CHE 7120 Exam I Oct. 6, 1993

Solution

1. $v = v^\circ - aP + bT$ (1) } are they consistent?

$h = cT - bPT - Pv$ (2)

we know that:

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

from (1) above:

$$\left.\frac{\partial V}{\partial T}\right)_P = b$$

$$\left.\frac{\partial h}{\partial P}\right)_T = v^\circ - aP + bT - bT = v^\circ - aP$$

from (2) above:

$$\left.\frac{\partial h}{\partial P}\right)_T = -bT - P\left.\frac{\partial V}{\partial P}\right)_T - V$$

five points for knowing about $\left.\frac{\partial V}{\partial P}\right)_T$

$$= -bT - P\left(-a\right) - v^\circ + aP - bT$$

$$\left.\frac{\partial h}{\partial P}\right)_T = -2bT + aP + aP - v^\circ = -bT + ap - V$$

.. is consistent if:

~~$v^\circ - aP = -bT + ap = V$~~

~~$V = -v^\circ + 2ap - bT$ ← not consistent!~~

must be equal [$V - T\left.\frac{\partial V}{\partial T}\right)_P = (v^\circ - aP + bT) - T(b) = v^\circ - aP$

$\left.\frac{\partial h}{\partial P}\right)_T = -bT + ap - V$ ~~$-bT + ap - (v^\circ - aP + bT)$~~

$-bT + ap - V \stackrel{?}{=} v^\circ - aP$

$-v^\circ - bT + 2ap \stackrel{?}{=} V$ no

BEST WAY (does not assume IG at 1 atm)

27) $\Delta S = \int_{T_1}^{T_2} \frac{c_p}{T} dT - R \ln P_2/P_1 + S_2^R - S_1^R$

$$\frac{S^R}{R} = -T \int_0^P \left.\frac{\partial z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (z-1) \frac{dP}{P}$$

$d(u^n) = nu^{n-1} du$

$P(v-b) = RT + aP^2/T$

$Pv - Pb = RT + aP^2/T$

$Pv = RT + Pb + aP^2/T$

$$\frac{Pv}{RT} = z = 1 + \frac{Pb}{RT} + \frac{aP^2}{RT^2}$$

$\int x\,dx$

$\frac{x^2}{2} dx$

$$\left.\frac{\partial z}{\partial T}\right)_P = -\frac{Pb}{RT^2} - \frac{2aP^2}{RT^3}$$

$$\frac{S^R}{R} = -T \int_0^P \left(-\frac{Pb}{RT^2} - \frac{2aP^2}{RT^3}\right) \frac{dP}{P} - \int_0^P \left(\frac{Pb}{RT} + \frac{aP^2}{RT^2}\right) \frac{dP}{P}$$

$$\frac{S^R}{R} = \int_0^P \left(\frac{b}{RT} + \frac{2aP}{RT^2}\right) dP - \int_0^P \left(\frac{b}{RT} + \frac{aP}{RT^2}\right) dP$$

$$\frac{S^R}{R} = \int_0^P \frac{aP}{RT^2} dP = \frac{aP^2}{2RT^2}$$

$\frac{16}{2 \cdot 90000}$

$$S^R = \frac{aP^2}{2T^2}$$

$$S_1^R = \left(1.0 \frac{\text{lt-K}}{\text{atm-mole}}\right)(4\,\text{atm})^2 / 2 \cdot 300^2 K = 8.89 \times 10^{-5} \frac{\text{lt-atm}}{\text{mole K}}$$

$$S_2^R = (1.0)(12^2) / 2 \cdot 400^2 = 4.5 \times 10^{-4} \frac{\text{lt-atm}}{\text{mole K}}$$

$$\Delta S = \left(8 \frac{\text{cal}}{\text{mole K}}\right)\left(\ln \frac{400}{300}\right) - 1.987 \ln \frac{12}{4} + 4.5 \times 10^{-4} \times \frac{1.987}{0.08203} - 8.89 \times 10^{-5} \frac{1.987}{0.08203}$$

$\Delta S = 2.3015 - 2.1829 + 0.01090 - 0.00215$

$$\boxed{\Delta S = 0.12735 \text{ cal/mole K}}$$

Not Bad:

(assumes IG at 1 atm)

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

$$\boxed{\begin{array}{c}4\text{atm}\\300K\end{array}} \xrightarrow{\Delta S_1} \boxed{\begin{array}{c}1\text{atm}\\300°K\end{array}} \xrightarrow{\Delta S_2} \boxed{\begin{array}{c}1\text{atm}\\400°K\end{array}} \xrightarrow{\Delta S_3} \boxed{\begin{array}{c}12\text{atm}\\400°K\end{array}}$$

ΔS_1:

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

$$v = b + \frac{RT}{P} + \frac{aP}{T}$$

$$\left.\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + aP\left(-\frac{1}{T^2}\right)$$

10 points for integrating both in P & T

$$-\left.\frac{\partial S}{\partial P}\right)_T = \frac{R}{P} - \frac{aP}{T^2}$$

$$\Delta S_1 = -\int_4^1 \left[\frac{R}{P} - \frac{aP}{T^2}\right] dP \qquad \text{const } T$$

$$\Delta S_1 = -R \ln 1/4 + \frac{a}{2T^2}(1^2 - 4^2)$$

$$= -\left(.08205 \frac{\text{lt-atm}}{\text{mole°K}}\right)(-1.386) + \frac{1 \text{ lt-K}}{\text{atm-mole}} \frac{1}{2(300°K)^2}(1^2-4^2)\text{atm}^2$$

$$= +.1137 \frac{\text{lt-atm}}{\text{mole°K}} - 8.3 \times 10^{-5} \frac{\text{lt-atm}}{\text{mole°K}}$$

$$\boxed{\Delta S_1 = +.1136 \frac{\text{lt-atm}}{\text{mole°K}}}$$

ΔS_2:

$$\left.\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\Delta S_2 = \int_{300}^{400} \frac{8 \text{ cal/mole°K}}{T} dT = 8 \text{ cal/mole°K} \ln 400/300 = 2.301 \frac{\text{cal}}{\text{mole°K}}$$

$$\Delta S_3 = -R\ln(12/1) + \frac{12^2 - 1^2}{2(400)^2} = -.2039 + 4.47\times10^{-4} = -.2035$$

a) $$\boxed{\Delta S = \left(.1136 \times \frac{1.987}{0.08205}\right) + 2.301 - 0.2035\left(\frac{1.987}{.08205}\right) = 0.124 \frac{\text{cal}}{\text{mole °K}}}$$

b. $RT \ln \phi_1 = \int_0^P \left[\bar{V}_1 - \frac{RT}{P} \right] dP$

$$v = b + \frac{RT}{P} + \frac{aP}{T}$$

$$V = nv = n_T b + n_T \frac{RT}{P} + n_T \frac{aP}{T}$$

$$\bar{V}_1 = \left.\frac{\partial V}{\partial n_1}\right)_{T,P,n_2} = \left.\frac{\partial (n_T b)}{\partial n_1}\right)_{T,P,n_2} + \frac{RT}{P} + \frac{P}{T} \left.\frac{\partial (n_T a)}{\partial n_1}\right)_{n_2}$$

<u>take:</u> $b = y_1 b_1 + y_2 b_2$

$$n_T b = n_1 b_1 + n_2 b_2$$

$$\left.\frac{\partial (n_T b)}{\partial n_1}\right)_{T,P,n_2} = b_1 \leftarrow$$

$$a = y_1^2 a_1 + 2 y_1 y_2 \sqrt{a_1 a_2} + y_2^2 a_2$$

$$n_T a = \frac{n_1^2 a_1}{n_T} + \frac{2 n_1 n_2 \sqrt{a_1 a_2}}{n_T} + \frac{n_2^2 a_2}{n_T}$$

$$\left.\frac{\partial (n_T a)}{\partial n_1}\right)_{n_2} = \frac{2 n_1 a_1}{n_T} - \frac{n_1^2 a_1}{n_T^2} + \frac{2 n_2 \sqrt{a_1 a_2}}{n_T} - \frac{2 n_1 n_2 \sqrt{a_1 a_2}}{n_T^2} - \frac{n_2^2 a_2}{n_T^2}$$

$$= 2 y_1 a_1 - y_1^2 a_1 + 2 y_2 \sqrt{a_1 a_2} - 2 y_1 y_2 \sqrt{a_1 a_2} - y_2^2 a_2$$

$$\left.\frac{\partial (n_T a)}{\partial n_1}\right)_{n_2} = 2 y_1 a_1 + 2 y_2 \sqrt{a_1 a_2} - a_{MIX} \leftarrow$$

$$RT \ln \phi_1 = \int_0^P \left[b_1 + \frac{P}{T} \left(2 y_1 a_1 + 2 y_2 \sqrt{a_1 a_2} - a_{MIX} \right) \right] dP$$

$$\boxed{RT \ln \phi_1 = b_1 P + \frac{P^2}{2T} \left(2 y_1 a_1 + 2 y_2 \sqrt{a_1 a_2} - a_{MIX} \right)}$$