Chemistry 217
Problem Set 1 Solution

1.1

(a) Ideal gas law

$$PV = nRT$$
$$\Rightarrow P = nRT/V$$

$n = 12.0\text{ mol}$

$T(K) = t(°C) + 273.15 = 30 + 273.15 = 303.15\text{ K}$

$V = 2.0\text{ L}$

$R = 8.314\times10^{-2}\text{ L.bar.K}^{-1}\text{.mol}^{-1}$

$P = (12.0\text{ mol})(8.314\times10^{-2}\text{ L.bar.K}^{-1}\text{.mol}^{-1})(303.15\text{ K})/2.0\text{ L}$
$= \underline{151.2\text{ bar}}$

(b) Van der Waals equation

$$P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$$

$a = 1.408\text{ L}^2\text{.bar.mol}^{-2}$

$b = 0.03913\text{ L.mol}^{-1}$

$n = 12.0\text{ mol}$

$T = 303.15\text{ K}$

$V = 2.0\text{ L}$

$R = 8.315\times10^{-2}\text{ L.bar.K}^{-1}\text{.mol}^{-1}$

$$P = \frac{12.01\text{ mol}\times8.315\times10^{-2}\text{ L.bar.K}^{-1}\text{mol}^{-1}\times303.15\text{ K}}{2.0\text{ L} - (12.0\text{ mol}\times0.03913\text{ L.mol}^{-1})} - \frac{1.408\text{ L}^2\text{.bar.mol}^{-2}\times(12.0\text{ mol})^2}{(2.0\text{ L})^2}$$

$P = 197.7 - 50.7 = \underline{147.0\text{ bar}}$

$$\%\text{error} = \frac{151.2\text{ bar} - 147.0\text{ bar}}{147.0\text{ bar}}\times100 = \underline{2.9\%}$$

1.2

(a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

	$N_2O_4(g)$	$2NO_2(g)$
initial	$(1.558/92)\,mol;$	0 mol
final	$(1.558/92 - x/2)\,mol;$	x mol

(Assume that there are x moles NO_2 at the final state – equilibrium)

$$P = nRT/V$$

$$P_{total} = P_{NO_2} + P_{N_2O_4}$$

$$n_{N_2O_4} = (1.558/92 - x/2)\,mol$$

$$n_{NO_2} = x\ mol$$

$$T = 298\,K$$

$$R = 8.3145\times10^{-2}\ L.bar.K^{-1}.mol^{-1}$$

$$V = 500\,cm^{-3} = 0.500\,L$$

$$P_{total} = 1.0133\ bar$$

$$\Rightarrow 1.0133 bar = \frac{(1.558/92 - x/2)\,mol\times8.3145\times10^{-2}\ L.bar.K^{-1}.mol^{-1}\times298\,K}{0.500\,L} + \frac{x\ mol\times8.3145\times10^{-2}\ L.bar.K^{-1}mol^{-1}\times298\,K}{0.500\,L}$$

$$\Rightarrow x = n_{NO_2} = 6.3747\times10^{-3}\ mol$$

$$\Rightarrow n_{N_2O_5} = \left(1.558/92 - \left(6.3747\times10^{-3}\right)/2\right) = 1.4074\times10^{-2}\ mol$$

$$\Rightarrow Y_{N_2O4} = \frac{1.4074\times10^{-2}}{1.4074\times10^{-2} + 6.3747\times10^{-3}} = \underline{0.6883}$$

$$and Y_{NO_2} = 1 - 0.6883 = \underline{0.3117}$$

(b)

$$\%\,undissociated = \frac{1.4074\times92}{1.588} = \underline{81.54\%}$$

$$\Rightarrow \%\,dissociated = 100 - 81.54 = \underline{18.46\%}$$

1.3

(a) $P = 1.0$ atm, $n = 1.0$ mol
$V_1 = 22401\ cm^3$, $t_1 = 0°C$
$V_2 = 30627\ cm^3$, $t_2 = 100°C$

$$\lim_{P\to 0}\left(P\overline{V}\right) = f(t)$$

$$f(t_1) = 1.0\ atm \times 22401\ cm^3.mol^{-1} = 22401\ cm^3.atm.mol^{-1}$$

$$f(t_2) = 1.0\ atm \times 30627\ cm^3.mol^{-1} = 30627\ cm^3.atm.mol^{-1}$$

$$f(t) = mt + b$$

$$m = \frac{\Delta f(t)}{\Delta t} = \frac{(30627 - 22401)\,cm^3.atm.mol^{-1}}{100°C - 0°C}$$

$$\Rightarrow m = 82.26\ cm^3.atm.mol^{-1}.°C^{-1}$$

when $f(t) = 0$, $b = 22401 cm^3.atm.mol^{-1}$
Substitue,

$$0 = \left(82.26\ cm^3.atm.mol^{-1}.°C\right)t + 22401\ cm^3.atm.mol^{-1}$$
$$\Rightarrow t = \underline{-272.3°C}$$

(b) $P = 0.1$ atm,
$t_1 = 0°C$, $\overline{V}_1 = 224130\ cm^3.mol^{-1}$
$t_2 = 100°C$, $\overline{V}_2 = 306200\ cm^3.mol^{-1}$

$$f(t_1) = 0.1\ atm \times 224130\ cm^3.mol^{-1} = 22413\ cm^3.atm.mol^{-1}$$

$$f(t_2) = 1.0\ atm \times 306200\ cm^3.mol^{-1} = 30620\ cm^3.atm.mol^{-1}$$

$$f(t) = mt + b$$

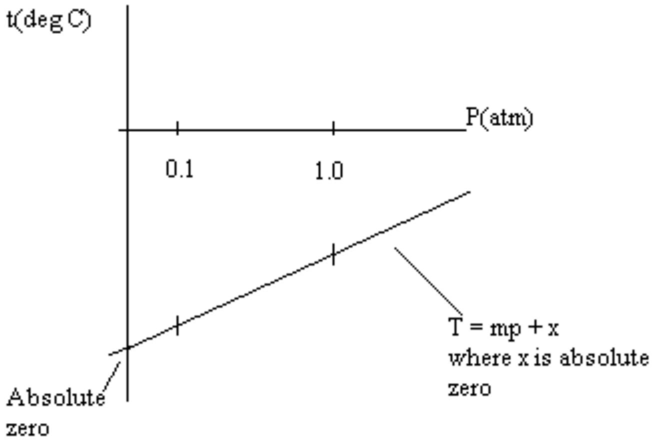
$$m = \frac{(30627 - 22413)\,cm^3.atm.mol^{-1}}{100°C - 0°C}$$

$$\Rightarrow m = 82.07\ cm^3.atm.mol^{-1}.°C^{-1}$$

when $f(t) = 0$, $b = 22413 cm^3.atm.mol^{-1}$
Substitue,

$$0 = (82.07\ \text{cm}^3.\text{atm.mol}^{-1}.°\text{C})t + 22413\ \text{cm}^3.\text{atm.mol}^{-1}$$
$$\Rightarrow t = \underline{-273.1°\text{C}}$$

(c)



$$m = \frac{\Delta T}{\Delta P} = \frac{-272.3\ °\text{C} - (-273.1\ °\text{C})}{1.0\ \text{atm} - 0.1\ \text{atm}} = 0.88889\ °\text{C.atm}^{-1}$$

when P = 1.0 atm, T = –272.3°C

x = T – mP = –272.3 – 0.88889 × 1.0 = –273.2°C

1.4

(a) for an ideal gas, $V = nRT/P$

$$\alpha_{ideal} = \frac{1}{V}(\partial V/\partial T)_P = \frac{P}{nRT} \times \frac{nR}{P} = \frac{1}{T}$$
$$\kappa_{ideal} = -\frac{1}{V}(\partial V/\partial P)_T = -\frac{P}{nRT} \times \left(\frac{-nRT}{P^2}\right) = \frac{1}{P}$$

(b)

$$P\overline{V} = RT + bP$$

$$P\frac{V}{n} = RT + bP \Rightarrow V = \frac{nRT + nbP}{P}$$

$$\alpha = \frac{P}{nRT + nbP}\left(\frac{nR}{P}\right) = \frac{R}{RT + bP}$$

$$\Rightarrow \alpha/\alpha_{idael} = \frac{R}{RT + bP}\bigg/\frac{1}{T} = \underline{\frac{RT}{RT + bP}}$$

$$\kappa = -\frac{P}{nRT + nbP}\left(\frac{-nRT}{P^2}\right) = \frac{RT}{RTP + bP^2}$$

$$\Rightarrow \kappa/\kappa_{ideal} = \frac{RT}{RTP + bP^2}\bigg/\frac{1}{P} = \underline{\frac{RT}{RT + bP}}$$

1.5

h = 29035 feet × 12 in.feet^{-1} × 2.54 cm.in^{-1} = 8.850 × 10^5 cm = 8.850 × 10^3 m

m = 0.781 × 28 + 0.209 × 32 + 0.010 × 40 = 28.956 g.mol^{-1} = 28.956 × 10^{-3} kg.mol^{-1}

$$P = P_0 e^{-gmh/RT}$$

$$P_{total} = 1.1013\ \text{bar} \times \exp\left[-\frac{9.8\ \text{m.s}^{-2} \times 28.956 \times 10^{-3} \times 10\ \text{g.mol}^{-1} \times 8.850 \times 10^3\ \text{m}}{8.315\ \text{J.K}^{-1}.\text{mol}^{-1} \times 273\ \text{K}}\right] = 0.335 bar$$

$$P_{O_2} = (1.013 \times 0.209)\ \text{bar} \times \exp\left[-\frac{9.8\ \text{m.s}^{-2} \times 32 \times 10^{-3}\ \text{kg.mol}^{-1} \times 8.850 \times 10^3\ \text{m}}{8.315\ \text{J.K.mol}^{-1} \times 273\ \text{K}}\right] = 0.07001 bar$$