Homework 1

1.1 From 1st law of thermodynamics

$$dQ = dU + p\,dV = C_v\,dT + P\,dV$$

Furthermore, we have:

$$dQ = dH - V\,dp = C_p\,dT - V\,dP$$

Since $dQ = 0$ for adiabatic $\Longrightarrow$ $\left.\begin{aligned} C_v\,dT &= -P\,dV \\ \text{and}\quad C_p\,dT &= V\,dP \end{aligned}\right\}$

$$\Longrightarrow \frac{C_p}{C_v} = \gamma = -\frac{V}{P}\frac{dP}{dV} \Longrightarrow -\frac{dP}{P} = \gamma\frac{dV}{V}$$

$$\Longrightarrow \ln P = -\gamma \ln V + \ln(\text{constant}) \Longrightarrow \boxed{PV^\gamma = \text{constant}}$$

Also since $PV = nRT \Longrightarrow$ $nRTV^{\gamma-1} = \text{constant}$

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1.3 In a free expansion, no work is done ($dW = 0$) -and there is no heat flow $dQ = 0$, and hence $dU = 0$ or $U = \text{constant}$:

Since we can write $U = U(T, V)$ (U is a state function), we can also write

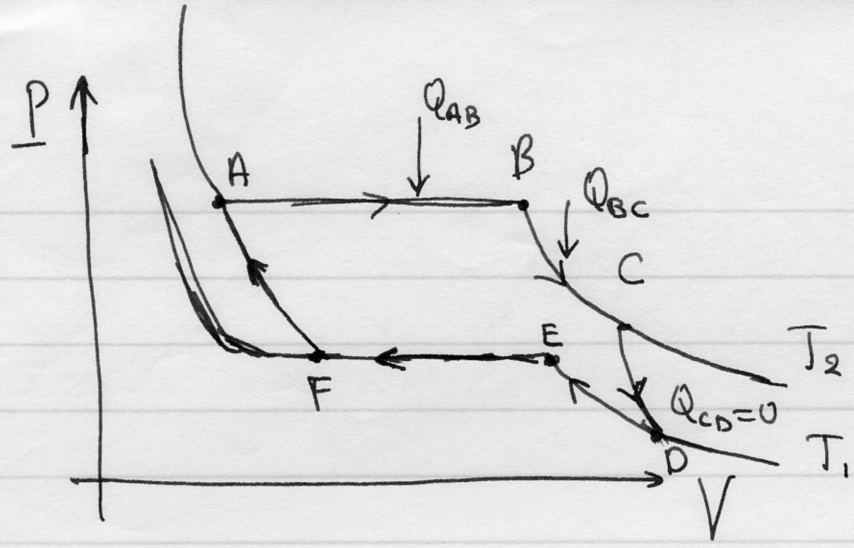
$$T = T(U, V)$$

$$\Longrightarrow dT = \left(\frac{\partial T}{\partial U}\right)_V dU + \left(\frac{\partial T}{\partial V}\right)_U dV \qquad \text{Since } dU = 0$$

$$\Longrightarrow dT = \left(\frac{\partial T}{\partial V}\right)_U dV \quad \text{or} \quad \Delta T = \left(\frac{\partial T}{\partial V}\right)_U \Delta V,$$

where ΔT and ΔV are small quantities. Since U is a state function and depends only on the initial and final states, ΔU is the same for both reversible and irreversible processes.

1.4



For any substance which goes through a reversible cyclic transformation, one has

$$\eta = \frac{W}{Q_2} = 1 - \frac{T_1}{T_2}$$

, where W is the net work done by the substance, Q_2 is the total amount of heat absorbed by the system, and T_2 and T_1 are the temperatures of the hot and cold reservoir, respectively.

During the expansion ABCD, heat is absorbed by the system during AB and during BC.

$$Q_{AB} = nL = (1\ \text{mol})(200\ \text{cal/mol}) = 200\ \text{cal}$$

Since BC is isothermal and the gas is ideal,

$$dU = 0 \Rightarrow dQ = p\,dV$$

$$\Rightarrow Q_{BC} = \int_{V_B}^{V_C} p\,dV = nRT_2 \int_{V_B}^{V_C} \frac{dV}{V} = RT_2 \ln \frac{V_c}{V_B}$$

$$\Rightarrow Q_{BC} = \left(1.986\ \frac{\text{cal}}{\text{deg}}\right)(300\ \text{K}) \ln\left(\frac{2.71828}{1}\right) = 595.7996\ \text{cal}$$

$$\Rightarrow Q_2 = Q_{AB} + Q_{BC} = 795.79\ \text{cal}$$

$$\Rightarrow W = Q_2\left[1 - T_1/T_2\right] = (795.79\ \text{cal})(0.5) = \underline{\underline{397.899\ \text{cal}}}$$

P 1.5 At constant $T = T_0$ the work done for the expansion $V_0 \to V$ is $W = R T_0 \ln \frac{V}{V_0}$.

The entropy is: $S = S(V,T) = R \frac{V_0}{V} \left(\frac{T}{T_0}\right)^a$, where V_0, T_0 and a are fixed constants.

(a) We have that $\left(\partial A/\partial T\right)_V = -S$ and $\left(\frac{\partial A}{\partial V}\right)_T = -P$

Thus: $dA_T = -(P\,dV)_T$ or $\int dA_T = \left(-\int P\,dV\right)_T = -W_T$

where W_T is the work done at constant

Thus: $A(T_0,V) - A(T_0,V_0) = -W_{T_0} =$

$$= -R T_0 \ln \frac{V}{V_0}$$

Thus: $\boxed{A(T_0,V) = A(T_0,V_0) - R T_0 \ln \frac{V}{V_0}}$ ① where $A(T_0,V_0)$ is a constant, which is the value of the Helmholtz free energy at T_0 and V_0.

Furthermore, from $S = -\left(\partial A/\partial T\right)_V$ one has

$$(dA)_V = -(S\,dT)_V \quad \text{or} \quad A(T,V) - A(T_0,V) = -\int_{T_0}^{T} S\,dT$$

$$\Rightarrow A(T,V) - A(T_0,V) = -\frac{R V_0}{V} \frac{\left(T^{a+1} - T_0^{a+1}\right)}{(a+1)\,T_0^a}$$

$$\Rightarrow \boxed{A(T,V) = A(T_0,V) - \frac{R V_0}{V} \frac{T^{a+1} - T_0^{a+1}}{(a+1)T_0^a}}$$

Combining with (1)

$\Rightarrow$

$$A(T,V) = A(T_0,V_0) - RT_0 \ln \frac{V}{V_0} - \frac{RV_0}{V} \frac{T^{a+1} - T_0^{a+1}}{(a+1)T_0^a}$$

(b) $$P = -\left(\frac{\partial A}{\partial V}\right)_T = \frac{RT_0}{V} - \frac{RV_0}{V^2} \frac{T^{a+1} - T_0^{a+1}}{(a+1)T_0^a}$$

(c) $$W = \int_{V_0}^{V} P\,dV = \int_{V_0}^{V} \frac{RT_0}{V} dV - \frac{\left(T^{a+1} - T_0^{a+1}\right)}{(a+1)T_0^a} RV_0 \int_{V_0}^{V} \frac{dV}{V^2} =$$

$$= RT_0 \ln \frac{V}{V_0} - \frac{\left(T^{a+1} - T_0^{a+1}\right)}{(a+1)T_0^a} RV_0 \left(\frac{1}{V_0} - \frac{1}{V}\right)$$

HOMEWORK

Extra 1: $S = A\,U^{3/4}\,V^{1/4}$ where $A = \text{const}$

(a) $$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = \frac{3}{4} A \left(\frac{V}{U}\right)^{1/4}$$

$$\boxed{\frac{U}{V} = \left(\frac{3A}{4}\right)^4 T^4}$$

(b) $$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_U = \frac{A}{4}\left(\frac{U}{V}\right)^{3/4}$$

$$P = T\,\frac{A}{4}\left(\frac{U}{V}\right)^{3/4}$$ From question (1)

However:

$$T = \frac{4}{3A}\left(\frac{U}{V}\right)^{1/4}$$

$$\Longrightarrow \quad P = \frac{4}{3A}\,\frac{A}{4}\left(\frac{U}{V}\right)^{1/4}\left(\frac{U}{V}\right)^{3/4} = \frac{1}{3}\,\frac{U}{V}$$

(c) $$\frac{S}{V} = A\left(\frac{U}{V}\right)^{3/4}$$ ← given by problem

$$\Longrightarrow \quad \frac{S}{V} = A\left(\frac{3A}{4}\right)^3 T^3 = \left(\frac{3}{4}\right)^3 A^4 T^3$$

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From thermal experiments one can link to equation of state measurements

$\text{đ}Q = T\,dS$

$\boxed{P\ V - T}$

$$\left\{\begin{aligned} C_v &= T\left(\frac{\partial S}{\partial T}\right)_{V,n} = \left(\frac{\text{đ}Q}{dT}\right)_{V,n} \\ C_p &= \left(\frac{\text{đ}Q}{dT}\right)_{p,n} = T\left(\frac{\partial S}{\partial T}\right)_{p,n} \end{aligned}\right.$$

Response functions

Intuitively, we expect the specific heats and compressibilities to be > 0.

This intuition will be justified in the following chapter in which we discuss thermodynamic stability

isothermal and adiabatic compressibilities

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

$$K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$

coefficient of thermal expansion

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

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· Example 1: $\left(\frac{\partial C_v}{\partial V}\right)_{T,n} = ?$

$$\left(\frac{\partial C_v}{\partial V}\right)_{T,n} = T\left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_{V,n}\right)_{T,n} =$$

$$= T\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_{T,n}\right)_{V,n} = T\left(\frac{\partial}{\partial T}\left(\frac{\partial p}{\partial T}\right)\right)_{V,n} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_{V,n}$$

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Example 2

$$(dS)_n = \left(\frac{\partial S}{\partial T}\right)_{V,n}(dT)_n + \left(\frac{\partial S}{\partial V}\right)_{T,n}(dV)_n$$

$$T\left(\frac{\partial S}{\partial T}\right)_{P,n} = T\left(\frac{\partial S}{\partial T}\right)_{V,n} + T\left(\frac{\partial S}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{P,n}$$

$$C_p = C_v + T\left(\frac{\partial P}{\partial T}\right)_{V,n}\left(\frac{\partial V}{\partial T}\right)_{P,n}$$

However for a function $f(x,y,z) = 0$

$$\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y = -1 \qquad f(P,V,T) = 0$$

$$\Rightarrow \left(\frac{\partial P}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{P,n}\left(\frac{\partial T}{\partial P}\right)_{V,n} = -1$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_{V,n} = -\left(\frac{\partial P}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{P,n}$$

$$\Rightarrow C_p = C_v - T\left(\frac{\partial P}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{P,n}^{2}$$

$$\boxed{C_p - C_v = +\frac{TV^{2}}{\cancel{V}K_T}\alpha^2 = \frac{TV}{K_T}\alpha^2}$$