Chemistry 230
Problem Set # 11 -- Answers

1. (a) 5.14% (b) x = 0.00985 (c) 0.985 mol %
   (d) 0.552 mol/kg (e) 0.539 mol/L

2. (a) Integrate and set V = 1002.94 cm^3 @ m = 0
   $V(\text{cm}^3) = 1002.94 + 32.280\ m + {}^2/_3\ 18.216\ m^{3/2} + 0.0111\ m^2$.
   (b) $\bar{V}_A = n_A^{-1}\ (V - n_B \bar{V}_B) = 18.068 - 0.10939\ m^{3/2} - 2.00\times10^{-4}\ m^2$.

3. (a) $\Delta H_{mix} = \Delta H_{mix,m}\ n = 1.403_4$ kJ/mol × 2.000 mol = 2.806_8 kJ.
   (b) Consider direct differentiation, starting with $\Delta H_{mix} = n_A \Delta H_{diff,A} + n_B \Delta H_{diff,B}$.
   $$\Delta H_{diff,A} = \left(\frac{\partial \Delta H_{mix}}{\partial n_A}\right)_{n_B} = \frac{\partial}{\partial n_A}\left[(n_A + n_B)\ \Delta H_{mix,m}\right]$$
   Let A = NaBr. $\Delta H_{diff,A} = \Delta H_{mix,m} + n \left(\frac{\partial \Delta H_{mix,m}}{\partial n_A}\right)_{n_B}$
   $$= \Delta H_{mix,m} + n \left(\frac{d \Delta H_{mix,m}}{d x_A}\right)\left(\frac{\partial x_A}{\partial n_A}\right)_{n_B} = \Delta H_{mix,m} + \left(\frac{d \Delta H_{mix,m}}{d x_A}\right) x_B$$
   = 1.403_4 kJ/mol – 0.19125 (0.50) = 1.307_8 kJ/mol.
   $\Delta H_{diff,B} = n_B^{-1}\ (\Delta H_{mix} - n_A \Delta H_{diff,A}) = 1.499_0$ kJ/mol.
   This is the "method of slopes." The method of intercepts yields the same results.

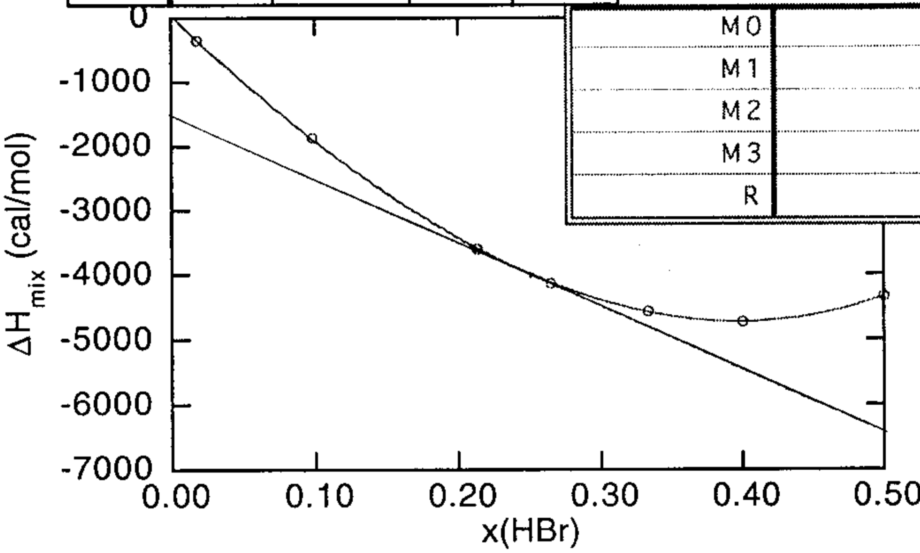
4. (a) $x_{b,l}$ = 0.5245 ; $x_{h,l}$ = 0.4755 $P_b = x_{b,l}\ P_b^*$ = 0.07108 atm; P_h = 0.10118 atm.
   (b) $P_{tot} = 0.1722_6$ atm; $x_{b,v}$ = 0.4126.
   (c) $\Delta V_{mix} = 0$ $V = V^* = n_b \bar{V}_b^* + n_h \bar{V}_h^* = m_b/\rho_b + m_h/\rho_h = 132.6_3$ cm^3.
   (d) $\Delta G_{mix} = RT\ (n_b \ln x_b + n_h \ln x_h)$ = –2106 J; ΔH_{mix} = 0;
   $\Delta S_{mix} = -R\ (n_b \ln x_b + n_h \ln x_h) = 7.020_6$ J/K.

5. Minimum work = $\Delta A = \Delta G - P\Delta V = \Delta G$ (since ΔV = 0 for ideal solutions). Here ΔG is the difference between ΔG_{mix} for $(n_A + n_B)$ *vs*. $(n_A - 1\ \text{mol} + n_B)$.
   (a) $\Delta G = RT$ (1 mol) $(1 \ln {}^1/_3 + 2 \ln {}^2/_3 - 4 \ln {}^1/_2)$ = 0.863 RT (1 mol) = 2.153 kJ.
   (b) $\Delta G = 0.719_5\ RT$(1 mol) = 1.795 kJ.
   (c) $\Delta G \quad -\left(\frac{\partial \Delta G_{mix}}{\partial n_A}\right)_{n_B}$(1 mol) = $(-\mu_A + \mu_A^*)$(1 mol) = $-RT \ln x_A$(1 mol)
   = $-RT \ln {}^1/_2$ (1 mol) = 1.729 kJ.

6. $n_{gas} = \frac{PV}{RT} = 0.817_5$ mol = $n_l + n_v$ @ equilibrium; n_{H_2O} = 5.551 mol; V_{gas} 19.9 L; P_{H_2O} = 23.76 torr;
   $P_g = K_H\ x_l$; 1.00 atm = $K_H \frac{2.00\ \text{mol}}{55.5+2\ \text{mol}}$ $K_H = 28.7_6$ atm.
   $n_{v,H_2O} = \frac{P_{H_2O} \bullet 19.9\ \text{L}}{RT}$ = 0.0254 mol (= 0.46 g) $n_{l,H_2O} = 5.52_6$ mol.
   At equilibrium, $P_g = K_H \bullet \frac{n_l}{5.526 + n_l} = \frac{(0.8175\ \text{mol} - n_l\ )RT}{19.9\ \text{L}}$ n_l = 0.1599 mol
   $P_g = 0.808_5$ atm. Also, x_{H_2O} = 0.972 P_{H_2O} = 23.1 torr P_{tot} = 0.839 atm.

7.

m	Φ_L	X_{HBr}	ΔH_{int}	$\Delta H_{mix}/n$ $(= \Delta H_{int} \cdot X_{HBr})$
1.000	314	0.017696	-20036	-354.56
6.000	1196	0.097547	-19154	-1868.4
15.000	3415	0.21274	-16935	-3602.7
20.000	4760	0.26487	-15590	-4129.3
27.753	6650	0.33332	-13700	-4566.5
37.004	8530	0.39999	-11820	-4727.8
55.506	11670	0.49999	-8680.0	-4339.9



$= M0 + M1*x + \ldots M8*x^8 + M9*x^9$

M0	26.565548
M1	-21503.43
M2	18055.653
M3	14984.458
R	0.99997526

@ $x = 0.25$

$$\frac{d\left(\frac{\Delta H_{mix}}{n}\right)}{dx} = -9666$$

$\Rightarrow \Delta H_{diff, H_2O} = -1.57$ kcal/mol

$\Delta H_{diff, HBr} = -11.24 \frac{kcal}{mol}$