ECHE363 Homework 6 - Due 03/21/25 **Trevor Swan (tcs94)**

1. From Textbook: Section 4.3: $\beta \equiv \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_P$ eq. 4.32, $\kappa \equiv -\frac{1}{V_m}\left(\frac{\partial V_m}{\partial P}\right)_T$ eq. 4.33

a) $\left(\frac{\partial P}{\partial T}\right)_{V_m} = \frac{\beta}{\kappa}$?

Cyclic Rule: $\left(\frac{\partial P}{\partial T}\right)_{V_m}\left(\frac{\partial V_m}{\partial P}\right)_T\left(\frac{\partial T}{\partial V_m}\right)_P = -1$

$$\left(\frac{\partial P}{\partial T}\right)_{V_m} \overset{\text{cyclic}}{=} -\frac{1}{\left(\frac{\partial V_m}{\partial P}\right)_T\left(\frac{\partial T}{\partial V_m}\right)_P} \overset{\text{reciprocal}}{=} -\frac{\left(\frac{\partial V_m}{\partial T}\right)_P^*}{\left(\frac{\partial V_m}{\partial P}\right)_T^*}$$

$$\beta = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_P \Rightarrow \left(\frac{\partial V_m}{\partial T}\right)_P = \beta(V_m)^*$$

$$\kappa = -\frac{1}{V_m}\left(\frac{\partial V_m}{\partial P}\right)_T \Rightarrow \left(\frac{\partial V_m}{\partial P}\right)_T = \kappa(-V_m)^*$$

$$\boxed{\therefore \left(\frac{\partial P}{\partial T}\right)_{V_m} = -\frac{\beta(V_m)}{\kappa(-V_m)} = \frac{\beta}{\kappa}}$$ Matches!

b) $C_{P,m} - C_{V,m} = \frac{V_m T\beta^2}{\kappa}$?

Use entropy (dS_m) expressions to relate $C_{P,m}$ & $C_{V,m}$: Both derived in class

(i) $dS_m = \frac{C_{V,m}}{T}dT + \left(\frac{\partial P}{\partial T}\right)_{V_m}dV_m$

(ii) $dS_m = \frac{C_{P,m}}{T}dT - \left(\frac{\partial V_m}{\partial T}\right)_P dP$

Equate dS_m expressions

$$\therefore \frac{C_{V,m}}{T}dT + \left(\frac{\partial P}{\partial T}\right)_{V_m}dV_m = \frac{C_{P,m}}{T}dT - \left(\frac{\partial V_m}{\partial T}\right)_P dP$$

$$\left(\frac{\partial P}{\partial T}\right)_{V_m}dV_m + \left(\frac{\partial V_m}{\partial T}\right)_P dP = \frac{C_{P,m}}{T}dT - \frac{C_{V,m}}{T}dT$$

$$dT = \left[\left(\frac{\partial P}{\partial T}\right)_{V_m}\cancel{dV_m} + \left(\frac{\partial V_m}{\partial T}\right)_P \cancel{dP}\right]\cdot\frac{T}{C_{P,m}-C_{V,m}}$$

'Divide' dT by dP, const. V_m: $\left(\frac{\partial T}{\partial P}\right)_{V_m} = \frac{T}{C_{P,m}-C_{V,m}}\left(\frac{\partial V_m}{\partial T}\right)_P$ Isn't necessary here!

'Divide' dT by dV_m, const. P: $\left(\frac{\partial T}{\partial V_m}\right)_P = \frac{T}{C_{P,m}-C_{V,m}}\left(\frac{\partial P}{\partial T}\right)_{V_m} = \frac{T}{C_{P,m}-C_{V,m}}\left(\frac{\beta}{\kappa}\right)$ Proved in part (a)

$$\hookrightarrow \beta = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_P \Rightarrow \left(\frac{\partial V_m}{\partial T}\right)_P = \beta(V_m)^* \Rightarrow \left(\frac{\partial T}{\partial V_m}\right)_P = \frac{1}{\beta V_m}$$

Make substitution

$$\therefore \frac{1}{\beta V_m} = \frac{T}{C_{P,m}-C_{V,m}}\left(\frac{\beta}{\kappa}\right) \Rightarrow \boxed{C_{P,m}-C_{V,m} = \frac{T\beta^2 V_m}{\kappa}}$$ Matches!

2. $Z = \frac{Pv_m}{RT} = 1 + B'P + C'P^2$ where B' & C' are constants, no T dependence!

(i) $\left(\frac{\partial h_m}{\partial P}\right)_T$, (ii) $\left(\frac{\partial h_m}{\partial P}\right)_{s_m}$, (iii) $\left(\frac{\partial h_m}{\partial T}\right)_P$, (iv) $\left(\frac{\partial h_m}{\partial T}\right)_{s_m}$ ~~in terms of~~ B', C', R, P, T, $c_{P,m}$

(i) $\left(\frac{\partial h_m}{\partial P}\right)_T$ FE: $dh_m = Tds_m + v_m dP$ → 'Divide' by dP, enforcing constant T

$$\left(\frac{\partial h_m}{\partial P}\right)_T = T\left(\frac{\partial s_m}{\partial P}\right)_T + v_m \xRightarrow[\text{relation}]{\text{maxwell}} \left(\frac{\partial h_m}{\partial P}\right)_T = -T\left(\frac{\partial v_m}{\partial T}\right)_P + v_m$$

$$\left(\frac{\partial v_m}{\partial T}\right)_P : \quad v_m = \frac{RT}{P}\left(1 + B'P + C'P^2\right)$$

$$\left(\frac{\partial h_m}{\partial P}\right)_T = 0$$

$$\left(\frac{\partial v_m}{\partial T}\right)_P = \frac{\partial}{\partial T}\left[\frac{RT}{P}\left(1 + B'P + C'P^2\right)\right] = \frac{R}{P}\left(1 + B'P + C'P^2\right)$$

$$\left(\frac{\partial h_m}{\partial P}\right)_T = -T\left[\frac{R}{P}\left(1 + B'P + C'P^2\right)\right] + v_m = -v_m + v_m = 0$$

(ii) $\left(\frac{\partial h_m}{\partial P}\right)_{s_m}$ FE: $dh_m = Tds_m + v_m dP$ → 'Divide' by dP, enforcing constant s_m

$$\left(\frac{\partial h_m}{\partial P}\right)_{s_m} = v_m = \frac{RT}{P}\left(1 + B'P + C'P^2\right)$$

(iii) $\left(\frac{\partial h_m}{\partial T}\right)_P$

$$\left(\frac{\partial h_m}{\partial T}\right)_P = c_{P,m}$$ This is the definition of $c_{P,m}$

(iv) $\left(\frac{\partial h_m}{\partial T}\right)_{s_m}$ FE: $dh_m = T\,ds_m + V_m\,dP$ → 'Divide' by dT, enforcing constant S_m

$$\left(\frac{\partial h_m}{\partial T}\right)_{s_m} = V_m\left(\frac{\partial P}{\partial T}\right)_{s_m}$$

No maxwell relation :: reciprocal

Cycle Rule: $\left(\frac{\partial P}{\partial T}\right)_{s_m}\left(\frac{\partial s_m}{\partial P}\right)_T\left(\frac{\partial T}{\partial s_m}\right)_P = -1$

$$\left(\frac{\partial P}{\partial T}\right)_{s_m} = \frac{-1}{\left(\frac{\partial s_m}{\partial P}\right)_T\left(\frac{\partial T}{\partial s_m}\right)_P} \overset{\text{reciprocal}}{=} -\frac{\left(\frac{\partial s_m}{\partial T}\right)_P}{\left(\frac{\partial s_m}{\partial P}\right)_T} \overset{\text{maxwell}}{=} \frac{\left(\frac{\partial s_m}{\partial T}\right)_P}{\left(\frac{\partial v_m}{\partial T}\right)_P}$$

FE: $dh_m = T\,ds_m + V_m\,dP$ → 'Divide' by dT, enforcing constant P

$$\left(\frac{\partial h_m}{\partial T}\right)_P = T\overbrace{\left(\frac{\partial s_m}{\partial T}\right)_P}^{C_{p,m}} \underset{\text{Definition}}{\Longrightarrow} \left(\frac{\partial s_m}{\partial T}\right)_P = \frac{C_{p,m}}{T}$$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_{s_m} = \frac{C_{p,m}}{T\left(\frac{\partial v_m}{\partial T}\right)_P} \underset{\text{into (iv)}}{\overset{\text{Plug back}}{\Longrightarrow}} \left(\frac{\partial h_m}{\partial T}\right)_{s_m} = v_m\left(\frac{C_{p,m}}{T\left(\frac{\partial v_m}{\partial T}\right)_P}\right) \overset{\text{reciprocal}}{=} \frac{V_m \cdot C_{p,m}}{T}\left(\frac{\partial T}{\partial V_m}\right)_P$$

$$\left(\frac{\partial T}{\partial V_m}\right)_P : T = \frac{P v_m}{R(1+B'P+C'P^2)}$$

$$\left(\frac{\partial T}{\partial V_m}\right)_P = \frac{\partial}{\partial v_m}\left[\frac{P v_m}{R(1+B'P+C'P^2)}\right] = \frac{P}{R(1+B'P+C'P^2)}$$

$$\Rightarrow \left(\frac{\partial h_m}{\partial T}\right)_{s_m} = \frac{C_{p,m}\cdot v_m}{T}\left[\frac{P}{R(1+B'P+C'P^2)}\right] = \frac{C_{p,m}}{T}\left[\frac{P v_m}{R(1+B'P+C'P^2)}\right]$$

$$\therefore \left(\frac{\partial h_m}{\partial T}\right)_{s_m} \overset{\text{Use EoS}}{=} \frac{C_{p,m}}{T}\cdot T = C_{p,m}$$

$$\left(\frac{\partial h_m}{\partial T}\right)_{s_m} = C_{p,m}$$

3. EoS: $P(v_m - b) = RT$ where b and $c_{v,m}$ are assumed to be constants

a) Show $u_m = u_m(T)$ Go w/ $u_m(T, v_m)$ total diff. to get a $c_{v,m}$ term!

$$du_m = \left(\frac{\partial u_m}{\partial T}\right)_{v_m} dT + \left(\frac{\partial u_m}{\partial v_m}\right)_T dv_m$$
$$= c_{v,m}\, dT + \left(\frac{\partial u_m}{\partial v_m}\right)_T dv_m$$

Use FE: $du_m = T\,dS_m - P\,dv_m$ 'Divide' by dv_m, enforcing constant T

$$\left(\frac{\partial u_m}{\partial v_m}\right)_T = T\left(\frac{\partial s_m}{\partial v_m}\right)_T - P \xrightarrow[\text{Relation}]{\text{Maxwell}} \left(\frac{\partial u_m}{\partial v_m}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_{v_m} - P$$

$\left(\frac{\partial P}{\partial T}\right)_{v_m}$: $P = \frac{RT}{v_m - b}$; $\left(\frac{\partial P}{\partial T}\right)_{v_m} = \frac{R}{v_m - b}$

$$\therefore \left(\frac{\partial u_m}{\partial v_m}\right)_T = T\left(\frac{R}{v_m - b}\right) - P = P - P = 0$$

$\Rightarrow$ $du_m = c_{v,m}\, dT + 0$ hence $u_m = u_m(T)$

b) Show $\frac{c_{p,m}}{c_{v,m}} = $ constant

Definition: $dh_m = du_m + P\,dv_m$ $\rightarrow$ 'Divide' by dT, enforcing constant P

Derived in class

$dh_m = c_{p,m}\, dT + \left[v_m - T\left(\frac{\partial v_m}{\partial T}\right)_P\right] dP$ We are looking for $c_{p,m}$, so hold P_{constant}!

$\xrightarrow[\text{Definitions}]{\text{Plug in}}$ $c_{p,m}\, dT = c_{v,m}\, dT + P\,dv_m$

dv_m: $v_m = \frac{RT}{P} + b$; $dv_m = \frac{R}{P} dT$

$$\therefore c_{p,m}\, dT = c_{v,m}\, dT + P\left(\frac{R}{P} dT\right) = c_{v,m}\, dT + R\, dT$$
$$c_{p,m}\, dT - c_{v,m}\, dT - R\, dT = 0$$
$$(c_{p,m} - c_{v,m} - R)\, dT = 0 \implies c_{p,m} - c_{v,m} - R = 0$$

$\therefore c_{p,m} = c_{v,m} + R \implies \frac{c_{p,m}}{c_{v,m}} = 1 + \frac{R}{c_{v,m}}$ constant as R is constant and $c_{v,m}$ is assumed constant

4. Expr. for dS_m in terms of $P, T, V_m, C_{P,m}, C_{V,m}$ Start with $S_m(P, V_m)$

$$S_m = S_m(P, V_m) \rightarrow dS_m = dS_m(P, V_m)$$

$$dS_m = \left(\frac{\partial S_m}{\partial P}\right)_{V_m} dP + \left(\frac{\partial S_m}{\partial V_m}\right)_P dV_m$$

$\left(\frac{\partial S_m}{\partial P}\right)_{V_m}$: • Use: $dU_m = TdS_m - PdV_m$ 'Divide' by dP, const. V_m

$$\left(\frac{\partial U_m}{\partial P}\right)_{V_m} = T\left(\frac{\partial S_m}{\partial P}\right)_{V_m} \Rightarrow \left(\frac{\partial S_m}{\partial P}\right)_{V_m} = \frac{1}{T}\left(\frac{\partial U_m}{\partial P}\right)_{V_m}$$

$\left(\frac{\partial S_m}{\partial V_m}\right)_P$: • Use: $dH_m = TdS_m - V_m dP$ 'Divide' by dV_m, const. P

$$\left(\frac{\partial H_m}{\partial V_m}\right)_P = T\left(\frac{\partial S_m}{\partial V_m}\right)_P \Rightarrow \left(\frac{\partial S_m}{\partial V_m}\right)_P = \frac{1}{T}\left(\frac{\partial H_m}{\partial V_m}\right)_P$$

$$\Rightarrow dS_m = \frac{1}{T}\left(\frac{\partial U_m}{\partial P}\right)_{V_m} dP + \frac{1}{T}\left(\frac{\partial H_m}{\partial V_m}\right)_P dV_m$$

$\left(\frac{\partial U_m}{\partial P}\right)_{V_m}$: • Use: (Derived in class) $dU_m = C_{V,m}dT + \left[T\left(\frac{\partial P}{\partial T}\right)_{V_m} - P\right]dV_m$

$$\left(\frac{\partial U_m}{\partial P}\right)_{V_m} = \frac{\partial}{\partial P}\left[C_{V,m}dT + \cancel{\left[T\left(\frac{\partial P}{\partial T}\right)_{V_m} - P\right]dV_m}\right]_{V_m} = C_{V,m}\left(\frac{\partial T}{\partial P}\right)_{V_m}$$

$\left(\frac{\partial H_m}{\partial V_m}\right)_P$: • Use: (Derived in class) $dH_m = C_{P,m}dT + \left[V_m - T\left(\frac{\partial V_m}{\partial T}\right)_P\right]dP$

$$\left(\frac{\partial H_m}{\partial V_m}\right)_P = \frac{\partial}{\partial V_m}\left[C_{P,m}dT + \cancel{\left[V_m - T\left(\frac{\partial V_m}{\partial T}\right)_P\right]dP}\right]_P = C_{P,m}\left(\frac{\partial T}{\partial V_m}\right)_P$$

$$\Rightarrow dS_m = \frac{C_{V,m}}{T}\left(\frac{\partial T}{\partial P}\right)_{V_m} dP + \frac{C_{P,m}}{T}\left(\frac{\partial T}{\partial V_m}\right)_P dV_m$$

Can be derived from a given EoS!

5. We are interested in the thermodynamic properties of a strip of rubber as it is stretched. Consider n moles of pure ethylene propylene rubber (EPR) that has an unstretched length z_0. If it is stretched by applying a force F, it will obtain an equilibrium length z given by $F = kT(z - z_0)$, where k is a positive constant.

Reversible Elastic Expansion

$$C_{z,m} = \left(\frac{\partial U_m}{\partial T}\right)_z = a + bT$$ for constant a, b

a) $dU = dQ_{rev} + dW_{rev}$

second law: $dQ_{rev} = TdS$

work from rubber: $dW_{rev} = Fdz$

$dU = TdS + Fdz$

Plug in F expr $\Rightarrow$ $dU = TdS + kT(z-z_0)dz$

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def free energy: $A = U - TS$

Total differential: $dA = dU - TdS - SdT$

Result from dU: $dA = (\cancel{TdS} + kT(z-z_0)dz) - \cancel{TdS} - SdT$

$\Rightarrow dA = kT(z-z_0)dz - SdT$

b) $S = S(T,z) \longrightarrow dS = dS(T,z)$

total differential: $dS = \left(\frac{\partial S}{\partial T}\right)_z dT + \left(\frac{\partial S}{\partial z}\right)_T dz$

$\left(\frac{\partial S}{\partial T}\right)_z$: Use: $dU = TdS + kT(z-z_0)dz$ 'Divide' by dT enforcing constant z

use dU!

$$\left(\frac{\partial U}{\partial T}\right)_z = T\left(\frac{\partial S}{\partial T}\right)_z \Rightarrow \left(\frac{\partial S}{\partial T}\right)_z = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_z = \frac{n}{T}\left(\frac{\partial U_m}{\partial T}\right)_z$$

$$\therefore \left(\frac{\partial S}{\partial T}\right)_z = \frac{n}{T}(a+bT) = \frac{nC_{v,m}}{T}$$

$\left(\frac{\partial S}{\partial z}\right)_T$: Use: $dA = kT(z-z_0)dz - SdT$

use dA!

'Divide' by dT enforcing constant z: $\left(\frac{\partial A}{\partial T}\right)_z = -S$

'Divide' by dz enforcing constant T: $\left(\frac{\partial A}{\partial z}\right)_T = kT(z-z_0)$

order of differentiation does not matter!

$$\left(\frac{\partial S}{\partial z}\right)_T: \quad -S = \left(\frac{\partial A}{\partial T}\right)_z \Rightarrow -\left(\frac{\partial S}{\partial z}\right)_T = \frac{\partial}{\partial z}\left[\left(\frac{\partial A}{\partial T}\right)_z\right]_T = \frac{\partial}{\partial T}\left[\left(\frac{\partial A}{\partial z}\right)_T\right]_z$$

$$\therefore -\left(\frac{\partial S}{\partial z}\right)_T = \frac{\partial}{\partial T}\left[kT(z-z_0)\right]_z \Rightarrow \left(\frac{\partial S}{\partial z}\right)_T = -k(z-z_0)$$

Combine!

$$dS = \frac{nC_{v,m}}{T}dT - k(z-z_0)dz$$

c) $U = U(T, z) \longrightarrow dU = dU(T, z)$

definition, also shown in b

total differential: $dU = \left(\frac{\partial U}{\partial T}\right)_z dT + \left(\frac{\partial U}{\partial z}\right)_T dz = nC_{v,m}\, dT + \left(\frac{\partial U}{\partial z}\right)_T dz$

$\left(\frac{\partial U}{\partial z}\right)_T$: Use: $dU = TdS + kT(z - z_0)\,dz$ 'Divide' by dz enforcing constant T

$$\left(\frac{\partial U}{\partial z}\right)_T = T\left(\frac{\partial S}{\partial z}\right)_T + kT(z - z_0)$$

$$= T\left(\underset{\text{(from b)}}{-k(z - z_0)}\right) + kT(z - z_0) = 0$$

$\therefore\ dU = nC_{v,m}\, dT$

d) $F_U = \left(\frac{\partial U}{\partial z}\right)_T = 0$ This was found in part c!

$$F_S = -T\left(\frac{\partial S}{\partial z}\right)_T = -T\left(\underset{\text{(from b)}}{-k(z - z_0)}\right) = kT(z - z_0)$$

$F_S = kT(z - z_0)$

e) Adiabatically $\rightarrow dQ_{rev} = 0 \quad \therefore\ dU = kT(z - z_0)\,dz$

$z_i \rightarrow z_f$ as we are stretching, T is a positive constant (initial T) by condition, k is a constant (positive), so $du > 0$ must be true! Therefore, the temperature will increase as the SPR's internal energy is increasing.

6. Answer the following reflection questions (5 points):

   a. What about the way this class is taught is helping your learning?

   b. What about the way this class is taught is inhibiting your learning?

A) The use of class time with examples and discussion helps my learning the most. The examples are challenging and serve as good parallels to the homework assignments. Being able to reference the notes, as I did through a lot of this assignment, makes the problems much more manageable. The enthusiasm Dr. Warburton has for the class's learning also encourages my learning, as I am more engaged and thus take in more of the information. The content is ever increasing in difficultly, but the way that the examples scale with this difficulty greatly helps my learning.

B) There is nothing currently inhibiting my learning. The class is not moving too fast, nor is it moving too slow. The examples are challenging but in a good way, discussion questions are helpful in engaging group discussion and invoking problem solving skills, and the homework enforces key topics from lecture. The way this class is taught currently does nothing but help my learning.