

**Tutorial 7: Expansion processes again****1. Exam style question - Free expansion and Joule-Kelvin coefficients**

- (a) Write down the van der Waals Equation of state, and explain briefly the physical meaning of a and b .
- (b) Derive the expression for the Joule coefficient of the van der Waals equation of state.

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{a}{C_V} \left(\frac{n}{V}\right)^2$$

- (c) The Joule-Kelvin expansion is an isenthalpic process, in which the change in temperature is given: by

$$\Delta T_{JK} = \int_{P_1}^{P_2} \left(\frac{\partial T}{\partial P}\right)_H dP$$

Show that the Joule-Kelvin coefficient can be written in terms of the heat capacity and the coefficient of thermal expansion:

$$\mu_{JK} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(\alpha T - 1)$$

- (d) Show that the Joule-Kelvin coefficient is zero for an ideal gas.
- (e) Evaluate the Joule-Kelvin coefficient for a van der Waals gas with specific heat capacity c_P .
- (f) Show that, for a van der Waals gas, the line dividing positive and negative values of μ_{JK} (the “inversion curve”) is given by:

$$T_{in} = \frac{2a}{Rb} \left(\frac{v_{in} - b}{v_{in}}\right)^2$$

Hint: The easiest way to get an expression for $(\partial v/\partial T)_P$ from the van der Waals equation is to write it as $T(P, V)$ and find $(\partial T/\partial v)_P$.

2. Cooling in an adiabatic expansion

Draw two isotherms and an adiabat for an ideal gas on an indicator (PV) diagram, and hence show that an ideal gas always cools when undergoing a reversible adiabatic expansion. You do not need to do any detailed mathematics.

Now show that the coefficient for cooling in an adiabatic expansion is:

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T}{C_P} \left(\frac{\partial V}{\partial T}\right)_P$$

Hence explain why an adiabatic expansion produces more cooling than an isenthalpic process, with a similar pressure change.

Discuss why the isenthalpic Joule-Kelvin process is used in real refrigerator, rather than the adiabatic Joule processes.

3. Expanding through a phase transition

In a throttling process we normally write

$$\Delta T_{JK} = \int \left(\frac{\partial T}{\partial P} \right)_H dP = \int \frac{V}{C_P} (\alpha T - 1) dP$$

In an evaporator, the cooling substance goes from liquid to gas in an isenthalpic process. With reference to the equation above, explain why this is a good thing to do, and why it creates a problem applying the equation. What happens in practice is that the system remains at constant pressure and temperature, while extracting heat from the surroundings to overcome latent heat and allow it to evaporate.

4. Gibbs Helmholtz

A system is heated from temperature T_1 to T_2 , show that

$$G_2 = \frac{G_1 T_2}{T_1} - T_2 \int_{T_1}^{T_2} \frac{H}{T^2} dT$$

If the interatomic forces are known, it is fairly simple to compute the internal energy of a system. Suppose a material at atmospheric pressure in its liquid phase has internal energy

$$U = U_l(V) + A_l T$$

and in its solid phase

$$U = U_s(V) + A_s T$$

Assume further that it has zero thermal expansion: $\left(\frac{dV}{dT} \right)_P = 0$ and melting point of 300K.

Write down the gibbs free energy difference at 300K, and calculate its value at any other temperature T_2 . Discuss each term in your final expression. By examining what happens at $T = 0$, prove that the given expressions for U are no longer valid in that limit.

5. **Critical point** At the critical point, where liquid and gas become indistinguishable, $(\partial P / \partial V)_T = 0$ and $(\partial^2 P / \partial V^2)_T = 0$. Sketch isotherms on a PV diagram showing these two conditions. Show that, for a van der Waals gas, the critical point is at:

$$P_c = \frac{a}{27b^2}, \quad V_c = 3nb, \quad T_c = \frac{8a}{27Rb}$$

For a van der Waals gas for which $a = 0.27 \text{ N m}^4 \text{ mole}^{-2}$ and $b = 3.1 \times 10^{-5} \text{ m}^3 \text{ mole}^{-1}$ (approximately the values for carbon dioxide) calculate the values of P_c , V_c and T_c . Compare the value of the critical temperature T_c with the value of the Boyle temperature T_B and comment.