CHM 4411 SOLUTIONS TO TEST 3

1. The Clausius-Clapeyron equation refers to a (l)/(g) equilibrium. For the $\mu(l) = \mu(g)$ condition for the chemical potentials of the two phases we can write

$$-\tilde{S}(l)dT + \tilde{V}(l)dp = -\tilde{S}(g) + \tilde{V}(g)dp, \tag{1}$$

and by rearrangement

$$\Delta_{vap}\tilde{S}(l)dT = \Delta\tilde{V}(l)dp \approx \tilde{V}(g)dp = RT\frac{dp}{p}, \tag{2}$$

from which follows

$$d(\ln p) = \frac{\Delta_{vap}H}{RT^2}dT, \tag{3}$$

which after integration yields

$$\ln\left(\frac{p_f}{p_i}\right) = \frac{\Delta_{vap}\tilde{H}}{R}\left(\frac{1}{T_i} - \frac{1}{T_f}\right) \tag{4}$$

Thus

$$\ln\left(\frac{40}{10}\right) = \frac{\Delta_{vap}\tilde{H}}{8.314\mathrm{JK^{-1}mol^{-1}}}\left(\frac{1}{359\mathrm{K}} - \frac{1}{392.5\mathrm{K}}\right), \tag{5}$$

so that (i) $\Delta_{vap}\tilde{H}$ =48.5kJmol^{-1}. (ii) The normal boiling point T_b occurs for 760 Torr, and we write

$$\ln\left(\frac{760}{40}\right) = \frac{48.5\times10^3\mathrm{Jmol^{-1}}}{8.314\mathrm{JK^{-1}mol^{-1}}}\left(\frac{1}{392.5K} - \frac{1}{T_b}\right), \tag{6}$$

or T_b =489.5K=216.3°C. (iii) Entropy of vaporization:

$$\Delta_{vap}\tilde{S} = \frac{\Delta_{vap}\tilde{H}}{T_b} = \frac{48.5\times10^3\mathrm{Jmol^{-1}}}{489.5\mathrm{K}} = 99.1\mathrm{JK^{-1}mol^{-1}}. \tag{7}$$

2. From Dalton's law we obtain

$$x_A(g) = \frac{p_A}{p_A + p_M} \tag{8}$$

or

$$0.516 = p_A/760\mathrm{Torr}, \tag{9}$$

from which we can compute p_A =392 Torr, and p_M =368 Torr. By definition the activity is

$$a_A = \frac{p_A}{p_A^*} = \frac{392}{786} = 0.499, \tag{10}$$

$$a_A = \frac{p_M}{p_M^*} = \frac{368}{551} = 0.668. \tag{11}$$

The activity coefficients are

$$\gamma_A = \frac{a_A}{x_A(l)} = \frac{0.499}{0.400} = 1.25, \tag{12}$$

$$\gamma_M = \frac{a_M}{x_M(l)} = \frac{0.668}{0.600} = 1.11. \tag{13}$$

3. From

$$2A + B \leftrightarrows 3C + 2D \tag{14}$$

and the final $n_C = 0.90$mol we can write

species	A	B	C	D	total
initial(mol)	1.0	2.0	0.0	1.0	4.0
change	-0.60	-0.30	0.90	0.60	0.60
equil.	0.40	1.70	0.90	1.60	4.60
final mol.fr	0.087	0.370	0.196	0.348	1.001

The equilibrium constant is

$$K = \frac{\left(\frac{p_C}{p^\theta}\right)^3 \left(\frac{p_D}{p^\theta}\right)^2}{\left(\frac{p_A}{p^\theta}\right)^2 \left(\frac{p_B}{p^\theta}\right)} = \frac{x_C^3 x_D^2}{x_A^2 x_B} \left(\frac{p}{p^\theta}\right)^2, \tag{15}$$

which fro $p = p^\theta = 1.0$bar computes to

$$K = \frac{(0.196)^3(0.348)^2}{(0.087)^2(0.370)} = 0.326. \tag{16}$$

Now we can obtain

$$\Delta_r G^\theta = (-8.314\text{JK}^{-1}\text{mol}^{-1}) \times (298\text{K}) \times (\ln 0.326)$$
$$= 2.8\text{kJmol}^{-1}$$

BONUS:From the expression for $\ln K$ and the Gibbs-Helmholtz equation we can write

$$\frac{d\ln K}{dT} = -\frac{1}{R}\frac{d(\Delta_r G^\theta/T)}{dT} = \frac{\Delta_r H^\theta}{RT^2}. \tag{17}$$

For exothermic reactions $\Delta_r H^\theta < 0$, and consequently

$$\frac{d\ln K}{dT} < 0, \tag{18}$$

and then also $dK/dT < 0$, so for $T \uparrow, K \downarrow$ and the equilibrium shifts toward reactants.

For endothermic reactions $\Delta_r H^\theta > 0$, and $dK/dT > 0$, so for $T \uparrow, K \uparrow$ and the equilibrium shifts towards products.