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Problem 3.1: Maxwell-Relations

[**Oral** | 3 pt(s)]

ID: ex_maxwell_relations:sm2627

Learning objective

In this exercise, you will derive Maxwell relations from thermodynamic potentials and use them to recover the equation of state of an ideal gas.

a) What is the differential of the Helmholtz free energy F, and what is the differential of the free enthalpy (also called Gibbs free energy) G? Derive the Maxwell relations following from these. **1**pt(s)

b) A substance satisfies the following two conditions at fixed particle number N and temperature T: **2**pt(s)

(i) The internal energy U is independent of the volume V.

(ii) The enthalpy H is independent of the pressure P.

Using these conditions and the Maxwell relations from (a), show that $PV \propto T$.

Problem 3.2: Joule–Thomson Process

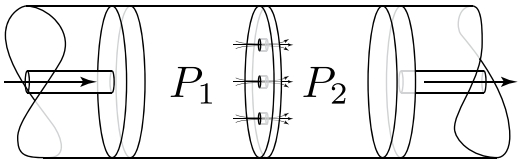
[**Oral** | 4 pt(s)]

ID: ex_joule_thomson_process:sm2627

Learning objective

This exercise is about the Joule-Thomson process used to change the temperature of a gas as it passes through a porous medium while preventing heat exchange with the surroundings.

In the Joule–Thomson process, a gas flowing through a pipe is forced through a porous membrane, with a higher pressure on the upstream side than on the downstream side ($P_2 < P_1$). The goal is to achieve a cooling of the gas by this means. The process is assumed to be adiabatic.



a) Show that this is a process at constant enthalpy, and derive an expression for the Joule–Thomson coefficient **2**pt(s)

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial P}\right)_H$$

as a function of the heat capacity C_P and the isobaric thermal expansion coefficient

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P .$$

b) Is cooling possible with an ideal gas? Why (not)? 1pt(s)

c) Assuming that $PV = NkT + B(T)\,P$ is a good approximation of the equation of state, determine μ_{JT} as a function of B. 1pt(s)

Problem 3.3: Clausius–Clapeyron Equation

[**Oral** | 4 pt(s)]

ID: ex_clausius_clapeyron_equation:sm2627

Learning objective

The Clausius-Clapeyron equation connects thermodynamic state functions to observable phase behavior, explaining how pressure governs boiling and melting points. Here you derive the equation from a cyclic process to build both mathematical rigor and physical intuition about phenomena such as pressure-dependent boiling and melting points.

We consider a substance that exists in two phases. To transfer the substance from phase 1 to phase 2 by changing its volume (at constant temperature T and pressure P_0), the latent heat $Q_L = T\Delta S$ is required. Here, $\Delta S = S_2 - S_1$ is the change in entropy during the phase transition of the entire substance. Furthermore, $\Delta V = V_2 - V_1$ denotes the corresponding change in volume.

a) The Clausius–Clapeyron equation determines the slope of a phase-boundary curve $P_0(T)$ in the pT-diagram according to 3pt(s)

$$\frac{dP_0}{dT} = \frac{\Delta S}{\Delta V}. \tag{1}$$

Derive this equation by considering the cyclic process of the complete phase transition (and its reverse, represented as a rectangle in the VT-diagram):

$$(V_1, T) \to (V_2, T) \to (V_2, T + \delta T) \to (V_1, T + \delta T) \to (V_1, T).$$

Hint: Use the equilibrium condition $\mu^{(1)}\big(P_0(T), T\big) = \mu^{(2)}\big(P_0(T), T\big)$ together with the fact that the free energy is a state function (i.e. $\oint dF = 0$).

b) Using the Clausius–Clapeyron equation, explain why (i) the boiling point of a liquid increases as the pressure increases, whereas (ii) the melting point of ice decreases as the pressure increases. 1pt(s)