Problem 3:

(2) a) $\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = -\frac{1}{\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T} = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\alpha_P}{\kappa_T}$$

b) $PV = nRT \qquad \alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\left(\frac{\partial}{\partial T}\frac{nRT}{P}\right)_P = \frac{nR}{PV}$ (1) $= \frac{1}{T}$ (1)

c) $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial}{\partial P}\frac{nRT}{P}\right)_T = +\frac{1}{V}\frac{nRT}{P^2}$ (1) $= \frac{1}{P}$ (1)

(2) d) $\frac{\alpha_P}{\kappa_T} = \frac{\frac{1}{T}}{\frac{1}{P}} = \frac{P}{T} \qquad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\frac{nRT}{V}\right)_V = \frac{nR}{V} = \frac{P}{T}$

e) $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

$$PV + \frac{an^2}{V} - Pnb - \frac{an^3b}{V^2} = nRT$$

$$\left.\frac{\partial}{\partial P}\right|_T \cdots \quad V + P\left(\frac{\partial V}{\partial P}\right)_T - \frac{an^2}{V^2}\left(\frac{\partial V}{\partial P}\right)_T - nb + \frac{2an^3b}{V^3}\left(\frac{\partial V}{\partial P}\right)_T = 0$$

$$V - nb = \left(\frac{an^2}{V^2} - \frac{2an^3b}{V^3} - P\right)\left(\frac{\partial V}{\partial P}\right)_T \quad (1)$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{V - nb}{PV + \frac{2an^3b}{V^2} - \frac{an^2}{V}} = \frac{V - nb}{V\left[\frac{nRT}{V-nb} - \frac{an^2}{V^2}\right] + \frac{2an^3b}{V^2} - \frac{an^2}{V}}$$

$$= \frac{V - nb}{V\frac{nRT}{V-nb} + \frac{2an^3b}{V^2} - \frac{2an^2}{V}} \quad (1)$$

f) ideal gas: $K_T = \frac{1}{P} = \frac{V}{nRT}$

$= \frac{V}{3076.18\ J}$

$n = 1$ mole

$R = 8.314\ \frac{J}{mol\,K}$

$T = 370\,K$

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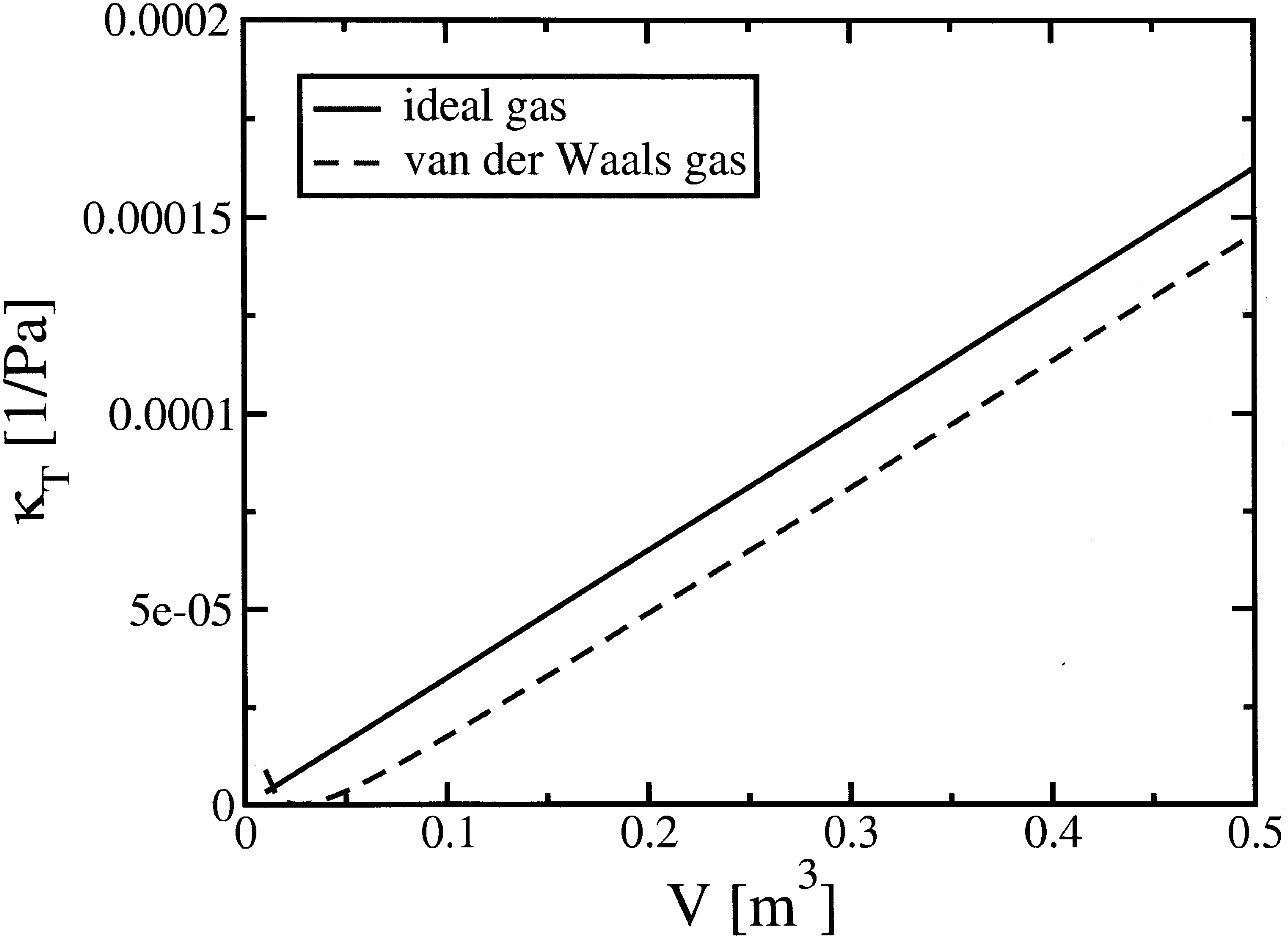
ideal gas
van der Waals gas
0.0002
0.00015
0.0001
5e-05
0
κ_T [1/Pa]
0
0.1
0.2
0.3
0.4
0.5
V [m^3]

Problem 4:

P and T are the experimentally controlled variables. Thus, we want to express everything in terms of P and T:

a) $$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\Delta W = -\int_i P\,dV = -\int_{P_1}^{P_2} P\left(\frac{\partial V}{\partial P}\right)_T dP = V \cdot \kappa_T \int_{P_1}^{P_2} P\,dP$$

neglect small change in volume

$$= V \cdot \frac{\kappa_T}{2}(P_1^2 - P_2^2) \approx 10^{-3}\, m^3 \cdot 0.5 \cdot 10^{-4} \frac{1}{atm} \frac{1}{2}(20^2 - 1^2)\, atm^2$$

2

$$\approx 10^{-5}\, m^3\, atm \approx 1\, m^3 \frac{N}{m^2} = 1\, J$$

2

b) $$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$\Delta Q = \int T\,dS = \int_{P_1}^{P_2} T\left(\frac{\partial S}{\partial P}\right)_T dP = -T\int_{P_1}^{P_2}\left(\frac{\partial V}{\partial T}\right)_P dP$$

$$= -TV\alpha_P \int_{P_1}^{P_2} dP = -TV\alpha_P (P_2 - P_1)$$ 2

neglect small change in V

$$\approx -293\,K \cdot 10^{-3} m^3\; 2 \cdot 10^{-4} \frac{1}{K}\,(20-1)\, atm$$

$$\approx -12 \cdot 10^{-4}\, m^3\, atm = -120\, m^3 \frac{N}{m^2} = -120\, J$$ 2

Problem 5:

a) $dU = \left(\frac{\partial U}{\partial \vec{M}}\right)_T d\vec{M} + \left(\frac{\partial U}{\partial T}\right)_{\vec{M}} dT$

We want to show that $\left(\frac{\partial U}{\partial \vec{M}}\right)_T = 0$.
Use identity for partial derivatives:

$$\left(\frac{\partial U}{\partial \vec{M}}\right)_T = \left(\frac{\partial U}{\partial \vec{M}}\right)_S + \left(\frac{\partial U}{\partial S}\right)_{\vec{M}} \left(\frac{\partial S}{\partial \vec{M}}\right)_T$$

$\vec{M}$ and S are the natural variables of U. Thus

$$\left(\frac{\partial U}{\partial \vec{M}}\right)_S = \vec{H} \qquad \left(\frac{\partial U}{\partial S}\right)_{\vec{M}} = T$$

Use Maxwell relation for $\left(\frac{\partial S}{\partial \vec{M}}\right)_T$

$$\Rightarrow \left(\frac{\partial U}{\partial \vec{M}}\right)_T = \vec{H} - T\left(\frac{\partial \vec{H}}{\partial T}\right)_{\vec{M}} \qquad \vec{H} = \frac{T}{nD}\vec{M} \Rightarrow \left(\frac{\partial \vec{H}}{\partial T}\right)_{\vec{M}} = \frac{\vec{M}}{nD} = \frac{\vec{H}}{T}$$

$$= \vec{H} - T\frac{\vec{H}}{T} = 0$$

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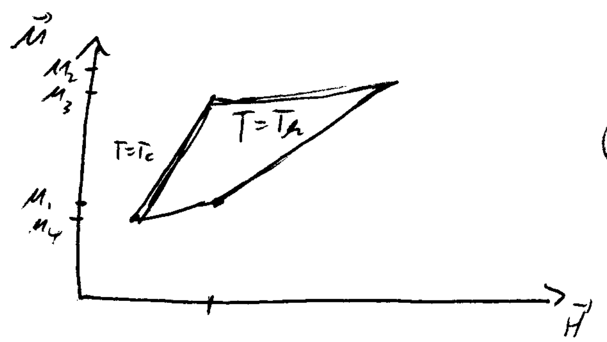
b) isotherm: $\vec{M} = \frac{nD\vec{H}}{T}$

adiabat: $dU = \vec{H}\, d\vec{M} = C\, dT$

$$\frac{\vec{M}}{nD}\, d\vec{M} = C\frac{dT}{T}$$

$$\frac{1}{2nD}\vec{M}^2 = C \ln T + \text{const}$$



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c) Heat is only exchanged along the isotherms:

$$\left.\begin{aligned} \Delta Q_h = \Delta W_a = \int_{M_1}^{M_2} \vec{H}\, d\vec{M} = \frac{T_h}{nD} \int_{\vec{M}_1}^{\vec{M}_2} \vec{M}\, d\vec{M} = \frac{T_h}{2nD} \left(\vec{M}_2^{\,2} - \vec{M}_1^{\,2}\right) \\ \Delta Q_c = \Delta W_c = \frac{T_c}{2nD} \left(\vec{M}_3^{\,2} - \vec{M}_4^{\,2}\right) \end{aligned}\right\} \textcircled{2}$$

$\uparrow$ since $dU = C\,dT = 0$

heat absorbed: ΔQ_h ①

work performed $\Delta Q_h - \Delta Q_c$ ① (since $\Delta U = 0$ over whole cycle)

d) $$\eta = 1 - \frac{\Delta Q_c}{\Delta Q_h} = 1 - \frac{T_c}{T_h} \frac{\vec{M}_3^{\,2} - \vec{M}_4^{\,2}}{\vec{M}_2^{\,2} - \vec{M}_1^{\,2}} \quad ①$$

adiabats: $$\frac{1}{2nD}\left(\vec{M}_2^{\,2} - \vec{M}_3^{\,2}\right) = C\left(\ln T_h - \ln T_c\right)$$

$$\frac{1}{2nD}\left(\vec{M}_1^{\,2} - \vec{M}_4^{\,2}\right) = C\left(\ln T_h - \ln T_c\right)$$

$$\vec{M}_3^{\,2} - \vec{M}_4^{\,2} = -2nD\, C\left(\ln T_h - \ln T_c\right) + \vec{M}_2^{\,2} - \vec{M}_4^{\,2}$$

$$\vec{M}_2^{\,2} - \vec{M}_1^{\,2} = \vec{M}_2^{\,2} - \left[\vec{M}_4^{\,2} + 2nDC\left(\ln T_h - \ln T_c\right)\right]$$

$$= \vec{M}_3^{\,2} - \vec{M}_4^{\,2}$$

$$\Rightarrow \eta = 1 - \frac{T_c}{T_h} \quad ①$$