Q4001 Thermodynamics of Materials September, 2019

Homework 5

Jesus Alberto Martínez Espinosa

A01750270 CEM

1. The Helmholtz function of a certain gas is

$$A = -\frac{n^2 a}{V} - nRT\ln(V-nb) + J(T)$$

where J is a function of T only. Derive an expression for the pressure of the gas.

We know that $dA = -SdT - PdV$

$$\left(\frac{\partial A}{\partial V}\right)_T = -S\cancelto{0}{dT} - PdV = -P\left(\frac{\partial V}{\partial V}\right)_T$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

Then,

$$\left(\frac{\partial A}{\partial V}\right)_T = \frac{n^2 a}{V^2} - nRT\left[\frac{1}{V-nb}\right] + \cancelto{0}{\frac{\partial J(T)}{\partial V}}$$

$$\left(\frac{\partial A}{\partial V}\right)_T = \frac{n^2 a}{V^2} - \frac{nRT}{V-nb} = -P$$

$$P = \frac{nRT}{V-nb} - \frac{n^2 a}{V^2}$$

2. The Gibbs function of a gas is given by

$$G = nRT\ln\left(\frac{P}{P_0}\right) - nBP$$

Where B is a function of T. Find the expression for:

(a) The equation of state

$$\partial G = -SdT + VdP$$

$$\left(\frac{\partial G}{\partial P}\right)_T = -\frac{S\partial T}{\partial P}^{0} + \frac{V\partial P}{\partial P} \rightarrow \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial G}{\partial P}\right)_T = nRT\left[\ln(P) - \ln(P_0)\right] - nB$$

$$\left(\frac{\partial G}{\partial P}\right)_T = nRT\left[\frac{1}{P}\right] - nB$$

$$\left(\frac{\partial G}{\partial P}\right)_T = \frac{nRT}{P} - nB$$

$$V = \frac{nRT}{P} - nB \rightarrow PV = nRT - nPB$$

(b) The entropy

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \left(\frac{\partial G}{\partial T}\right)_P = nR\ln\left(\frac{P}{P_0}\right) - nP\frac{\partial B}{\partial T}$$

$$\left(\frac{\partial G}{\partial T}\right)_P = nR\ln\left(\frac{P}{P_0}\right) - nP\frac{\partial B}{\partial T}$$

$$S = nP\frac{\partial B}{\partial T} - nR\ln\left(\frac{P}{P_0}\right)$$

c) The Helmholtz function

Using $A = U - TS$, $H = U + PV$, $G = H - TS$

$G = U + PV - TS \rightarrow G = U - TS + PV$

$G = A + PV$

$A = G - PV$ from (a) and

$A = nRT\ln\left(\frac{P}{P_0}\right) - nBP - PV$

$A = nRT\ln\left(\frac{P}{P_0}\right) - nBP - nRT + nPB$

$A = nRT\left[\ln\left(\frac{P}{P_0}\right) - 1\right]$

3. Read the article by J. Pellicer et al. "Thermodynamics of Rubber Elasticity".

4. With the information from Pellicer's paper

(a) Write an expression for conformation work for a elastic system at constant volume.

We can use the following equations from the appendix.

$dU = TdS - pdV + \tau dL$

the term $-PdV = 0$ owing to V constant, then

$dw = \tau dL$

$w = \tau \int_{L_0}^{L} dL$

(b) What is the relation between the constant k in this paper and the Young's modulus of the elastic material?

k is a constant (intensive) and is not possible to determine

$$F = -k\Delta x$$

$$E = \sigma E$$

E is an intensive quantity and depends on the material, E is determined experimentally. In the equation $\tau = kT\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right]$ and L_0 without stress.

k depends only on the composition and geometry and geometry In Hooke's Law, the constant is defined by the composition and geometry as well.

(c) Derive equations 2, 3, 6, 7, 9 and 10.

Equation (2)

$$dU = TdS - \cancel{pdV}^{\,0} + \tau dL$$

$$dU = TdS + \tau dL$$

$$\left(\frac{\partial U}{\partial L}\right)_{T,V} = T\left(\frac{\partial S}{\partial L}\right)_{T,V} + \tau\left(\frac{\partial L}{\partial L}\right)_{T,V}$$

$$\left(\frac{\partial U}{\partial L}\right)_{T,V} = \tau + T\left(\frac{\partial S}{\partial L}\right)_{T,V}$$

Equation (3) $\tau = kT\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right]$ $\left(\frac{\partial U}{\partial L}\right)_{T,V} = \tau + T\left(\frac{\partial S}{\partial L}\right)_{T,V}$

$$\left(\frac{\partial S}{\partial L}\right)_{T,V} = -\left(\frac{\partial \tau}{\partial T}\right)_{L,V}$$

$$\left(\frac{\partial \tau}{\partial T}\right)_{L,V} = kT\left[\frac{-L\frac{\partial L_0}{\partial T}}{L_0^2} - \frac{2}{L}\left(\frac{L_0}{L}\right)\frac{\partial L_0}{\partial T}\right]$$

$$\tau_0 = \frac{1}{L_0}\frac{\partial L_0}{\partial T}$$

Is the coefficient of linear expansion of rubber under zero stress

$$\tau = 0$$

$$\left(\frac{\partial \tau}{\partial T}\right)_{L,V} = kT\left[-\frac{1}{L_0}\left(\frac{L}{L_0}\right)\frac{\partial L_0}{\partial T} - \frac{2L_0}{L^2}\frac{\partial L_0}{\partial T}\left(\frac{L_0}{L_0}\right)\right]$$

$$\left(\frac{\partial \tau}{\partial T}\right)_{L,V} = kT\left[-\left(\frac{L}{L_0}\right)\frac{1}{L_0}\frac{\partial L_0}{\partial T} - \frac{2L_0^2}{L^2}\left(\frac{1}{L_0}\right)\frac{\partial L_0}{\partial T}\right]$$

$$\left(\frac{\partial \tau}{\partial T}\right)_{L,V} = kT\left[-\left(\frac{L}{L_0}\right)\tau_0 - 2\left(\frac{L_0}{L}\right)^2\tau_0\right]$$

$$-T\left(\frac{\partial \tau}{\partial T}\right)_{L,V} = kT^2\left(\frac{L}{L_0}\right)\tau_0 + 2kT^2\left(\frac{L_0}{L}\right)^2\tau_0$$

$$-T\left(\frac{\partial \tau}{\partial T}\right)_{L,V} = kT^2\tau_0\left[\frac{L}{L_0} + 2\left(\frac{L_0}{L}\right)^2\right]$$

$$\left(\frac{\partial U}{\partial L}\right)_{T,V} = \cancel{\tau}^{\,0} + T\left(\frac{\partial S}{\partial L}\right)_{T,V}$$

$$\left(\frac{\partial U}{\partial L}\right)_{T,V} = kT^2\tau_0\left[\frac{L}{L_0} + 2\left(\frac{L_0}{L}\right)^2\right]$$

Equation (6)

$$\lambda_{\tau,V} = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_{\tau,V} = \lambda_0 - \frac{1}{T}\frac{\left(\frac{L}{L_0}\right)^3 - 1}{\left(\frac{L}{L_0}\right)^3 + 2}$$

$$-\left(\frac{\partial \tau}{\partial T}\right)_{L,V} = kT\left[\left(L(-1)\left(\frac{1}{L_0^2}\right)\frac{\partial L_0}{\partial T} + \frac{1}{L_0}\frac{\partial L}{\partial T}\right) - \left(L_0^2(-2)\left(\frac{1}{L^3}\right)\frac{\partial L}{\partial T} + \frac{2L_0}{L^2}\frac{\partial L_0}{\partial T}\right)\right]$$

$$-\left(\frac{\partial \tau}{\partial T}\right)_{L,V} = kT\left[-\frac{L}{L_0}\lambda_0 + \frac{1}{L_0}\frac{\partial L}{\partial T} + \frac{2L_0^2}{L^3}\frac{\partial L}{\partial T} - \frac{2L_0^2}{L^2}\lambda_0\right]$$

$$0 = kT\left[-\frac{L}{L_0}\lambda_0 + \frac{1}{L_0}\frac{\partial L}{\partial T} + \frac{2L_0^2}{L^3}\frac{\partial L}{\partial T} - \frac{2L_0^2}{L^2}\lambda_0\right] + \frac{\partial \tau}{\partial T}$$

$$0 = kT\left[-\frac{1}{L_0}\lambda_0 + \frac{1}{L_0}\frac{\partial L}{\partial T} + \frac{2L_0^2}{L^3}\frac{\partial L}{\partial T} - \frac{2L_0^2}{L^2}\lambda_0\right] + \frac{\partial}{\partial T}kT\left[\frac{L}{L_0} - \frac{L_0^3}{L^2}\right]$$

$$0 = kT\left[-\frac{1}{L_0}\lambda_0 + \frac{1}{L_0}\frac{\partial L}{\partial T} + \frac{2L_0^2}{L^3}\frac{\partial L}{\partial T} - \frac{2L_0^2}{L^2}\lambda_0\right] + k\left[\frac{L}{L_0} - \frac{L_0^2}{L^2}\right]\frac{\partial T}{\partial T}$$

$$0 = -\frac{TL}{L_0}\lambda_0 + \frac{T}{L_0}\frac{\partial L}{\partial T} + \frac{2TL_0^2}{L^3}\frac{\partial L}{\partial T} - \frac{2TL_0^2}{L^2}\lambda_0 + \frac{L}{L_0} - \frac{L_0^2}{L^2}$$

$$\left(\frac{L^2}{L_0^2}\right)0 = \left[\lambda_0\left(-\frac{TL}{L_0} - \frac{2TL_0^2}{L^2}\right) + \frac{\partial L}{\partial T}\left(\frac{T}{L_0} + \frac{2TL_0^2}{L^3}\right) + \frac{L}{L_0} - \frac{L_0^2}{L^2}\right]\frac{L^2}{L_0^2}$$

$$0 = \lambda_0\left(-\frac{TL^3}{L_0^3} - 2T\right) + \frac{\partial L}{\partial T}\left(\frac{TL^2}{L_0^3} + \frac{2T}{L}\right) + \left(\frac{L^3}{L_0^3} - 1\right)$$

$$\frac{1}{L}\frac{\partial L}{\partial T}\left(\frac{TL^3}{L_0^3} + 2T\right) = \lambda_0\left(\frac{TL^3}{L_0^3} + 2T\right) - \left(\frac{L^3}{L_0^3} - 1\right)$$

$$\frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_{\tau,V} = \lambda_0\frac{\left(\frac{TL^3}{L_0^3} + 2T\right)}{\left(\frac{TL^3}{L_0^3} + 2T\right)} - \frac{\left(\frac{L^3}{L_0^3} - 1\right)}{\left(T\frac{L^3}{L_0^3} + 2T\right)}$$

$$\frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_{\tau,V} = \lambda_0 - \frac{1}{T}\frac{\left[\left(\frac{L}{L_0}\right)^3 - 1\right]}{\left[\left(\frac{L}{L_0}\right)^3 + 2\right]}$$

Equation (7)

$$L_o(T) = L_o(T_o)\exp[\chi_o(T-T_o)]$$

using (4)

$$\chi_o = \frac{1}{L_o}\frac{\partial L_o}{\partial T}$$

$$\int_{T_o}^{T} \chi_o \, \partial T = \int \frac{\partial L_o}{L_o} \rightarrow \chi_o(T-T_o) + C = \ln(L_o)$$

$$\rightarrow e^{\chi_o(T-T_o)+C} = e^{\ln(L_o)}$$

$$e^{\chi_o(T-T_o)} e^{C} = L_o$$

$$e^{\chi_o(T-T_o)} K = L_o$$

where K may take the initial conditions of the rubber, then

$$e^{\chi_o(T-T_o)} L_o(T_o) = L_o(T)$$

Equation 9.

Using equations 7 and 6

$$\lambda_0 = \lambda_{\tau,v} + \frac{1}{T}\frac{[L/L_0(T)]^3 - 1}{[L/L_0(T)]^3 + 2}$$

$$L_0(T) = L_0(T_0)\exp[\lambda_0(T-T_0)]$$

Then

$$L_0(T) = L_0(T_0)\exp\left\{\lambda_{\tau,v} + \frac{1}{T}\frac{\left[\frac{L}{L_0(T)}\right]^3 - 1}{\left[\frac{L}{L_0(T)}\right]^3 + 2}(T-T_0)\right\}$$

Substituting in eq. (1)

$$\tau = kT\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right] = kT\left[e^{(T-T_0)\lambda_{T,v}} - \left(\frac{1}{e^{(T-T_0)\lambda_{T,v}}}\right)^2\right]$$

$$\left(\frac{\partial\tau}{\partial T}\right)_{L,v} = kT\left[e^{(T-T_0)\lambda_{T,v}} - \left(\frac{1}{e^{(T-T_0)\lambda_{T,v}}}\right)^2\right] - kT\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right]$$

$$\left(\frac{\partial\tau}{\partial T}\right)_{L,v} = k\left\{e^{(T-T_0)\lambda_{T,v}} - \left(\frac{1}{e^{(T-T_0)\lambda_{T,v}}}\right)^2 + T\left[e^{(T-T_0)\lambda}(T-T_0)\right.\right.$$
$$+ 2\left(e^{(T-T_0)\lambda}\right)^3 \exp^{(T-T_0)}\lambda_{\tau,v}(T-T_0)$$

$$\left(\frac{\partial\tau}{\partial T}\right) = -k\lambda_{\gamma,v}T\left[\alpha_0 e^{[-\lambda_0(T-T_0)]} + \frac{2}{\alpha_0^2}e^{[2\lambda_0(T-T_0)]}\right]$$

(10) $\tau = kT\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right]$

$$\left(\frac{\partial \tau}{\partial T}\right)_{L,V} = k\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right] + kT\left[-\frac{L}{L_0^2}\left(\frac{\partial L_0}{\partial T}\right)_{L,V} + \frac{2L_0}{L^2}\left(\frac{\partial L_0}{\partial T}\right)_{L,V}\right]$$

Using $L_0(T) = L_0(T_0)\, e^{[T-T_0]}$

$$\left(\frac{\partial L_0(T)}{\partial T}\right)_{T,V} = \gamma_0 L_0(T)$$

$$\left(\frac{\partial \tau}{\partial T}\right)_{L,V} = k\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right] + kT\left[-\frac{L}{L_0^2}(\gamma_0 L_0) + \frac{2L_0^2 \gamma_0}{L^2}\right]$$

$$S(T,L) = S_0(T) + \int_{L_0}^{L}\left(\frac{\partial S}{\partial L}\right)_{T,V} dL$$

$$\int\left(\frac{\partial S}{\partial L}\right)_{T,V} dL = -\int_{L_0}^{L}\left(\frac{\partial \tau}{\partial T}\right)_{L,V} dL$$

$$= -k\int_{L_0}^{L}\left[\left(\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right) - T\left[\frac{\gamma_0 L}{L_0} - 2\gamma_0\left(\frac{L_0}{L}\right)^2\right]\right] dL$$

$$-kL_0\left[\frac{L^2}{2L_0^2} + \frac{L_0}{L} - \frac{3}{2} - \gamma_0 T\left(\frac{L^2}{2L_0^2} - \frac{2L_0}{L} + \frac{3}{2}\right)\right]$$

$$S(T,L) = S_0(T) + \int_{L_0}^{L}\left(\frac{\partial S}{\partial L}\right)_{T,V} dL$$

$$\rightarrow S_0(T) - \int_{L_0}^{L}\left(\frac{\partial \tau}{\partial T}\right)_{L,V} dL$$

$$S(T,L) = S_0(T) - kL_0\left[\frac{L^2}{2L_0^2} + \frac{L_0}{L} - \frac{3}{2} - \gamma_0 T\left(\frac{L^2}{2L_0^2} - \frac{2L_0}{L} + \frac{3}{2}\right)\right]$$

(e) Why is it that rubberlike elasticity is an entropic effect?

According to (1)

$$\left(\frac{\partial S}{\partial L}\right)_T = \left(\frac{\partial L}{\partial T}\right)_F \left(\frac{\partial F}{\partial L}\right)_T$$

If we consider a change is the sign, determined by observing the temperature dependence of the elastic band length under the condition of constant tension $\left(\frac{\partial L}{\partial T}\right)_\tau$. The determination of $\left(\frac{\partial L}{\partial T}\right)_\tau$ will give the sign of $\left(\frac{\partial S}{\partial L}\right)_T$.

Using deformation force, whic has an energetic and entropic effect

$$f = \left(\frac{\partial U}{\partial L}\right)_{V,T} - T\left(\frac{\partial S}{\partial L}\right)_{V,T}$$

When stretching a rubber, the force exerted is not used to vary the internal energy but to make variations of conformation that decrease entropy. Then

$$f = \cancel{\left(\frac{\partial U}{\partial L}\right)_{V,T}}^{\,0} - T\left(\frac{\partial S}{\partial L}\right)_{V,T}$$

$$f = -T\left(\frac{\partial S}{\partial L}\right)_{V,T}$$

5. Demonstrate the following thermodynamic relations:

(a) $C_p = C_v + \frac{\alpha^2 TV}{K_T}$

We can modify the equation

$$C_p - C_v = \frac{\alpha^2 TV}{K_T} \qquad S = S(V,T) \quad V = V(T,P)$$

$$\partial S = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

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

$$\partial S = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T \cdot \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP\right]$$

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

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

1) Deriving at P constant

$$\left(\frac{\partial S}{\partial T}\right)_P = \left[\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P\right]\left(\frac{\partial T}{\partial T}\right)_P + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T \cancel{\left(\frac{\partial P}{\partial T}\right)_P}^{\,0}$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

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

$$\frac{C_p - C_v}{T} = \frac{\alpha}{K_T}(V\alpha)$$

$$C_p - C_v = \frac{TV\alpha^2}{K_T}$$

(b) $k_T - k_S = \frac{\alpha^2 \bar{V} T}{C_p}$ where $k_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$

$$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T + \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$

$$\frac{1}{V}\left[-\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial V}{\partial P}\right)_S\right]$$

$$\frac{1}{V}\left[k_T V + \left(\frac{\partial V}{\partial P}\right)_S\right]$$

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

$$\left(\frac{\partial V}{\partial P}\right)_S = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_S + \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial P}\right)_S$$

$$\left(\frac{\partial V}{\partial P}\right)_S = \bar{V}\alpha \left(\frac{\partial T}{\partial P}\right)_S + (-k_T V)$$

Finding $\left(\frac{\partial T}{\partial P}\right)_S = \frac{-\left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_P} = \frac{\bar{V}\alpha}{\frac{C_p}{T}} = \frac{T\bar{V}\alpha}{C_p}$

$$\left(\frac{\partial V}{\partial P}\right)_S = \bar{V}\alpha\left(\frac{T\bar{V}\alpha}{C_p}\right) - k_T V$$

$$\frac{1}{V}\left[k_T V + \frac{\bar{V}^2\alpha^2 T}{C_p} - k_T V\right]$$

$$\frac{1}{V}\left[\frac{\bar{V}^2\alpha^2 T}{C_p}\right] = \frac{V\alpha^2 T}{C_p}$$

(c) $\frac{K_T}{K_S} = \frac{\bar{C_p}}{\bar{C_v}}$

We know that $\frac{C_p}{T} = \left(\frac{\partial S}{\partial T}\right)_p$ and $\frac{C_v}{T} = \left(\frac{\partial S}{\partial T}\right)_V$

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

$$\frac{C_p}{C_v} = \frac{T\left(\frac{\partial S}{\partial T}\right)_p}{T\left(\frac{\partial S}{\partial T}\right)_V} = \frac{\left(\frac{\partial S}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_V}$$

But, It is necessary to find other expression for

$$\left(\frac{\partial S}{\partial T}\right)_p \text{ and } \left(\frac{\partial S}{\partial T}\right)_V$$

Using $\left(\frac{\partial y}{\partial x}\right)_z\left(\frac{\partial z}{\partial y}\right)_x\left(\frac{\partial x}{\partial z}\right)_y = -1$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{-1}{\left(\frac{\partial p}{\partial S}\right)_T\left(\frac{\partial T}{\partial p}\right)_S} \quad \text{and}$$

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

Then

$$\frac{\left(\frac{\partial S}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_V} = \frac{\dfrac{-1}{\left(\frac{\partial p}{\partial S}\right)_T\left(\frac{\partial T}{\partial p}\right)_S}}{\dfrac{-1}{\left(\frac{\partial V}{\partial S}\right)_T\left(\frac{\partial T}{\partial V}\right)_S}} = \frac{-\left(\frac{\partial V}{\partial S}\right)_T\left(\frac{\partial T}{\partial V}\right)_S}{-\left(\frac{\partial p}{\partial S}\right)_T\left(\frac{\partial T}{\partial p}\right)_S}$$

$$\rightarrow \frac{\left(\frac{\partial V}{\partial S}\right)_T\left(\frac{\partial T}{\partial V}\right)_S}{\left(\frac{\partial p}{\partial S}\right)_T\left(\frac{\partial T}{\partial p}\right)_S} = \text{using } \left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \text{ and } \left(\frac{\partial y}{\partial t}\right)_z\left(\frac{\partial t}{\partial x}\right)_z = \left(\frac{\partial y}{\partial x}\right)_z$$

$$\rightarrow \frac{\left(\frac{\partial V}{\partial S}\right)_T \cdot \left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_S \cdot \left(\frac{\partial T}{\partial p}\right)_S} = \frac{\left(\frac{\partial V}{\partial p}\right)_T}{\left(\frac{\partial V}{\partial p}\right)_S} \cdot \left(\frac{-\frac{1}{V}}{-\frac{1}{V}}\right) = \frac{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T}{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S} = \frac{K_T}{K_S}$$

(d) $\left(\frac{\partial H}{\partial V}\right)_S = \frac{-C_p}{K_T C_V}$

$\partial H = TdS + VdP$

$\left(\frac{\partial H}{\partial V}\right)_S = T\left(\frac{\partial S}{\partial V}\right)_S + V\left(\frac{\partial P}{\partial V}\right)_S$ $\left(\frac{\partial S}{\partial V}\right)_S \to 0$

$\left(\frac{\partial H}{\partial V}\right)_S = V\left(\frac{\partial P}{\partial V}\right)_S$

$\left(\frac{\partial V}{\partial P}\right)_S = \frac{\bar{V}^2\alpha^2 T}{C_p} - K_T V$ → from exercise two

$\left(\frac{\partial P}{\partial V}\right)_S = \frac{1}{\frac{\bar{V}^2\alpha^2 T}{C_p} - K_T V\left(\frac{C_p}{C_p}\right)} = \frac{1}{\frac{\bar{V}^2\alpha^2 T - K\bar{V}C_p}{C_p}}$

$\left(\frac{\partial P}{\partial V}\right)_S = \frac{C_p}{\bar{V}^2\alpha^2 T - K_T\bar{V}C_p}$

$\left(\frac{\partial H}{\partial V}\right)_S = \bar{V}\left(\frac{C_p}{\bar{V}^2\alpha^2 T - K_T\bar{V}C_p}\right)$

$\left(\frac{\partial H}{\partial V}\right)_S = \frac{C_p}{V\alpha^2 T - K_T C_p}$

from exercise (1)

$K_T\left(C_V\right) = \left(C_p - \frac{\alpha^2 TV}{K_T}\right)K_T$

$(-1)\left(K_T C_V\right) = \left(C_p K_T - \alpha^2 TV\right)(-1)$

$-K_T C_V = \alpha^2 TV - C_p K_T$

$\left(\frac{\partial H}{\partial V}\right)_S = \frac{C_p}{-K_T C_V}$

$\left(\frac{\partial H}{\partial V}\right)_S = -\frac{C_p}{K_T C_V}$

(e) $\left(\frac{\partial C_p}{\partial P}\right)_T = -TV\left(\alpha^2 + \frac{\partial \alpha}{\partial T}\right)$

$\frac{C_p}{T} = \left(\frac{\partial S}{\partial T}\right)_P \rightarrow C_p = T\left(\frac{\partial S}{\partial T}\right)_P$

$\left(\frac{\partial C_p}{\partial P}\right)_T = T \frac{\partial}{\partial P}\Big|_T \left(\frac{\partial S}{\partial T}\right)_P$

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

$\left(\frac{\partial C_p}{\partial P}\right)_T = T\frac{\partial}{\partial T}\left(-\frac{\partial V}{\partial T}\right)_P \qquad \partial S = \frac{C_p}{T} dT - \alpha V dP$

$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)$

$\partial V = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \searrow 0$

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

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

$\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P = \bar{V}\left(\frac{\partial \alpha}{\partial T}\right)_P + \left(\frac{\partial V}{\partial T}\right)_P \alpha$

$= -T\left(\bar{V}\left(\frac{\partial \alpha}{\partial T}\right)_P + V\alpha \cdot \alpha\right)$

$-T\bar{V}\left[\left(\frac{\partial \alpha}{\partial T}\right)_P + \alpha^2\right]$