Physical Chemistry Assignment One:
1.4, 1.5, 1.14, 1.17, 1.18, 1.20, 1.26, 1.31, 1.33, 1.34

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1.4

Mass: 1.588g
$n_t = \frac{1.588g}{92.08\frac{g}{molN_2O_4}} = 0.0172\ molN_2O_4$
P: 1.0133 bar $*\frac{10^5 Pa}{bar} = 1.0133 * 10^5 Pa$
T: 298K
V_{tot}: 500 $cm^3 * \frac{m}{100cm}^3 = 5 * 10^{-4} m^3$

Goal: find n_1 and n_2, the mols of N_2O_4 and NO_2, respectively.

$n_1 = n_t - x$
$n_2 = 2x$

$PV_1 = (n_t - x)RT$
$PV_2 = 2xRT$

We add these equations and see that:

$P(V_1 + V_2) = (n_t + x)RT$
$(1.0133 * 10^5 \frac{N}{m^2})(5 * 10^{-4} m^3) = (0.0172mol + x)(8.314\frac{J}{mol*K})(298K)$

From this we can see that $x = 0.00325$

Therefore we end up with 0.01395 mol N_2O_4 and 0.0065 mol NO_2, for a total of 0.02045.

Mole fractions: 0.68 and 0.32.

Percent dissociated: 19%.

1.5

$$Z = 1 + B'P + C'P^2 + ... = 1 + \frac{B}{RT}P + \frac{C - B^2}{(RT)^2)} \tag{1}$$
$$\frac{\partial}{\partial P}\Big(1 + \frac{B}{RT}P + \frac{C - B^2}{(RT)^2}P^2\Big) = \frac{B}{RT} + \frac{2C - 2B^2}{(RT)^2}P \tag{2}$$
$$\lim_{P\to 0} \frac{B}{RT} + \frac{2C - 2B^2}{(RT)^2}P = \frac{B}{RT} = B' \tag{3}$$
$$\tag{4}$$

1.14

$$\kappa = -V^{-1}\frac{dV}{dP}_T \tag{5}$$

$$nRT = (P + \frac{an^2}{V^2})(V - nb) \tag{6}$$

$$nRT = PV - Pnb + \frac{an^2}{V} - \frac{abn^3}{V^2} \tag{7}$$

$$\frac{\partial}{\partial P}nRT = \frac{\partial}{\partial P}\Big(PV - Pnb + \frac{an^2}{V} - \frac{abn^3}{V^2}\Big) \tag{8}$$

$$0 = P\frac{\partial V}{\partial P}_T + V - nb + \frac{-an^2}{V^2}\frac{\partial V}{\partial P}_T - \frac{-2abn^3}{V^3}\frac{\partial V}{\partial P}_T \tag{9}$$

$$nb - V = (P + \frac{-an^2}{V^2} - \frac{-2abn^3}{V^3})\frac{\partial V}{\partial P}_T \tag{10}$$

$$\frac{nb - V}{P + \frac{-an^2}{V^2} - \frac{-2abn^3}{V^3}} = \frac{\partial V}{\partial P}_T \tag{11}$$

$$\kappa = \frac{-1}{V}\frac{\partial V}{\partial P}_T = \frac{-1}{V}\frac{nb - V}{P + \frac{-an^2}{V^2} - \frac{-2abn^3}{V^3}} \tag{12}$$

$$\tag{13}$$

We then look at the limiting case when volume goes to infinity, using L'Hospital's Rule:

$$\lim_{V\to\infty}\kappa = \lim_{V\to\infty}\frac{-1}{V}\frac{nb - V}{P + \frac{-an^2}{V^2} - \frac{-2abn^3}{V^3}} \tag{14}$$

$$= \frac{\frac{\partial}{\partial V}}{\frac{\partial}{\partial V}}\frac{nb - V}{PV + \frac{-an^2}{V} - \frac{-2abn^3}{V^2}} \tag{15}$$

$$= \frac{-1}{P + \frac{an^2}{V^2} + \frac{-4abn^3}{V^3}} \tag{16}$$

$$= \frac{-1}{P} \tag{17}$$

$$\tag{18}$$

This is identical to the answer we found in problem 1.17.

1.17

$$\alpha = \frac{1}{V}(\frac{\partial V}{\partial T})_P \tag{19}$$

$$= \frac{1}{\frac{nRT}{P}}(\frac{\partial\frac{nRT}{P}}{\partial T})_P \tag{20}$$

$$= \frac{P}{nRT}\frac{nR}{P} \tag{21}$$

$$= \frac{1}{T} \tag{22}$$

$$\tag{23}$$

$$\kappa = \frac{-1}{V}(\frac{\partial V}{\partial P})_T \tag{24}$$
$$= \frac{-1}{\frac{nRT}{P}}(\frac{\partial \frac{nRT}{P}}{\partial P})_T \tag{25}$$
$$= \frac{-P}{nRT}\frac{-nRT}{P^2} \tag{26}$$
$$= \frac{1}{P} \tag{27}$$
$$\tag{28}$$

1.18

$$\alpha = (\frac{\partial V}{\partial T})_P \frac{1}{V} = c_P \tag{29}$$
$$(\frac{\partial V}{\partial T})_P \frac{1}{V} = c_P \tag{30}$$
$$\int \frac{1}{V} dV = \int c_P dT \tag{31}$$
$$ln(V) = c_P T + C \tag{32}$$
$$e^{c_P T + C} = V \tag{33}$$
$$V = Ce^{\alpha T} \tag{34}$$
$$\tag{35}$$

This is true at constant P.

$$\kappa = (\frac{\partial V}{\partial P})_T \frac{-1}{V} = c_T \tag{36}$$
$$(\frac{\partial V}{\partial P})_T \frac{1}{V} = -c_T \tag{37}$$
$$\int frac1V dV = \int -c_T dP \tag{38}$$
$$ln(V) = -c_T P + C \tag{39}$$
$$V = e^{-c_T P + C} \tag{40}$$
$$V = Ce^{-c_T P} = Ce^{-\kappa P} \tag{41}$$
$$\tag{42}$$

This is only true at constant T.

We can then see by combining these two derivations for the general, non-constant case that $V = Ce^{\alpha T - \kappa P}$.

1.20

$$\frac{\partial P}{\partial V}_T = (\frac{\partial}{\partial V}_T)\frac{nRT}{V - nb} \tag{43}$$
$$= \frac{-nRT}{(V - nb)^2} \tag{44}$$
$$\tag{45}$$

and

$$\frac{\partial P}{\partial T}_T = (\frac{\partial}{\partial T})_V \frac{nRT}{V-nb} \tag{46}$$
$$= \frac{nR}{V-nb} \tag{47}$$
$$\tag{48}$$

Then we can see that:

$$\frac{\partial^2 P}{\partial V \partial T} = \frac{\partial}{\partial T}\frac{-nRT}{(V-nb)^2} = \frac{-nr}{(V-nb)^2} \tag{49}$$
$$\tag{50}$$

and

$$\frac{\partial^2 P}{\partial T \partial V} = \frac{\partial}{\partial V}\frac{nR}{V-nb} = \frac{-nr}{(V-nb)^2} \tag{51}$$
$$\tag{52}$$

and so

$$\frac{\partial^2 P}{\partial T \partial V} = \frac{\partial^2 P}{\partial V \partial T} \tag{53}$$

1.26

$$B = \sum_{i=1}^{2}\sum_{j=1}^{2} y_i y_j B_{ij} = y_1 y_1 B_{11} + y_1 y_2 B_{12} + y_2 y_1 B_{12} + y_2 y_2 B_{22} \tag{54}$$
$$= y_1^2 B_{11} + y_2^2 B_{22} + 2 y_1 y_2 B_{12} \tag{55}$$
$$\tag{56}$$

1.31

(a)

$$PV = nRT \tag{57}$$
$$P(0.5L) = (1mol)R(600K) \tag{58}$$
$$P(0.5L * \frac{m^3}{1000L}) = (1mol)(8.314\frac{N*m}{mol*K})(600K) \tag{59}$$
$$P = \frac{8.314*600}{0.0005}\frac{N}{m^2} = 9.976e6Pa \tag{60}$$
$$\tag{61}$$

(b)
From Wikipedia (en.wikipedia.org/wiki/Van_der_Waals_constants_(data_page)):

$$a = 24.71\frac{L^2 bar}{mol^2} = 24.71\frac{L^2 bar}{mol^2} * \frac{m^3}{10^3 L}^2 * \frac{10^5 Pa}{bar} = 2.471\frac{m^6 Pa}{mol^2}$$

$$b = 0.1735\frac{L}{mol} = 0.1735\frac{L}{mol} * \frac{m^3}{1000L} = 1.6 * 10^{-4}\frac{m^3}{mol}$$

$$(P+\frac{a}{\bar{V}^2})(\bar{V}-b)=RT \tag{62}$$
$$(P+\frac{2.471}{\bar{V}^2})(\bar{V}-1.6*10^{-4})=RT \tag{63}$$
$$(P+\frac{2.471}{0.0005^2})(0.0005-1.6*10^{-4})=(8.314)(600) \tag{64}$$
$$(P+9884000)=\frac{(8.314)(600)}{(0.00034)} \tag{65}$$
$$P=\frac{(8.314)(600)}{(0.00034)}-9884000 \tag{66}$$
$$P=4.787764*10^6 Pa \tag{67}$$
$$\tag{68}$$

1.33

$$\kappa=-V^{-1}(\frac{\partial V}{\partial P_)}T \tag{69}$$
$$-\kappa V=\frac{\partial V}{\partial P}_T \tag{70}$$
$$\int -\kappa V\partial P_T=\int \partial V \tag{71}$$
$$\int -\kappa\partial P_T=\int \frac{1}{V}\partial V \tag{72}$$
$$-P\kappa+C=ln(V) \tag{73}$$
$$V=e^{-\kappa P}e^C \tag{74}$$
$$V=C_0e^{-\kappa P} \tag{75}$$
$$\tag{76}$$

1.34

$$P(\bar{V}-b)=RT \tag{77}$$
$$\bar{V}-b=\frac{RT}{P} \tag{78}$$
$$\bar{V}=\frac{RT}{P}+b \tag{79}$$
$$V=\frac{nRT}{P}+nb \tag{80}$$
$$\tag{81}$$

$$\alpha=\frac{1}{V}\frac{\partial V}{\partial T}_P \tag{82}$$
$$=\frac{1}{V}\frac{\partial\frac{nRT}{P}+nb}{\partial T}_P \tag{83}$$
$$=\frac{1}{V}\frac{nR}{P} \tag{84}$$
$$=\frac{nR}{PV} \tag{85}$$
$$\tag{86}$$

$$\kappa = \frac{-1}{V}\frac{\partial V}{\partial P}_T \tag{87}$$

$$= \frac{-1}{V}\left(\frac{\partial \frac{nRT}{P} + nb}{\partial P}\right)_T \tag{88}$$

$$= \frac{-1}{V}\frac{-nRT}{P^2} \tag{89}$$

$$= \frac{nRT}{VP^2} \tag{90}$$

$$\tag{91}$$