Homework 9

Due by 10pm on Wednesday, November 18th, 2020

Reading: Schroeder Ch. 6, Secs. 6.1-5. Class notes.

1. Measured heat capacities of solids and liquids are almost always at constant pressure, not constant volume. To see why, estimate the pressure needed to keep V fixed as T increases, as follows.

(a) First imagine slightly increasing the temperature of a material at constant pressure. Write the change in volume, dV_1, in terms of dT and the thermal expansion coefficient β introduced in Problem 3 of Hw1.

(b) Now imagine slightly compressing the material, holding its temperature fixed. Write the change in volume for *this* process, dV_2, in terms of dP and the **isothermal compressibility** κ_T, defined as

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

(This is the reciprocal of the isothermal bulk modulus defined in Problem 4 of Hw2.)

(c) Finally, imagine that you compress the material just enough in part (b) to offset the expansion in part (a). Then the ratio of dP to dT is equal to $(\partial P/\partial T)_V$, since there is no net change in volume. Express this partial derivative in terms of β and κ_T. Then express it more abstractly in terms of the partial derivatives used to define β and κ_T. For the second expression you should obtain

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}.$$

This result is actually a purely mathematical relation, true for any three quantities that are related in such a way that any two determine the third.

(d) Compute β, κ_T, and $(\partial P/\partial T)_V$ for an ideal gas, and check that the three expressions satisfy the identity you found in part (c).

(e) For water at 25°C, $\beta = 2.57 \times 10^{-4}$ K^{-1} and $\kappa_T = 4.52 \times 10^{-10}$ Pa^{-1}. Suppose you increase the temperature of some water from 20°C to 30°C. How much pressure must you apply to prevent it from expanding? Repeat the calculation for mercury, for which (at 25°C) $\beta = 1.81 \times 10^{-4}$ K^{-1} and $\kappa_T = 4.04 \times 10^{-11}$ Pa^{-1}. Given the choice, would you rather measure the heat capacities of these substances at constant V or at constant P?

2. Use one of the Maxwell relations you derived and the third law of thermodynamics to prove that the thermal expansion coefficient β must be zero at $T = 0$. (If you don't remember β return to problem 3 of Hw1.)

You've now accumulated many results on partial derivatives, adding in a little more partial-derivative trickery, you can derive a completely general relation between C_P and C_V. The calculation has several steps, so we'll break it up between problems 3 and 4.

3. (a) Use the original thermodynamic identity to derive the heat capacity formula

$$C_V = T \left(\partial S / \partial T \right)_V,$$

which is occasionally more convenient than the more familiar expression in terms of U. Then derive a similar formula for C_P, by first writing dH in terms of dS and dP.

(b) With the heat capacity expressions from part (a) in mind, first consider S to be a function of T and V. Expand dS in terms of the partial derivatives $(\partial S / \partial T)_V$ and $(\partial S / \partial V)_T$. Note that one of these derivatives is related to C_V.

(c) To bring in C_P, consider V to be a function of T and P and expand dV in terms of partial derivatives in a similar way. Plug this expression for dV into the result of part (b), then set $dP = 0$ and note that you have derived a nontrivial expression for $(\partial S / \partial T)_P$. This derivative is related to C_P, so you now have a formula for the difference $C_P - C_V$.

4. (a) Write the remaining partial derivatives in terms of measurable quantities using a Maxwell relation and the result of Problem 1 above. Your final result should be

$$C_P = C_V + \frac{TV\beta^2}{\kappa_T}.$$

(b) Check that this formula gives the correct value of $C_P - C_V$ for an ideal gas.

(c) Use this formula to argue that C_P cannot be less than C_V.

(d) Use the data in Problem 1 above to evaluate $C_P - C_V$ for water and for mercury at room temperature. By what percentage do the two heat capacities differ?

(e) Schroeder's Figure 1.14 shows measured values of C_P for three elemental solids, compared to predicted values of C_V. It turns out that a graph of β vs. T for a solid has same general appearance as a graph of heat capacity. Use this fact to explain why C_P and C_V agree at low temperatures but diverge in the way they do at higher temperatures.

5. The density of ice is 917 kg/m³. (a) Use the Clausius-Clapeyron relation to explain why the slope of the phase boundary between water and ice is negative.

(b) How much pressure would you have to put on an ice cube to make it melt at $-1°$C?

(c) Approximately how deep under a glacier would you have to be before the weight of the ice above gives the pressure you found in part (b)? (Note that the pressure can be greater at some locations, as where the glacier flows over a protruding rock.)

(d) Make a rough estimate of the pressure under the blade of an ice skate, and calculate the melting temperature of ice at this pressure. Some authors have claimed that skaters glide with very little friction because the increased pressure under the blade melts the ice to create a thin layer of water. What do you think of this explanation?

6. (a) As you can see from Schroeder's Figure 5.20, the critical point is the unique point on the original van der Walls isotherms (before the Maxwell construction) where both the first and second derivatives of P with respect to V (at fixed T) are zero. Use this fact to show that

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

(b) Use the result of the previous part and the approximate values of a and b given on p181 of Schroeder's book to estimate T_c, P_c, and V_c/N for N_2, H_2O, and He. (Tabulated values of a and b are often determined by working backward from the measured critical temperature and pressure.)