Name Solution

Wednesday, April 12th

ECHE 363 – Thermodynamics of Chemical Systems
Midterm #2

Rules:

- 75 minutes total time. Once time is up, put aside answer sheets.
- Be sure to show all work to obtain maximum credit.
- There is one bonus question on the exam. This will be graded "all or nothing" (i.e., no partial credit).
- Closed book and no notes.
- Write your name on every page.
- Please only write on the front side of each page. Ask for additional paper if necessary.

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1. (35 points) A mysterious fluid obeys the Renner–renneR equation of state:

$$P(v_m - b) = RT + \frac{aP^2}{T}$$

where the constants are:

$$a = 10^{-7}\ \text{m}^3\ \text{K}/(\text{Pa mol})$$
$$b = 8 \times 10^{-5}\ \text{m}^3/\text{mol}$$
$$c_{p,m}^{\text{ideal}} = 33.5\ \text{J}/(\text{mol K})$$

Using the provided property data, calculate the molar entropy change of the fluid for a change from $P_1 = 12$ bar, $T_1 = 300$ K to $P_2 = 12$ bar, $T_2 = 400$ K.

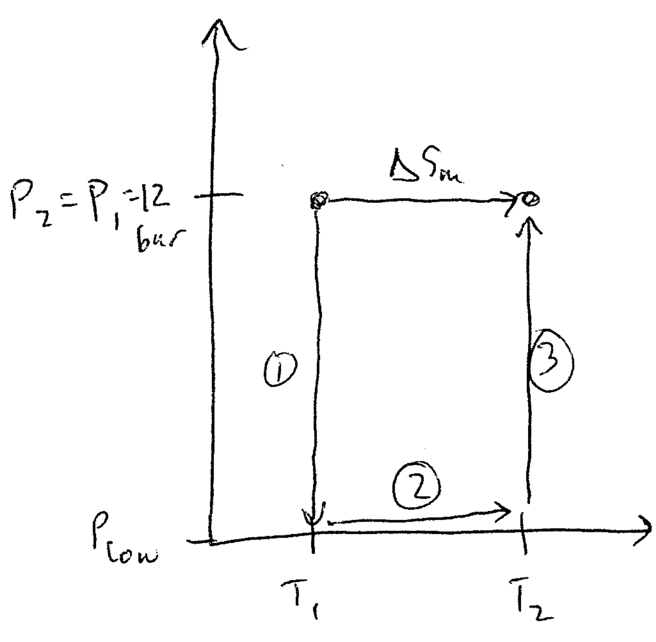
$$\Delta s_m = \int ds_m$$

$$ds_m = \frac{c_{p,m}}{T} dT - \left(\frac{\partial v_m}{\partial T}\right)_P dP$$

$\left(\frac{\partial v_m}{\partial T}\right)_P$: EOS $\rightarrow$ $v_m = \frac{RT}{P} + \frac{aP}{T} + b$

$$\left(\frac{\partial v_m}{\partial T}\right)_P = \frac{R}{P} - \frac{aP}{T^2}$$

$$ds_m = \frac{c_{p,m}}{T} dT - \left(\frac{R}{P} - \frac{aP}{T^2}\right) dP$$



$$\Delta s_m = \Delta s_{m,1} + \Delta s_{m,2} + \Delta s_{m,3}$$

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$T = T_1,\ P_1 \rightarrow P_{Low}$

$$\Delta S_{m,①} = \int_{P_1}^{P_{low}} dS_m = -\int_{P_1}^{P_{Low}} \left(\frac{R}{P} - \frac{aP}{T_1^2} \right) dP$$

$$\Delta S_{m,①} = -\ln\left(\frac{P_{Low}}{P_1}\right) + \frac{a}{2T_1^2}\left(\underbrace{P_{Low}^2}_{\approx 0} - P_1^2\right)$$

$$\Delta S_{m,①} = -\ln\left(\frac{P_{Low}}{P_1}\right) - \frac{aP_1^2}{2T_1^2}$$

$T = T_2,\ P_{low} \rightarrow P_2 = P_1$

$$\Delta S_{m,③} = -\int_{P_{Low}}^{P_2} \left(\frac{R}{P} - \frac{aP}{T_2^2} \right) dP$$

$$= -\ln\left(\frac{P_2}{P_{low}}\right) + \frac{a}{2T_2^2}\left(P_2^2 - \underbrace{P_{low}^2}_{\approx 0}\right)$$

$$\Delta S_{m,③} = -\ln\left(\frac{P_1}{P_{Low}}\right) + \frac{aP_1^2}{2T_2^2} \leftarrow P_2 = P_1$$

$P = P_{Low},\ T_1 \rightarrow T_2$

$$\Delta S_{m,②} = \int_{T_1}^{T_2} \frac{C_{p,m}^{ideal}}{T} dT = C_{p,m}^{ideal} \ln\left(\frac{T_2}{T_1}\right)$$

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$$\Delta S_m = C_{p,m}^{ideal} \ln\left(\frac{T_2}{T_1}\right) - R \underbrace{\cancel{\ln}\left(\frac{P_1}{P_1}\right)}_{=0} + \frac{a P_1^2}{2}\left(\frac{1}{T_2^2} - \frac{1}{T_1^2}\right)$$

$$\boxed{\Delta S_m = 9.29 \quad J/mol}$$

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2. (25 points) We are interested in the thermodynamic properties of a gas-phase system that contains charged molecules under the influence of an external electrostatic potential. These charged species have a molar charge of α_m. For a system where work can be done through both "PV work" and electrical work, the reversible work is: $dw_{m,rev} = -Pdv_m + \psi d\alpha_m$, where ψ is the potential and α is the charge per mole.

   a) (5 points) Come up with a fundamental equation for du_m for this system.

   b) (10 points) Come up with a fundamental equation for dg_m for this system.

   c) (10 points) Derive a Maxwell Relation equivalent to the partial derivative $\left(\frac{\partial s_m}{\partial \alpha_m}\right)_{T,P}$

   d) **Bonus** (10 extra points): Derive a Maxwell Relation equal to the partial derivative $\left(\frac{\partial \alpha_m}{\partial v_m}\right)_{s_m,\psi}$. You may need to define a new thermodynamic state function, χ_m.

a) $du_m = dq_{rev} + dw_{m,rev}$

$du_m = T\,ds_m \underbrace{- P\,dv_m + \psi\,d\alpha_m}$

b) $g_m = u_m + Pv_m - Ts_m$

$dg_m = du_m + P\,dv_m + v_m\,dP - T\,ds_m - s_m\,dT$

$dg_m = \cancel{T\,ds_m} - \cancel{P\,dv_m} + \psi\,d\alpha_m$

$\quad + \cancel{P\,dv_m} + v_m\,dP$

$\quad - \cancel{T\,ds_m} - s_m\,dT$

$\rightarrow \boxed{dg_m = -s_m\,dT + v_m\,dP + \psi\,d\alpha_m}$

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c) $s_m = -\left(\frac{\partial g_m}{\partial T}\right)_{P, \alpha_m}$ $\psi = \left(\frac{\partial g_m}{\partial \alpha_m}\right)_{T, P}$

$$\left[\frac{\partial}{\partial \alpha_m}\left(\frac{\partial g_m}{\partial T}\right)_{P,\alpha_m}\right]_{T,P} = \left[\frac{\partial}{\partial T}\left(\frac{\partial g_m}{\partial \alpha_m}\right)_{T,P}\right]_{P,\alpha_m}$$

$$\left[\frac{\partial}{\partial \alpha_m}\left(-s_m\right)\right]_{T,P} = \left[\frac{\partial}{\partial T}\left(\psi\right)\right]_{P,\alpha_m}$$

$$\boxed{\left(\frac{\partial s_m}{\partial \alpha_m}\right)_{T,P} = -\left(\frac{\partial \psi}{\partial T}\right)_{P,\alpha_m}}$$

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d) Define $\chi_m = u_m - \psi \alpha_m$

$$d\chi_m = T\,ds_m - P\,dv_m + \cancel{\psi\,d\alpha_m} - \cancel{\psi\,d\alpha_m} - \alpha_m\,d\psi$$

$$\boxed{d\chi_m = T\,ds_m - P\,dv_m - \alpha_m\,d\psi}$$

$$-\alpha_m = \left(\frac{\partial \chi_m}{\partial \psi}\right)_{s_m, v_m} \qquad -P = \left(\frac{\partial \chi_m}{\partial v_m}\right)_{s_m, \psi}$$

$$\left[\frac{\partial}{\partial v_m}\left(\frac{\partial \chi_m}{\partial \psi}\right)_{s_m, v_m}\right]_{s_m, \psi} = \left[\frac{\partial}{\partial \psi}\left(\frac{\partial \chi_m}{\partial v_m}\right)_{s_m, \psi}\right]_{s_m, v_m}$$

$$\boxed{\left(\frac{\partial \alpha_m}{\partial v_m}\right)_{s_m, \psi} = \left(\frac{\partial P}{\partial \psi}\right)_{s_m, v_m}}$$

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3. (40 Points) Two solid phases, α and β, of a pure species exist in equilibrium. It is assumed that the molar volumes of both phases (v_m^α and v_m^β) are constant, as are the heat capacities ($c_{p,m}^\alpha$ and $c_{p,m}^\beta$). The enthalpy of the phase change, $\Delta h_m^{\alpha\to\beta} = h_m^\beta - h_m^\alpha$, is known at T_o and is equal to $\Delta h_m^{\alpha\to\beta}(T_o)$. Using the measured equilibrium point of (P_o, T_o) as an integration constant, derive an equation to relate the temperature and pressure of phase equilibrium assuming:

a) (15 points) The enthalpy of phase change is a constant.

b) (25 points) The enthalpy of phase change depends on temperature.

a) $$\frac{dP}{dT} = \frac{h_m^\beta - h_m^\alpha}{T(v_m^\beta - v_m^\alpha)}$$

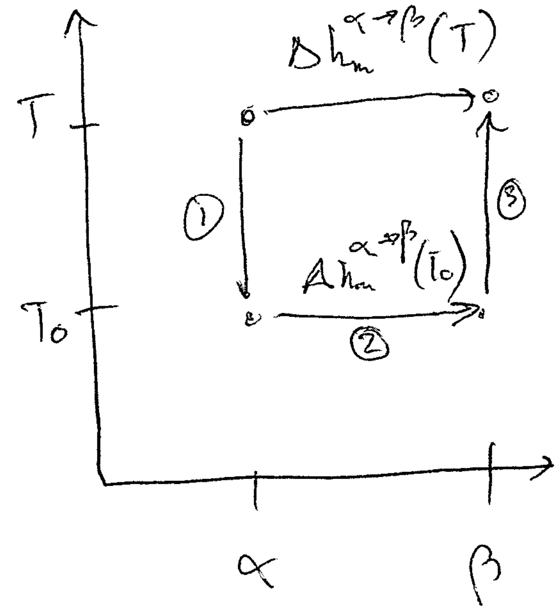
$$\frac{dP}{dT} = \frac{\Delta h_m^{\alpha\to\beta} \leftarrow \text{const}}{T(v_m^\beta - v_m^\alpha) \leftarrow \text{const}}$$

$$\int_{P_o}^{P} dP = \frac{\Delta h_m^{\alpha\to\beta}}{v_m^\beta - v_m^\alpha} \int_{T_o}^{T} \frac{dT}{T}$$

$$P - P_o = \frac{\Delta h_m^{\alpha\to\beta}}{v_m^\beta - v_m^\alpha} \ln\left(\frac{T}{T_o}\right)$$

where $\Delta h_m^{\alpha\to\beta} = \text{constant} = \Delta h_m^{\alpha\to\beta}(T_o)$

b)



$$\Delta h_m^{\alpha\to\beta}(T) = \Delta h_m^{\alpha\to\beta}(T_0) + C_{p,m}^{\alpha}(T_0 - T) + C_{p,m}^{\beta}(T - T_0)$$

$$\Delta h_m^{\alpha\to\beta}(T) = \Delta h_m^{\alpha\to\beta}(T_0) + \left(C_{p,m}^{\beta} - C_{p,m}^{\alpha}\right)(T - T_0)$$

$$\frac{dP}{dT} = \frac{\Delta h_m^{\alpha\to\beta}(T)}{T\left(v_m^{\beta} - v_m^{\alpha}\right)} = \frac{\Delta h_m^{\alpha\to\beta}(T_0) + \left(C_{p,m}^{\beta} - C_{p,m}^{\alpha}\right)(T - T_0)}{T\left(v_m^{\beta} - v_m^{\alpha}\right)}$$

$$\int_{P_0}^{P} dP = \int_{T_0}^{T} \left[\frac{\Delta h_m^{\alpha\to\beta}(T_0) - \left(C_{p,m}^{\beta} - C_{p,m}^{\alpha}\right)T_0}{T\left(v_m^{\beta} - v_m^{\alpha}\right)} + \frac{C_{p,m}^{\beta} - C_{p,m}^{\alpha}}{v_m^{\beta} - v_m^{\alpha}}\right] dT$$

$$\boxed{P - P_0 = \frac{\Delta h_m^{\alpha\to\beta}(T_0)}{v_m^{\beta} - v_m^{\alpha}} \ln\left(\frac{T}{T_0}\right) + \left(\frac{C_{p,m}^{\beta} - C_{p,m}^{\alpha}}{v_m^{\beta} - v_m^{\alpha}}\right)\left(T - T_0 - T_0 \ln\frac{T}{T_0}\right)}$$