Problem 5.3–1 Fundamental Relation for Ideal Gas in Different Representations

Fundamental relation in the entropy representation for monoatomic ideal gas:

$$S = Ns_0 + NR\ln\left(\left(\frac{U}{U_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\left(\frac{N}{N_0}\right)^{-5/2}\right)$$

Solving for U, we get internal energy representation of the fundamental relation:

$$U = U_0\left(\frac{V_0}{V}\right)^{2/3}\left(\frac{N}{N_0}\right)^{5/3}\exp\left(\frac{2S}{3NR}-\frac{2s_0}{3R}\right)$$

For calculation of the Helmholtz potential, calculate temperature:

$$T = \frac{\partial U}{\partial S} = \frac{2U_0}{3NR}\left(\frac{V_0}{V}\right)^{2/3}\left(\frac{N}{N_0}\right)^{5/3}\exp\left(\frac{2S}{3NR}-\frac{2s_0}{3R}\right)$$

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Therefore: $$U = \frac{3}{2} NRT$$

and
$$S = Ns_0 + NR \ln\left(\left(\frac{3NRT}{2U_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\left(\frac{N}{N_0}\right)^{-5/2}\right)$$

Substituting these expressions into the Legendre transform for S: $F = U - TS$

$$F = \frac{3}{2} NRT - NT\left(s_0 + R \ln\left(\left(\frac{3NRT}{2U_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\left(\frac{N}{N_0}\right)^{-5/2}\right)\right)$$

Problem 5.3–1 Fundamental Relation for Ideal Gas in Different Representations

For calculation of the enthalpy, calculate pressure:

$$P = -\frac{\partial U}{\partial V} = \frac{2}{3} U_0 \frac{V_0^{2/3}}{V^{5/3}} \left(\frac{N}{N_0} \right)^{5/3} \exp\left(\frac{2S}{3NR} - \frac{2s_0}{3R} \right)$$

Therefore: $$U = \frac{3}{2} PV$$

Express volume as a function of pressure:

$$V = \left(\frac{2}{3} \frac{U_0}{P} \right)^{3/5} V_0^{2/5} \left(\frac{N}{N_0} \right) \exp\left(\frac{2S}{5NR} - \frac{2s_0}{5R} \right)$$

The appropriate Legendre transformation is:

$$H = U + PV = \frac{3}{2} PV + PV = \frac{5}{2} PV$$

Problem 5.3–1 Fundamental Relation for Ideal Gas in Different Representations

$$H=\frac{5}{2}PV=\frac{5}{2}\left(\frac{2U_0}{3}\right)^{3/5}(PV_0)^{2/5}\left(\frac{N}{N_0}\right)\exp\left(\frac{2S}{5NR}-\frac{2s_0}{5R}\right)$$

For the Gibbs potential calculation: $U=\frac{3}{2}NRT$

$$\left.\begin{aligned}T&=\frac{\partial U}{\partial S}=\frac{2U_0}{3NR}\left(\frac{V_0}{V}\right)^{2/3}\left(\frac{N}{N_0}\right)^{5/3}\exp\left(\frac{2S}{3NR}-\frac{2s_0}{3R}\right)\\ P&=-\frac{\partial U}{\partial V}=\frac{2}{3}U_0\frac{V_0^{2/3}}{V^{5/3}}\left(\frac{N}{N_0}\right)^{5/3}\exp\left(\frac{2S}{3NR}-\frac{2s_0}{3R}\right)\end{aligned}\right\}\quad PV=NRT$$

$$G=U-TS+PV=\frac{3}{2}NRT-TS+PV=\frac{5}{2}NRT-TS$$

Problem 5.3–1 Fundamental Relation for Ideal Gas in Different Representations

$$G = \frac{5}{2}NRT - T\left(Ns_0 + NR\ln\left(\left(\frac{U}{U_0}\right)^{3/2} \left(\frac{V}{V_0}\right) \left(\frac{N}{N_0}\right)^{-5/2} \right) \right)$$

$$\Downarrow$$

$$G = \frac{5}{2}NRT - TN\left(s_0 + R\ln\left(\left(\frac{3NRT}{2U_0}\right)^{3/2} \left(\frac{NRT}{PV_0}\right) \left(\frac{N}{N_0}\right)^{-5/2} \right) \right)$$

Problem 5.3– 5 Calculation of Gibbs potential and α, κ_T, c_P

We are given the fundamental relation: $$S = \left(\frac{R^2}{v_0\theta}\right)^{1/3}(NVU)^{1/3}$$

Solve it for U to obtain the fundamental relation in the energy representation:

$$U = \frac{v_0\theta}{R^2 NV} S^3$$

To obtain the Gibbs potential via a Legendre transformation:

$$G(T,P) = U - TS + PV$$

We need to express U, S and V as functions of T and P. There fore, we need three equations to eliminate U, S and V :

$$U = \frac{v_0\theta}{R^2 NV} S^3 \qquad T = \frac{\partial U}{\partial S} = 3\frac{v_0\theta}{R^2 NV} S^2 \qquad P = -\frac{\partial U}{\partial S} = \frac{v_0\theta}{R^2 NV^2} S^3$$

Problem 5.3 – 5 Calculation of Gibbs potential and α, κ_T, c_P

Solving these three equations for U, S and V, we obtain:

$$U = \frac{R^2 N T^3}{27 v_0 \theta P} \qquad S = \frac{R^2 N T^2}{9 v_0 \theta P} \qquad V = \frac{R^2 N T^3}{27 v_0 \theta P^2}$$

Substituting them into the Legendre transformation for G and simplifying:

$$G(T, P) = U - TS + PV = -\frac{R^2 N T^3}{27 v_0 \theta P}$$

Writing the differential of G: $$dG = -SdT + VdP + \mu dN$$

we note that: $$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} = \frac{R^2 N T^2}{9 v_0 \theta P} \qquad V = \left(\frac{\partial G}{\partial P}\right)_{T,N} = \frac{2R^2 N T^3}{27 v_0 \theta P^2}$$

We can use these equations in calculations of α, κ_T, c_P

Problem 5.3 – 5 Calculation of Gibbs potential and α, κ_T, c_P

Recalling the definitions of α, κ_T, c_P:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} = \frac{1}{V}\left(\frac{\partial}{\partial T}\frac{2R^2NT^3}{27v_0\theta P^2}\right)_{P,N} = \frac{1}{V}\frac{2R^2NT^2}{9v_0\theta P} = \frac{1}{\frac{2R^2NT^3}{27v_0\theta P^2}}\frac{2R^2NT^2}{9v_0\theta P} = \frac{3}{T}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{P,N} = -\frac{1}{V}\left(\frac{\partial}{\partial P}\frac{2R^2NT^3}{27v_0\theta P^2}\right)_{P,N} = \frac{1}{V}\frac{4R^2NT^3}{27v_0\theta P^3} = \frac{1}{\frac{2R^2NT^3}{27v_0\theta P^2}}\frac{4R^2NT^3}{27v_0\theta P^3} = \frac{2}{P}$$

$$c_P = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{P,N} = \frac{T}{N}\left(\frac{\partial}{\partial T}\frac{R^2NT^2}{9v_0\theta P}\right)_{P,N} = \frac{2R^2T^2}{9v_0\theta P}$$

Problem 5.3 – 6 Fundamental Relation in the Enthalpy Representation

The second good fundamental relation:

$$S = \left(\frac{R}{\theta}\right)^{1/2}\left(NU + \frac{R\theta V^2}{v_0^2}\right)^{1/2} \Rightarrow U = \frac{\theta S^2}{NR} - \frac{R\theta V^2}{N v_0^2}$$

$$P = -\frac{\partial U}{\partial V} = 2\frac{R\theta V}{N v_0^2} \Rightarrow V = \frac{N P v_0^2}{2R\theta}$$

$$H = U + PV \Rightarrow H = \frac{\theta S^2}{NR} - \frac{R\theta}{N v_0^2}\left(\frac{N P v_0^2}{2R\theta}\right)^2 + P\frac{N P v_0^2}{2R\theta}$$

$$H = \frac{\theta S^2}{NR} - \frac{N P^2 v_0^2}{4R\theta} + \frac{N P^2 v_0^2}{2R\theta} = \frac{\theta S^2}{NR} + \frac{N P^2 v_0^2}{4R\theta} \Rightarrow V = \left(\frac{\partial H}{\partial P}\right)_{S,N} = \frac{N P v_0^2}{2R\theta}$$

Problem 5.3 – 7 Calculation c_V from given enthalpy H

$$H = \frac{AS^2}{N}\ln\left(\frac{P}{P_0}\right) \qquad\qquad c_V = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_V$$

$$dH = TdS + VdP + \ldots \quad\Rightarrow\quad T = \left(\frac{\partial H}{\partial S}\right)_P = \frac{2AS}{N}\ln\left(\frac{P}{P_0}\right)$$

$$V = \left(\frac{\partial H}{\partial P}\right)_S = \frac{AS^2}{NP} \quad\Rightarrow\quad P = \frac{AS^2}{NV}$$

Using this expression for P in the expression for T, we obtain T as a function of S and V

$$T = \frac{2AS}{N}\ln\left(\frac{AS^2}{NVP_0}\right)$$

Problem 5.3 – 7 Calculation c_V from given enthalpy H

$$T = \frac{2AS}{N}\ln\left(\frac{AS^2}{NVP_0}\right)$$

Differentiating the above expression with respect to T at constant V, we obtain:

$$\left(\frac{\partial T}{\partial T}\right)_V = \frac{2A}{N}\ln\left(\frac{AS^2}{NVP_0}\right)\left(\frac{\partial S}{\partial T}\right)_V + \frac{2AS}{N}\left(\frac{\partial \ln\left(S^2\right)}{\partial T}\right)_V =$$

$$\frac{2A}{N}\ln\left(\frac{AS^2}{NVP_0}\right)\left(\frac{\partial S}{\partial T}\right)_V + \frac{4A}{N}\left(\frac{\partial S}{\partial T}\right)_V = 1 \quad \Rightarrow$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{N}{2A\left(\ln\left(\dfrac{P}{P_0}\right)+2\right)} \quad \Rightarrow \quad c_V = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_V = \frac{T}{2A\left(\ln\left(\dfrac{P}{P_0}\right)+2\right)}$$

Problem 5.3 – 12 Gibbs Potential

$$(s - s_0)^4 = Avu^2 \quad \Rightarrow \quad U = \frac{(S - Ns_0)^2}{A^{1/2}V^{1/2}N^{1/2}}$$

$$T = \frac{\partial U}{\partial S} = \frac{2(S - Ns_0)}{A^{1/2}V^{1/2}N^{1/2}} \qquad P = -\frac{\partial U}{\partial V} = \frac{(S - Ns_0)^2}{2A^{1/2}V^{3/2}N^{1/2}}$$

$$\Downarrow \qquad \Downarrow$$

$$T = \frac{2U}{(S - Ns_0)} \qquad P = -\frac{\partial U}{\partial V} = \frac{U}{2V}$$

$$U = \frac{4U^2(2P)^{1/2}}{T^2A^{1/2}U^{1/2}N^{1/2}} \quad \Rightarrow \quad U = \frac{ANT^4}{32P}$$

$$G = U - TS + PV = U - 2U + \frac{U}{2} - TNs_0 = -\frac{U}{2} - TNs_0$$

$$G = -\frac{ANT^4}{64P} - TNs_0$$

Problem 5.3 – 13 Gibbs and Helmholtz Potentials

$$\left.\begin{aligned} u &= \frac{3}{2}Pv \\ P &= AvT^4 \end{aligned}\right\} \Rightarrow \left.\begin{aligned} \frac{1}{T} &= \left(\frac{3A}{2}\right)^{1/4}\frac{v^{1/2}}{u^{1/4}} \\ \frac{P}{T} &= \left(\frac{2}{3}\right)^{3/4}A^{1/4}\frac{u^{3/4}}{v^{1/2}} \end{aligned}\right\} \Rightarrow$$

$$ds = \frac{1}{T}du + \frac{P}{T}dv = \left(\frac{3A}{2}\right)^{1/4}\frac{v^{1/2}}{u^{1/4}}du + \left(\frac{2}{3}\right)^{3/4}A^{1/4}\frac{u^{3/4}}{v^{1/2}}dv$$

$$ds = \left(\frac{3A}{2}\right)^{1/4}\left(\frac{v^{1/2}}{u^{1/4}}du + \frac{2u^{3/4}}{3v^{1/2}}dv\right) = \left(\frac{3A}{2}\right)^{1/4} d\left(\frac{4}{3}u^{3/4}v^{1/2}\right)$$

$$s = \left(\frac{3A}{2}\right)^{1/4}\frac{4}{3}u^{3/4}v^{1/2} + s_0$$

Problem 5.3 – 13 Gibbs and Helmholtz Potentials

$$(s-s_0)^4 = 2A\left(\frac{4}{3}\right)^3 u^3 v^2 \quad \Rightarrow \quad u = \frac{3}{4}\frac{(s-s_0)^{4/3}}{(2A)^{1/3} v^{2/3}}$$

$$T = \frac{\partial u}{\partial s} = \frac{(s-s_0)^{1/3}}{(2A)^{1/3} v^{2/3}} = \frac{4}{3}\frac{u}{(s-s_0)} \quad \Rightarrow \quad s = s_0 + 2AT^3 v^2$$

$$f = u - Ts = \frac{3}{4}\frac{(s-s_0)^{4/3}}{(2A)^{1/3} v^{2/3}} - \frac{(s-s_0)^{1/3}}{(2A)^{1/3} v^{2/3}} s$$

$$f = u - Ts = \frac{3}{2}AT^4 v^2 - T\left(s_0 + 2AT^3 v^2\right) = -\frac{1}{2}AT^4 v^2 - Ts_0$$

$$F = -\frac{1}{2}NAT^4 v^2 - NTs_0$$

Problem 5.3 – 13 Gibbs and Helmholtz Potentials

$$P = -\frac{\partial u}{\partial v} = \frac{1}{2}\frac{\left(s - s_0\right)^{4/3}}{\left(2A\right)^{1/3} v^{5/3}} = \frac{2}{3}\frac{u}{v} \quad \Rightarrow$$

$$g = u + Pv - Ts = \frac{5}{2}Pv - T\left(s_0 + 2AT^3 v^2\right) \qquad v = \frac{P}{AT^4}$$

$$g = \frac{5}{2}\frac{P^2}{AT^4} - T\left(s_0 + 2AT^3\left(\frac{P}{AT^4}\right)^2\right)$$

$$g = \frac{1}{2}\frac{P^2}{AT^4} - Ts_0$$