

$$1) \text{ Show that: } \left. \frac{\partial U}{\partial P} \right|_T = -T \left. \frac{\partial V}{\partial T} \right|_P - P \left. \frac{\partial V}{\partial P} \right|_T$$

This relation is obtain in the following steps, —

$$\textcircled{1} \quad dU = Tds - pdv$$

differentiating both sides w.r.t. P at cont. T

$$\left. \frac{\partial U}{\partial P} \right|_T = T \cdot \left. \frac{\partial S}{\partial P} \right|_T - P \cdot \left. \frac{\partial v}{\partial P} \right|_T$$

$$\textcircled{2} \quad \text{Maxwell's heat relation: } \left. \frac{\partial v}{\partial T} \right|_P = - \left. \frac{\partial S}{\partial P} \right|_T$$

From $\textcircled{1}$ and $\textcircled{2}$ the result is obtained

$$2) \text{ By definition: } C_V = -T \left. \frac{\partial S}{\partial T} \right|_V$$

$$\text{By Aux \& eqn: } dA = -pdV - SdT$$

$$\text{from this eqn: } S = - \left. \frac{\partial A}{\partial T} \right|_V$$

Substituting in the above eqn for C_V gives, —

$$C_V = -T \frac{\partial}{\partial T} \left[- \left. \frac{\partial A}{\partial T} \right|_V \right]_V$$

$$\therefore C_V = -T \left. \frac{\partial^2 A}{\partial T^2} \right|_V$$

3) This example is solved in the following steps. Since C_V and C_P occur in two Tds eqn the soln begins with them.

$$\textcircled{1} \quad TdS = mC_VdT + T \left. \frac{\partial P}{\partial T} \right|_V dV$$

For an isentropic process $\Rightarrow dS = 0$ ~~($S = \text{const}$)~~

$$\therefore mC_V = -T \left. \frac{\partial P}{\partial T} \right|_V \cdot \left. \frac{\partial V}{\partial T} \right|_S$$

$$\textcircled{2} \quad \text{Again, } TdS = mC_PdT + T \left. \frac{\partial V}{\partial T} \right|_P dP$$

isentropic pros.
OR, $mC_P = T \left. \frac{\partial V}{\partial T} \right|_P \left. \frac{\partial P}{\partial T} \right|_S$

$$\textcircled{3} \quad \frac{C_P}{C_V} = \frac{mC_P}{mC_V} = - \left. \frac{\partial V}{\partial T} \right|_P \left. \frac{\partial T}{\partial P} \right|_V \left. \frac{\partial P}{\partial V} \right|_S$$

$$\textcircled{4} \quad \text{cyclic relation gives: } \left. \frac{\partial V}{\partial T} \right|_P \left. \frac{\partial T}{\partial P} \right|_V \left. \frac{\partial P}{\partial V} \right|_T = -1$$

$$\therefore \left. \frac{\partial V}{\partial T} \right|_P \left. \frac{\partial T}{\partial P} \right|_V = -\frac{1}{\left. \frac{\partial P}{\partial V} \right|_T}$$

$\textcircled{5}$ From step $\textcircled{3}$ & $\textcircled{4}$

$$\frac{C_P}{C_V} = \frac{\left. \frac{\partial P}{\partial V} \right|_S}{\left. \frac{\partial P}{\partial V} \right|_T} \quad (\text{proved})$$

B_S
isentropic
Bulk modulus

B_T
isothermal
Bulk modulus

$$4) \quad ds = \frac{C_v}{T} dt + \left. \frac{\partial P}{\partial T} \right|_V dV$$

Similarly it can be shown using forth Maxwell's relation that

$$ds = \frac{C_p}{T} dt + \left. \frac{\partial V}{\partial T} \right|_P dP$$

Using the above two eqn. and solving for dP ,

$$dP = \frac{\frac{C_p - C_v}{T}}{\left. \frac{\partial V}{\partial T} \right|_P} dt - \left. \frac{\frac{\partial P}{\partial T} \Big|_V}{\frac{\partial V}{\partial T} \Big|_P} \right. dV$$

Considering P as a func of T and V , we can see that

$$\frac{\frac{C_p - C_v}{T}}{\left. \frac{\partial V}{\partial T} \right|_P} = \left. \frac{\partial P}{\partial T} \right|_V$$

Two thermodynamic properties can be defined at this stage,

$$\beta \equiv \frac{1}{V} \cdot \left. \frac{\partial V}{\partial T} \right|_P$$

$$\alpha R \equiv -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T$$

β is called isobaric compressibility

αR is " isothermal "

now $\left. \frac{\partial P}{\partial T} \right|_V \cdot \left. \frac{\partial T}{\partial V} \right|_P \cdot \left. \frac{\partial V}{\partial P} \right|_T = -1$

$$\left. \frac{\partial P}{\partial T} \right|_V = - \frac{\left. \frac{\partial V}{\partial P} \right|_T}{\left. \frac{\partial V}{\partial T} \right|_P} = \frac{\beta}{R}$$

$$\text{Therefore, } C_p - C_v = - \frac{T \left(\frac{\partial V}{\partial P} \Big|_P \right)^2}{\frac{\partial V}{\partial P} \Big|_T}$$

Since $\frac{\partial V}{\partial P} \Big|_T$ is always -ve for all stable substances, C_p is always greater than C_v

∴ we wish to produce the derivative: $\frac{\partial U}{\partial V} \Big|_T$

$$\text{we start with: } U = A + TS$$

Then form the needed derivative:

$$\frac{\partial U}{\partial V} \Big|_T = \frac{\partial A}{\partial V} \Big|_T + T \frac{\partial S}{\partial V} \Big|_T$$

Now, we apply an appropriate Maxwell relation

$$\frac{\partial S}{\partial V} \Big|_T = \frac{\partial P}{\partial T} \Big|_V$$

and get:

$$\frac{\partial U}{\partial V} \Big|_T = \frac{\partial A}{\partial V} \Big|_T + T \frac{\partial P}{\partial T} \Big|_V$$

Finally, we recognize:

$$\frac{\partial A}{\partial V} \Big|_T = -P \quad \text{and} \quad \frac{\partial P}{\partial T} \Big|_V = \frac{\alpha}{R}$$

This then gives:

$$\frac{\partial U}{\partial V} \Big|_T = -P + T \frac{\partial P}{\partial T} \Big|_V = -P + \frac{T\alpha}{R}$$

Notice we have converted the need to make U vs V measurements ~~into~~ into making measurements of α and R , which are much easier for a van der Waals Gas:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\text{So, } \left. \frac{\partial P}{\partial T} \right|_V = \frac{R}{V-b}$$

$$\text{And, } \left. \frac{\partial U}{\partial V} \right|_T = -P + T \cdot \frac{R}{V-b}$$

$$\therefore \left. \frac{\partial U}{\partial V} \right|_T = -\frac{RT}{V-b} + \frac{a}{V^2} + \frac{RT}{V-b}$$

$$\therefore \left. \frac{\partial U}{\partial V} \right|_T = \frac{a}{V^2}$$

7) ① By definition: $G_1 = H - TS$ or, $dG_1 = Vdp - SdT$

② Since G_1 is a property, $S = -\left. \frac{\partial G_1}{\partial T} \right|_p$

③ Substituting for S in the defining relation for G_1 gives, $G_1 = H + T \left. \frac{\partial G_1}{\partial T} \right|_p$ and transposing

this gives, $\frac{G_1}{T} - \left. \frac{\partial G_1}{\partial T} \right|_p = \frac{H}{T}$

④ Now, $\frac{\partial}{\partial T} \left(\frac{G_1}{T} \right)_p = \frac{1}{T} \cdot \left. \frac{\partial G_1}{\partial T} \right|_p - \frac{G_1}{T^2}$

$$\textcircled{5} \text{ Hence, } \frac{G}{T} - \left. \frac{\partial G}{\partial T} \right|_P = -T \left. \frac{\partial}{\partial T} \left(\frac{d}{T} \right) \right|_P$$

\textcircled{6} Combining with step \textcircled{3} above, step \textcircled{5} becomes

$$-T \left. \frac{\partial}{\partial T} \left(\frac{d}{T} \right) \right|_P = \frac{H}{T}$$

$$\therefore \left. \frac{\partial (d/T)}{\partial T} \right|_P = -\frac{H}{T^2}$$

8) Initial temp 298K, $\alpha = 2.2 \times 10^{-5} \text{ K}^{-1}$
 $C_p = 80 \text{ J mol}^{-1} \text{ K}^{-1}$

The problem requires calculation of the variation in temp. with pres. at cont. entropy i.e. $\left. \frac{\partial T}{\partial P} \right|_S$

Using variable T, P, S : $\left. \frac{\partial T}{\partial P} \right|_S \left. \frac{\partial P}{\partial S} \right|_T \left. \frac{\partial S}{\partial T} \right|_P = -1 \quad \text{(i)}$

The definition of the molal cont. pres. heat capacity

$$C_p = T \left. \frac{\partial S}{\partial T} \right|_P \text{ gives } \left. \frac{\partial S}{\partial T} \right|_P = \frac{C_p}{T} \quad \text{(ii)}$$

The inverse of Maxwell's eqn 4 i.e. eqn #13 in sheet

$$\left. \frac{\partial P}{\partial S} \right|_T = - \left. \frac{\partial T}{\partial V} \right|_P \quad \text{(iii)}$$

and the isobaric thermal expansivity is defined as

$$\alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P \text{ or, } \left. \frac{\partial V}{\partial T} \right|_P = \alpha V \quad \text{(iv)}$$

Substituting Eqn. (ii) - (iv) into Eqn. (i) and rearranging gives, —

$$\left. \frac{\partial T}{\partial P} \right|_S \left. \frac{\partial P}{\partial S} \right|_T \frac{C_P}{T} = 1$$

$$\text{or, } \left. \frac{\partial T}{\partial P} \right|_S \left(-\frac{1}{V\alpha} \right) \frac{C_P}{T} = -1$$

$$\text{or, } \left. \frac{\partial T}{\partial P} \right|_S = \frac{T V\alpha}{C_P}$$

It is reasonable to assume that Al_2O_3 is an incompressible solid and that its heat capacity does not vary significantly over small ranges of temp. and pres. Thus, the variables can be separated for integration

$$\left. \frac{\partial T}{\partial P} \right|_S = \frac{T V\alpha}{C_P}$$

$$\text{or, } \frac{dT}{T} = \frac{V\alpha dP}{C_P} \quad \text{at cont. } S \quad (\text{ans adiabatic pres.})$$

$$\text{or, } \ln \frac{T_2}{T_1} = \left(\frac{V\alpha}{C_P} \right) \Delta P$$

$$\text{or, } \ln \frac{T_2}{298} = \frac{2.56 \times 10^{-5} \frac{m^3}{mol}}{80 \frac{J}{mol \cdot K}} \frac{2.2 \times 10^{-5} \frac{1}{K}}{x 500 \times 10^6 \frac{N}{m^2}}$$

$$\text{or, } \ln \left(\frac{T_2}{298} \right) = 0.00352$$

$$\therefore T_2 = 299 \text{ K} \quad \text{and} \quad \Delta T = (299 - 298) \text{ K} = 1 \text{ K}$$