Thermo | HW #2 | Tanner Corrado

10/10

Problem 1

1. $U = \left(\frac{v_0 \theta}{R^2}\right)\frac{S^3}{NV}$ where R, θ, v_0 are all positive constants

a. $P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$ $\quad T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$ $\quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V,N_j \neq i}$

$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = -\left(\frac{v_0 \theta}{R^2}\frac{S^3}{N}\right)\frac{-1}{V^2}$ $\quad \boxed{P = -\frac{v_0 \theta S^3}{R^2 N}\cdot\frac{-1}{V^2}}$

$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \frac{v_0 \theta}{R^2 NV}\cdot 3S^2$ $\quad \boxed{T = \frac{v_0 \theta}{R^2 NV}\cdot 3S^2}$

$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V,N_{i\neq j}} = \frac{v_0 \theta}{R^2}\frac{S^3}{V}\cdot\frac{-1}{N^2}$ $\quad \boxed{\mu = \frac{v_0 \theta S^3}{R^2 V}\cdot\frac{-1}{N^2}}$

b. $P(\lambda S, \lambda N, \lambda V) = \frac{-v_0 \theta (\lambda S)^3}{R^2 (\lambda V)^2 (\lambda N)} = \frac{\lambda^3}{\lambda^3}\left(\frac{-v_0 \theta S^3}{R^2 V^2 N}\right) = \lambda^0 P(S,N,V)$

$T(\lambda S, \lambda N, \lambda V) = \frac{v_0 \theta 3(\lambda S)^2}{R^2(\lambda N)(\lambda V)} = \frac{\lambda^2}{\lambda^2}\left(\frac{3 v_0 \theta S^2}{R^2 NV}\right) = \lambda^0 T(S,N,V)$

$\mu(\lambda S, \lambda N, \lambda V) = \frac{-v_0 \theta (\lambda S)^3}{R^2(\lambda V)(\lambda N)^2} = \frac{\lambda^3}{\lambda^3}\left(\frac{-v_0 \theta S^3}{R^2 V N^2}\right) = \lambda^0 \mu(S,N,V)$

The three equations are all zero-order homogeneous. $T(S,V,N)$ is intrinsically positive since N, V will always be >0 (you can't have negative moles or volume, R, v_0, and θ are all positive constants, and the S term is squared. Nothing else in the function is negative so $T(S,V,N)$ cannot be negative. Also, S must be >0.

c. $U = \left(\frac{v_0 \theta}{R^2}\right)\frac{S^3}{NV}$ $\quad S = \text{constant} \quad dS = 0 \quad dU = đW_{ad} = -P\,dV$

$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = \frac{v_0 \theta}{R^2}\frac{S^3}{N}\cdot\frac{1}{V^2} = \frac{v_0 \theta}{R^2}\frac{\left(\frac{S}{N}\right)^3}{\frac{N}{N}}\cdot\frac{1}{\left(\frac{V}{N}\right)^2} = \frac{v_0 \theta}{R^2}\frac{s^3}{v^2}$

$P = \frac{v_0 \theta}{R^2}\cdot\frac{s^3}{v^2}$ so for adiobat $Pv^2 = \frac{v_0 \theta}{R^2}\cdot s^3$ = constant since s is constant.

$Pv^2 = \text{constant.}$

d. $P = \frac{v_0 \theta}{R^2}\frac{s^3}{v^2}$ $\quad T = \frac{v_0 \theta}{R^2 NV}\cdot 3S^2 = \frac{v_0 \theta}{R^2}\cdot\frac{3\left(\frac{S}{N}\right)^2}{\frac{N}{N}\frac{V}{N}} = \frac{v_0 \theta}{R^2}\cdot\frac{s^2}{v} = T$

$s = \sqrt{\frac{vTR^2}{v_0 \theta}} \Rightarrow P = \frac{v_0 \theta}{R^2}\cdot\frac{1}{v^2}\cdot\left(\frac{vTR^2}{v_0 \theta}\right)^{3/2}$ $\quad P = \frac{v_0 \theta}{R^2}\cdot\frac{1}{v^2}\cdot\frac{v^{3/2}T^{3/2}R^3}{v_0^{3/2}\theta^{3/2}}$

$P = \frac{v_0 \theta R^3}{v_0^{3/2}\theta^{3/2}R^2}\cdot\frac{T^{3/2}}{v^{1/2}}$ $\quad Pv^{1/2} = \text{constant}\cdot T^{3/2}$

Since plotting isotherms, T is constant, so $Pv^{1/2} = \text{constant.}$

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In[37]:= ContourPlot[{P * v ^ 1 / 2 == 1, P * v ^ 1 / 2 == 2, P * v ^ 1 / 2 == 3, P * v ^ 1 / 2 == 4, P * v ^ 1 / 2 == 5, P * v ^ 1 / 2 =
         P * v ^ 1 / 2 == 7, P * v ^ 1 / 2 == 8, P * v ^ 1 / 2 == 9, P * v ^ 1 / 2 == 10, P * v ^ 1 / 2 == 11, P * v ^ 1 / 2 == 12}, {
         0, 10}, {v, 0, 10}]
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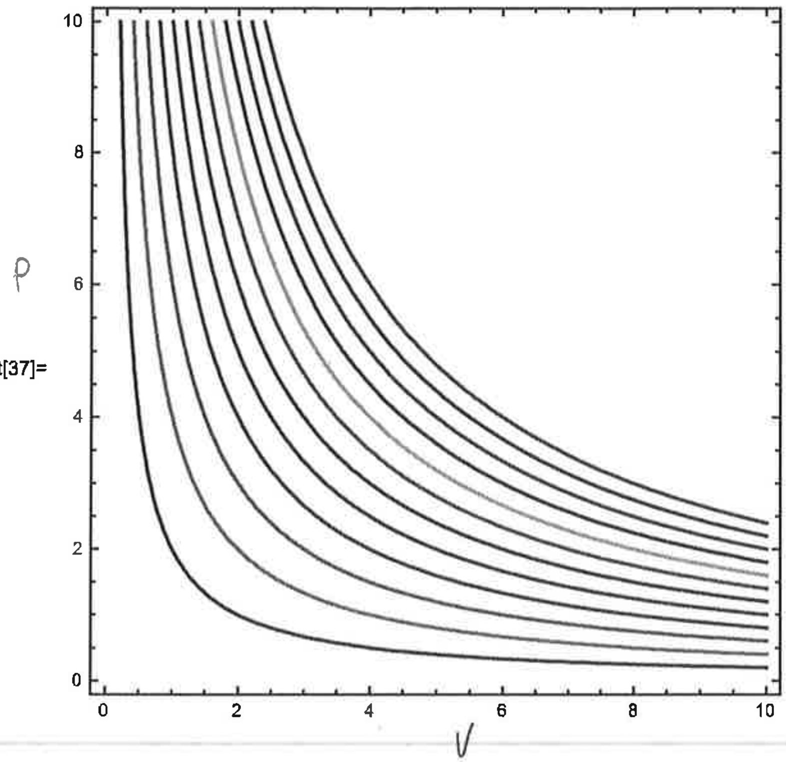
Out[37]=



Isotherms

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    v ^ 2 == 8, P * v ^ 2 == 9, P * v ^ 2 == 10, P * v ^ 2 == 11, P * v ^ 2 == 12} , {P, 0, 10} , {v, 0, 10} ]
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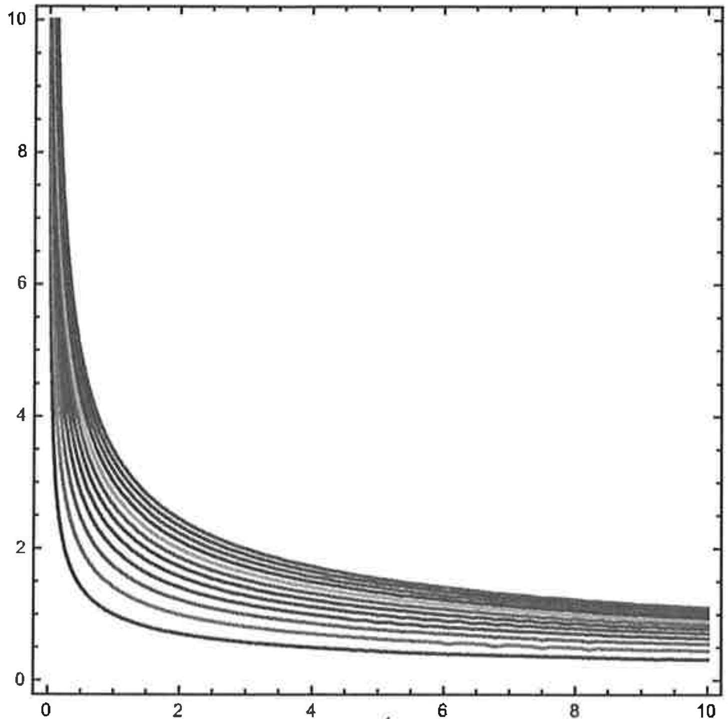
P

Out[36]=



V

Adiabats

2. $T = \frac{3As^2}{v}$ $P = \frac{As^3}{v^2}$ where A is a positive constant

1. Find corresponding chemical potential, $\mu(s,v)$.

$$d\mu = -s\,dT + v\,dP$$

$$dT(s,v) = \left(\frac{\partial T}{\partial s}\right)_v ds + \left(\frac{\partial T}{\partial v}\right)_s dv \qquad dP(s,v) = \left(\frac{\partial P}{\partial s}\right)_v ds + \left(\frac{\partial P}{\partial v}\right)_s dv$$

$$dT(s,v) = \frac{6As}{v}ds - \frac{3As^2}{v^2}dv \qquad dP(s,v) = \frac{3As^2}{v^2}ds - \frac{2As^3}{v^3}dv$$

$$d\mu = -s\left(\frac{6As}{v}ds - \frac{3As^2}{v^2}dv\right) + v\left(\frac{3As^2}{v^2}ds - \frac{2As^3}{v^3}dv\right)$$

$$= -6\frac{As^2}{v}ds + \frac{3As^3}{v^2}dv + \frac{3As^2}{v}ds - \frac{2As^3}{v^2}dv$$

$$d\mu = -\frac{3As^2}{v}ds + \frac{As^3}{v^2}dv$$

$$\mu = -\frac{As^3}{v} + f(v) \longrightarrow \left(\frac{\partial \mu}{\partial v}\right)_s = \frac{As^3}{v^2} = \frac{As^3}{v^2} + f'(v)$$

$\Rightarrow f'(v) = 0$; $f(v) = $ constant

$$\mu = -\frac{As^3}{v} + C$$

$$\mu = \frac{-As^3}{v} + C \text{ where } C \text{ is a constant}$$

2. $T = \frac{3As^2}{v} = \left(\frac{\partial u}{\partial s}\right)_v$ $-P = -\frac{As^3}{v^2} = \left(\frac{\partial u}{\partial v}\right)_s$

$$\int\left(\frac{\partial u}{\partial s}\right)_v = \int\frac{3As^2}{v} \Rightarrow u(s,v) = \frac{3A}{v}\left(\frac{s^3}{3}\right) + c_2 - c_1$$

$$u(s,v) = \frac{As^3}{v} + C \text{ where } C = \text{constant}$$

$$\int\left(\frac{\partial u}{\partial v}\right)_s = \int\frac{-As^3}{v^2} \qquad u(s,v) + c_1 = -As^3\left(\frac{v^{-1}}{-1}\right) + c_2$$

$$u(s,v) = \frac{As^3}{v} + C \text{ where } C = \text{constant}$$

← Equal ✓

3. $U_1 = \frac{3}{2} R n_1 T_1$ $\quad U_2 = \frac{5}{2} R n_2 T_2$

System 1: $n_1 = 2$ (mol) $\quad T_1 = 250\ k$ $\quad$ System 2: $n_2 = 3$ (mol) $\quad T_2 = 350\ k$

At equilibrium: $T_1 = T_2$ $\quad$ What are the energies and temperatures at equilibrium?

$U_1 = \frac{3}{2} \cdot 8.314 \frac{J}{mol\ K} \cdot 2\ mol \cdot 250\ k$ $\quad U_1 = 6235.5\ J$ $\quad U_1 = 6.236\ kJ$

$U_2 = \frac{5}{2} \cdot 8.314 \frac{J}{mol\ k} \cdot 3\ mol \cdot 350\ k$ $\quad U_2 = 21824.3\ J$ $\quad U_2 = 21.82\ kJ$

$U_T = U_1 + U_2 = 6.236\ kJ + 21.82\ kJ$ $\quad U_T = 28.06\ kJ$

Constants: n_1, n_2, U_T, V_1, V_2 $\quad$ Variables: $T_1, T_2, U_1, U_2, S_1, S_2$

$U_1 + U_2 = \frac{3}{2} R n_1 T_1 + \frac{5}{2} R n_2 T_2$ $\quad$ At equilibrium, $T_1 = T_2$

$U_1 + U_2 = \frac{3}{2} R n_1 T_1 + \frac{5}{2} R n_2 T_1$

$U_1 + U_2 = T_1 \left(\frac{3}{2} R n_1 + \frac{5}{2} R n_2 \right)$

$T_1 = \dfrac{U_1 + U_2}{R\left(\frac{3}{2} n_1 + \frac{5}{2} n_2\right)}$ $\quad T_1 = \dfrac{28.06\ kJ}{0.008314 \frac{kJ}{mol\ k} \cdot \left(\frac{3}{2} \cdot 2\ mol + \frac{5}{2} \cdot 3\ mol\right)}$

$T_1 = \dfrac{28.06\ kJ}{0.008314 \frac{kJ}{mol\ k} \cdot 10.5\ mol}$ $\quad \boxed{T_1 = 321.4\ K}$

$\boxed{T = 321.4\ K \text{ at equilibrium.}}$ $\quad (T_1 = T_2 = 321.4k)$

$U_1 = \frac{3}{2} R n_1 T = \frac{3}{2} \cdot 0.008314 \frac{kJ}{mol\ k} \cdot 2\ mol \cdot 321.4k$ $\quad \boxed{U_1 = 8.016\ kJ}$

$U_2 = \frac{5}{2} R n_2 T = \frac{5}{2} \cdot 0.008314 \frac{kJ}{mol\ k} \cdot 3\ mol \cdot 321.4k$ $\quad \boxed{U_2 = 20.04\ kJ}$

4. $T = \left(\frac{V}{V_0}\right)^n T_0$ where n is constant, Ideal, monoatomic gas, compressed quasi-statically

1. Find work $-w$ done when one mole compressed from V_0 to $V_1 < V_0$

$$dW = -PdV \qquad P = \frac{NRT}{V} = \frac{NR}{V}\left(\frac{V}{V_0}\right)^n T_0 = \frac{NRT_0}{V_0^n} V^{n-1}$$

$$dW = \frac{-NRT_0}{V_0^n} V^{n-1} dV \Rightarrow \Delta W = \frac{-NRT_0}{V_0^n}\int_{V_0}^{V_1} V^{n-1} dV$$

$$\Delta W = \frac{-NRT_0}{nV_0^n} V^n \Big|_{V_0}^{V_1} \qquad \Delta W = \frac{-NRT_0}{nV_0^n}\left(V_1^n - V_0^n\right)$$

2. Find ΔU

$$\Delta U = U_1 - U_0 = \frac{3}{2}NR(T_1 - T_0)$$

$$\Delta U = \frac{3}{2}NR\left(\frac{V_1^n}{V_0^n}T_0 - T_0\right) = \frac{3}{2}NRT_0\left(\frac{V_1^n}{V_0^n} - 1\right)$$

3. $\Delta q = \Delta U - \Delta W$

$$\Delta q = \frac{3}{2}NRT_0\left(\frac{V_1^n}{V_0^n} - 1\right) - \frac{-NRT_0}{nV_0^n}\left(V_1^n - V_0^n\right)$$

$$= \frac{3}{2}NRT_0\left(\frac{V_1^n}{V_0^n} - 1\right) + \frac{NRT_0}{n}\left(\frac{V_1^n}{V_0^n} - 1\right)$$

$$= \left(\frac{3}{2}NRT_0 + \frac{NRT_0}{n}\right)\left[\frac{V_1^n}{V_0^n} - 1\right)$$

$$\Delta q = NRT_0\left(\frac{3}{2} + \frac{1}{n}\right)\left[\frac{V_1^n}{V_0^n} - 1\right]$$

4. q by integrating $dq = TdS$

$$dq = TdS = du - PdV \longrightarrow q = \int_{U_0}^{U_1} dU + \int_{V_0}^{V_1} PdV$$

$$q = U_1 - U_0 + \int_{V_0}^{V_1} \frac{NRT_0}{nV_1} V^{n-1} dV = \frac{3}{2}NR(T_1 - T_0) + \frac{NRT_0}{nV_0^n}\left(V_1^n - V_0^n\right)$$

$$= \frac{3}{2}NRT_0\left(\frac{V_1^n}{V_0^n} - 1\right) + \frac{NRT_0}{n}\left(\frac{V_1^n}{V_0^n} - 1\right)$$

$$q = NRT_0\left(\frac{3}{2} + \frac{1}{n}\right)\left[\frac{V_1^n}{V_0^n} - 1\right]$$

4.

5. Calculate η for $q=0$

$q=0 \Rightarrow \Delta U = \Delta W$

$$\frac{3}{2} N R T_0 \left(\frac{V_1^{\eta}}{V_0^{\eta}} - 1 \right) = \frac{-N R T_0}{\eta} \left(\frac{V_1^{\eta}}{V_0^{\eta}} - 1 \right)$$

$$\frac{3}{2} = \frac{-1}{\eta} \Rightarrow \eta = -\frac{2}{3}$$

Thermo | HW #2 | Tanner Corrado

5\. 1. $n = 1$ ideal monoatomic: $c = \frac{3}{2}$ $V = 10^{-3}\ m^3$ $T = 400\ K$

Gas brought to final state of twice the volume and same temp.

$T_0 = 400K \rightarrow T_1 = 400\ K$ $v_0 \rightarrow v_1 = 2v_0$ $dw_{rws} > 0$ for work done by system

$\Delta U^{\,0} + q_{rhs} + w_{rws} = 0$ since T doesn't change. $dq_{rhs} > 0$ for heat taken from system

$\underline{w_{rws} = -q_{rhs}}$ $\Delta S + \frac{q_{rhs}}{T_{rhs}} = 0$ $\Delta S = \frac{-q_{rhs}}{T_{rhs}}$ $\underline{q_{rhs} = -T_{rhs}\Delta S}$

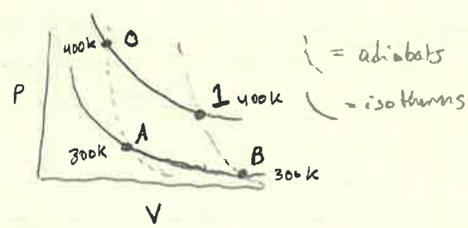
$\Delta S = nR \ln \frac{v}{v_0}$ $n = 1$ $\Delta S = R \ln \frac{2v_0}{v_0}$ $\Delta S = R \ln 2$

$\Delta S = 0.008314 \frac{kJ}{mol\,k} \cdot \ln 2$ $\Delta S = 0.005763 \frac{kJ}{mol\,k}$

$q_{rhs} = -T_{rhs}\Delta S$ $q_{rhs} = -300K \cdot 0.005763 \frac{kJ}{mol\,k}$ $q_{rhs} = -1.729 \frac{kJ}{mol}$

$w_{rws} = -q_{rhs}$ $\boxed{w_{rws} = 1.729 \frac{kJ}{mol}}$

2\.



$\underline{0 \rightarrow A}$

$T_0 = 400\ k \rightarrow T_A = 300\ k$ $\Delta U = -w_{rws} = cnR(\Delta T) = \frac{3}{2}(1\,mol)(0.008314 \frac{kJ}{mol\,k})(300-400k)$

$\Delta U = -1.247\ kJ$ $\Delta S = 0$, $\boxed{q_{rhs} = 0}$ since adiabatic $\boxed{w_{rws} = 1.247\ kJ}$

$\underline{A \rightarrow B}$ $T_A = T_B = 300k$ $\Delta U = 0$ since isothermal

$w_{rws} = -q_{rhs}$ $q_{rhs} = -T_{rhs}\Delta S$ $\Delta S = 0.005763 \frac{kJ}{mol\,k}$

$q_{rhs} = -300\ k \cdot 0.005763 \frac{kJ}{mol\,K}$ $\boxed{q_{rhs} = -1.729 \frac{kJ}{mol} \quad w_{rws} = 1.729 \frac{kJ}{mol}}$

$\underline{B \rightarrow 1}$ $T_B = 300\ k \rightarrow T_1 = 400\ k$ $\Delta U = -w_{rws} = cnR(\Delta T) = \frac{3}{2}(1\,mol)(0.008314 \frac{kJ}{mol\,k})(400-300k)$

$\Delta U = 1.247\ kJ$ $\Delta S = 0$, $\boxed{q_{rhs} = 0}$ adiabatic $\boxed{w_{rws} = -1.247\ kJ}$

So: $0 \rightarrow A \rightarrow B \rightarrow 1$

$w_{rws} = 1.247\ kJ + 1.729\ kJ - 1.247\ kJ = \boxed{1.729 \frac{kJ}{mol}}$

$\boxed{q_{rhs} = -1.729 \frac{kJ}{mol}}$

$\Delta U = -1.247\ kJ + 1.247\ kJ = 0$

3\. The minimum work necessary to return to the initial state would be $1.729 \frac{kJ}{mol}$ (putting in that work) due to conservation of energy, using the same reservoir.