

Homework 3

Hand in

1. By combining the first law, $du = \delta w + \delta Q$, with $\delta Q = TdS$ and $\delta W = -PdV$, and thinking of U as a function of T and V, so that

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

we derived in class

$$TdS = C_v dT + T \left(\frac{\partial P}{\partial T} \Big|_V \right) dV. \quad (1)$$

Now think of U as a function of T and P and derive the following equation:

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \Big|_P \right) dP. \quad (2)$$

Along the way, it will be useful to think of V also being a function of T and P. In addition, you'll need to show that

$$c_p = \frac{\partial U}{\partial T} \Big|_P + P \frac{\partial V}{\partial T} \Big|_P.$$

2. Now derive (2) in the following much simpler way: think of the entropy S as a function of T and P, argue that c_p is equal to an appropriate partial derivative of S, and use the Maxwell chart.

(continued)

Don't hand in (but may be on the exam)

3. For the ideal gas, obtain the entropy (example 2.3 in the book, page 42) and the chemical potential (example 2.8 on page 60). Also, obtain an relationship between the additive undetermined constants in these expressions using Euler's equation (exercise 2.9 on page 61).

4. In class we derived

$$dU = C_V dT + \left(T \left. \frac{\partial P}{\partial T} \right|_V - P \right) dV.$$

Use this to obtain $U(T, V)$ for the van der Waals gas (exercise 3.8 in the book). Similarly, use equation (1) to obtain $S(T, V)$ (exercise 3.9).

5. Prove that if $f(x, y, z) = 0$,

$$\left. \frac{\partial x}{\partial y} \right|_z \left. \frac{\partial y}{\partial z} \right|_x \left. \frac{\partial z}{\partial x} \right|_y = -1.$$

6. Using Equations (1), (2), and the result in problem 5, along with the following definitions of experimentally measurable quantities:

$$\begin{aligned} \alpha &\equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p && \text{coefficient of thermal expansion} \\ \kappa_T &\equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T && \text{isothermal compressibility} \\ \kappa_S &\equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S && \text{adiabatic compressibility} \end{aligned}$$

show that:

$$(a) \quad TdS = C_V dT + \frac{\alpha T}{\kappa_T} dV \quad \text{and} \quad TdS = C_P dT - \alpha TV dP,$$

$$(b) \quad C_P - C_V = \frac{TV\alpha^2}{\kappa_T},$$

and

$$(c) \quad \frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S} \quad (\text{assuming an adiabatic process}).$$