the result of Problem 2.17, find a formula for the temperature of an Einstein solid in the limit $q \ll N$. Solve for the energy as a function of temperature to obtain $U = N\epsilon e^{-\epsilon/k_B T}$, where ϵ is the size of an energy unit.

Problem 3.6 In a system with only quadratic degrees of freedom in the high-temperature limit, i.e. where the number of energy units is much larger than the number of degrees of freedom, the multiplicity is proportional to $U^{Nf/2}$, where Nf is the total number of degrees of freedom. Find an expression for the energy of such a system in terms of its temperature and comment on the result. How can you tell that this formula for Ω cannot be valid when the total energy is very small?

Problem 3.8 Starting with the result of Problem 3.5, calculate the heat capacity of an Einstein solid in the low-temperature limit. Sketch the predicted heat capacity as a function of temperature. (Note: Measurements of heat capacities of actual solids at low temperatures do not confirm the prediction that you will make in this problem.)

Problem 3.10 An ice cube (mass 30g) at 0°C is left sitting on the kitchen table, where it gradually melts. The temperature in the kitchen is 25°C.

(a) Calculate the change in the entropy of the ice cube as it melts into water at 0°C. (Don't worry about the fact that the volume changes somewhat.)

(b) Calculate the change in the entropy of the water (from the melted ice) as its temperature rises from 0°C to 25°C.

(c) Calculate the change in the entropy of the kitchen as it gives up heat to the melting ice/water

(d) Calculate the net change in the entropy of the universe during this process. Is the net change positive, negative, or zero? Is this what you would expect?

Problem 3.25a–d In Problem 2.18 it is found that the multiplicity of an Einstein solid with N oscillators and q energy units is approximately

$$\Omega(N, q) \approx \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N .$$

(a) Starting with this formula, find an expression for the entropy of an Einstein solid as a function of N and q. Explain why the factors omitted from the formula have no effect on the entropy when N and q are large.

(b) Use the result of part (a) to calculate the temperature of an Einstein solid as a function of its energy. (The energy is $U = q\epsilon$, where ϵ is a constant.) Be sure to simplify your result as much as possible.

(c) Invert the relation you found in part (b) to find the energy as a function of temperature, then differentiate to find a formula for the heat capacity.

(d) Show that in the limit $T \to \infty$, the heat capacity is $C = Nk_B$. (Hint: when x is very small $e^x \approx 1 + x$.) Is this the result you would expect? Explain.

Problem 3.31 Experimental measurements of heat capacities are often represented in reference works as empirical formulas. For graphite, a formula that works well over a fairly wide range of temperatures is (for one mole)

$$C_P = a + bT - c/T^2,$$

where $a = 16.86$ J/K, $b = 4.77 \times 10^{-3}$ J/K^2, and $c = 8.54 \times 10^5$ JK. Suppose then that a mole of graphite is heated at constant pressure from 298 K to 500 K. Calculate the increase in its entropy during this process. Add on the tabulated value of $S(298 \text{ K})$ from the table of the book[1] to obtain $S(500 \text{ K})$.

Problem 3.36 Consider an Einstein solid for which both N and q are much greater than 1. Think of each oscillator as a separate "particle".

(a) Show that the chemical potential is

$$\mu = -k_B T \ln\left(\frac{N+q}{N}\right).$$

(b) discuss this result in the limits $N \gg q$ and $N \ll q$, concentrating on the question of how much S increases when another particle carrying no energy is added to the system. Does the formula make intuitive sense?

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[1] The table may also be found at the end of this document.

Problem 4.1 Recall Problem 1.34, which concerned an ideal diatomic gas taken around a rectangular cycle on a PV diagram. Suppose now that this system is used as a heat engine, to convert the heat added into mechanical work.

(a) Evaluate the efficiency of this engine for the case $V_2 = 3V_1$, $P_2 = 2P_1$.

(b) Calculate the efficiency of an "ideal" engine operating between the same temperature extremes.

Problem 4.5 Prove directly—by calculating the heat taken in and the heat expelled—that a Carnot engine using an ideal gas as the working substance has an efficiency of $1 - T_c/T_h$.

Problem 4.14 a–c A **heat pump** is an electrical device that heats a building by pumping heat in from the cold outside. In other words, it's the same as a refrigerator, but its purpose is to warm the hot reservoir rather than to cool the cold reservoir (even though it does both). Let us define the following standard symbols, all taken to be positive by convention:

T_h = temperature inside building,
T_c = temperature outside,
Q_h = heat pumped into building in 1 day,
Q_c = heat taken from outdoors in 1 day,
W = electrical energy used by heat pump in 1 day.

(a) Explain why the "coefficient of performance" (COP) for a heat pump should be defined as Q_h/W.

(b) What relation among Q_h, Q_c, and W is implied by energy conservation along? Will energy conservation permit the COP to be greater than 1?

(c) Use the second law of thermodynamics to derive an upper limit on the COP, in terms of the temperatures T_h and T_c alone.

Problem 4.18 Derive the following equation for the efficiency of the Otto cycle,

$$e = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}.$$

Problem 4.20 Derive a formula for the efficiency of the Diesel cycle, described in Fig. 4.6, in terms of the compression ratio V_1/V_2 and the cutoff ratio V_3/V_2. Show that for a given compression ratio, the Diesel cycle is less efficient than the Otto cycle. Evaluate the theoretical efficiency of a Diesel engine with a compression ratio of 18 and a cutoff ratio of 2.

Problem 4.21 The ingenious **Stirling engine** is a true heat engine that absorbs heat from an external source. See p. 133–134 for a description of its workings.

(a) Draw a PV diagram for this idealized Stirling cycle.

(b) Forget about the regenerator for the moment. Then, during step 2, the gas will give up heat to the cold reservoir instead of to the regenerator; during step 4 the gas will absorb heat from the hot reservoir. Calculate the efficiency of the engine in this case, assuming that the gas is ideal. Express your answer in terms of the temperature ratio T_c/T_h and the compression ratio (the ratio of the maximum and minimum volumes). Show that the effficiency is less than that of a Carnot engine operating between the same temperatures. Work out a numerical example.

(c) Now put the regenerator back. Argue that, if it works perfectly, the efficiency of a Stirling engine is the same as that of a Carnot engine.

(d) Discuss, in some detail, the various advantages and disadvantages of a Stirling engine, compared to other engines.

Problem 5.5 Consider a fuel cell that uses methane ("nattural gas") as fuel. The reaction is

$$\mathrm{CH_4}{+}2\mathrm{O_2} \longrightarrow 2\mathrm{H_2O} + \mathrm{CO_2}.$$

(a) Use the data at the back of this book to determine the values of ΔH and ΔG for this reaction, for one mole of methane. assume that the reaction takes place at room temperature and atmospheric pressure.

(b) Assuming ideal performance, how much electrical work can you get out of the cell, for each mole of methande fuel?

(c) How much waste heat is produced, for each mole of methane fuel?

(d) The steps of this reaction are

$$\begin{aligned}&\text{at } - \text{ electrode: } CH_4{+}2H_2O \longrightarrow CO_2 + 8H^+ + 8e^-,\\ &\text{at } + \text{ electrode: } 2O_2 + 8H^+ + 8e^- \longrightarrow 4H_2O.\end{aligned}$$

what is the voltage of the cell?

Problem 5.11 Suppose that a hydrogen fuel cell, as described in the text, is to be operated at 75°C and atmospheric pressure. We wish to estimate the maximum electrical work done by the cell, using only the room-temperature data at the back of this book. It is convenient to first establish a zero-point for each off the three substances, H_2, O_2, and H_2O. Let us take G for both H_2 and O_2 to be zero at 25°C, so that G for a mole of H_2O is -237 kJ at 25°C.

(a) Using these conventions, estimate the Gibbs free energy of a mole of H_2 at 75°C. Repeat for O_2, and H_2O.

(b) Using the results of part (a), calculte the maximum electrical work done by the cell at 75°C, for one mole of hydrogen fuel. Compare to the ideal performance of the cell at 25°C.

Problem 5.23a–c By subtracting μN from U, H, F, or G, one can obtain four new thermodynamic potentials. Of the four, the most useful is the **grand free energy** (or **grand potential**),

$$\Phi \equiv U - TS - \mu N.$$

(a) Derive the thermodynamic identity for Φ, and the related formulas for the partial derivatives of Φ with respect to T, V, and μ.

(b) Prove that, for a system in thermal and diffusive equilibrium (with a reservoir that can supply both energy and particles), Φ tends to decrease.

(c) Prove that $\Phi = -PV$.

Problem 5.35 The Clausius-Clapeyron relation 5.47 is a differential equation that can, in principle, be solved to find the shape of the entire phase-boundary curve. To solve it, however, you have to know how both L and ΔV depend on temperature and pressure. Often, over a reasonably small section of the curve, you can take L to be constant. Moreover, if one of the phases is a gas, you can usually neglect the volume of the condensed phase and just take ΔV to be the volume of the gas, expressed in terms of temperature and pressure using the ideal gas law. Making all these assumptions, solve the differential equation explicitly to obtain the folowing formula for the phase boundary curve:

$$P = \text{const} \times e^{-L/RT}.$$

This result is called the **vapor pressure equation**. Caution: Be sure to use this formula only when all the assumptions just listed are valid.

Problem 5.47

Problem 5.48 As can be seen in Fig. 5.20, the critical point is the unique point on the original van der Waals isotherms (before the Maxwell construction) where both the first and second derivaties of P with respect to V (at fixed T) are zero. Use this fact to show that

$$V_c = 3Nb, \quad P_c = \frac{1}{27}\frac{a}{b^2}, \quad \text{and} \quad k_B T_c = \frac{8}{27}\frac{a}{b}.$$

Problem 5.51 When plotting graphs and performing numerical calculations, it is convenient to work in terms of **reduced variables**,

$$t = T/T_c, \quad p = P/P_c, \quad v = V/V_c.$$

Rewrite the van der Waals equation in terms of these variables, and notice that the constants a and b disappear.

Problem 1.69 Imagine a narrow pipe, filled with fluid, in which the concentration of a certain type of molecule varies only along the length of the pipe (in the x direction). By considering the flux of these particles from both directions into a short segment Δx, derive **Fick's second law**,

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2}.$$

Noting the similarity to the heat equation derived in Problem 1.62, discuss the implications of this equation in some detail.

Problem 1.70 In analogy with the thermal conductivity, derive an approximate formula for the diffusion coefficient of an ideal gas in terms of the mean free path and the average thermal speed. Evaluate your formula numerically for air at room temperature and atmospheric pressure, and compare to the experimental value quoted in the text. How doew D depend on T, at fixed pressure?

Thermodynamic Properties of Selected Substances

All of the values in this table are for one mole of material at 298 K and 1 bar. Following the chemical formula is the form of the substance, either solid (s), liquid (l), gas (g), or aqueous solution (aq). When there is more than one common solid form, the mineral name or crystal structure is indicated. Data for aqueous solutions are at a standard concentration of 1 mole per kilogram water. The enthalpy and Gibbs free energy of formation, $\Delta_f H$ and $\Delta_f G$, represent the changes in H and G upon forming one mole of the material starting with elements in their most stable pure states (e.g., C (graphite), O_2 (g), etc.). To obtain the value of ΔH or ΔG for another reaction, subtract Δ_f of the reactants from Δ_f of the products. For ions in solution there is an ambiguity in dividing thermodynamic quantities between the positive and negative ions; by convention, H^+ is assigned the value zero and all others are chosen to be consistent with this value. Data from Atkins (1998), Lide (1994), and Anderson (1996). Please note that, while these data are sufficiently accurate and consistent for the examples and problems in this textbook, not all of the digits shown are necessarily significant; for research purposes you should always consult original literature to determine experimental uncertainties.

Substance (form)	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)	C_P (J/K)	V (cm^3)
Al (s)	0	0	28.33	24.35	9.99
Al_2SiO_5 (kyanite)	−2594.29	−2443.88	83.81	121.71	44.09
Al_2SiO_5 (andalusite)	−2590.27	−2442.66	93.22	122.72	51.53
Al_2SiO_5 (sillimanite)	−2587.76	−2440.99	96.11	124.52	49.90
Ar (g)	0	0	154.84	20.79	
C (graphite)	0	0	5.74	8.53	5.30
C (diamond)	1.895	2.900	2.38	6.11	3.42
CH_4 (g)	−74.81	−50.72	186.26	35.31	
C_2H_6 (g)	−84.68	−32.82	229.60	52.63	
C_3H_8 (g)	−103.85	−23.49	269.91	73.5	
C_2H_5OH (l)	−277.69	−174.78	160.7	111.46	58.4
$C_6H_{12}O_6$ (glucose)	−1268	−910	212	115	
CO (g)	−110.53	−137.17	197.67	29.14	
CO_2 (g)	−393.51	−394.36	213.74	37.11	
H_2CO_3 (aq)	−699.65	−623.08	187.4		
HCO_3^- (aq)	−691.99	−586.77	91.2		
Ca^{2+} (aq)	−542.83	−553.58	−53.1		
$CaCO_3$ (calcite)	−1206.9	−1128.8	92.9	81.88	36.93
$CaCO_3$ (aragonite)	−1207.1	−1127.8	88.7	81.25	34.15
$CaCl_2$ (s)	−795.8	−748.1	104.6	72.59	51.6
Cl_2 (g)	0	0	223.07	33.91	
Cl^- (aq)	−167.16	−131.23	56.5	−136.4	17.3
Cu (s)	0	0	33.150	24.44	7.12
Fe (s)	0	0	27.28	25.10	7.11

Substance (form)	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)	C_P (J/K)	V (cm^3)
H_2 (g)	0	0	130.68	28.82	
H (g)	217.97	203.25	114.71	20.78	
H^+ (aq)	0	0	0	0	
H_2O (l)	−285.83	−237.13	69.91	75.29	18.068
H_2O (g)	−241.82	−228.57	188.83	33.58	
He (g)	0	0	126.15	20.79	
Hg (l)	0	0	76.02	27.98	14.81
N_2 (g)	0	0	191.61	29.12	
NH_3 (g)	−46.11	−16.45	192.45	35.06	
Na^+ (aq)	−240.12	−261.91	59.0	46.4	−1.2
NaCl (s)	−411.15	−384.14	72.13	50.50	27.01
$NaAlSi_3O_8$ (albite)	−3935.1	−3711.5	207.40	205.10	100.07
$NaAlSi_2O_6$ (jadeite)	−3030.9	−2852.1	133.5	160.0	60.40
Ne (g)	0	0	146.33	20.79	
O_2 (g)	0	0	205.14	29.38	
O_2 (aq)	−11.7	16.4	110.9		
OH^- (aq)	−229.99	−157.24	−10.75	−148.5	
Pb (s)	0	0	64.81	26.44	18.3
PbO_2 (s)	−277.4	−217.33	68.6	64.64	
$PbSO_4$ (s)	−920.0	−813.0	148.5	103.2	
SO_4^{2-} (aq)	−909.27	−744.53	20.1	−293	
HSO_4^- (aq)	−887.34	−755.91	131.8	−84	
SiO_2 (α quartz)	−910.94	−856.64	41.84	44.43	22.69
H_4SiO_4 (aq)	−1449.36	−1307.67	215.13	468.98	