ASSIGNMENT 1 : SOLUTIONS

1(a) USE $PV = nRT$

$$\Rightarrow n = P_0V/(RT)$$

$$\simeq (1.5 \times 10^6\ Pa)(0.5\ m^3)/[(8.315\ \tfrac{J}{mol \cdot K})(\underbrace{293.15\ K}_{273.15+20})]$$

$$\Rightarrow \boxed{n \simeq 308\ mol}$$

b) FOR O_2 THE MASS/MOL IS $2 \times (15.9994\ g/mol) = 31.999\ g/mol$

THE MASS OF 308 MOL IS

$$m = (308\ mol)(31.999\ g/mol)(1\ kg/1000\ g)$$

$$\Rightarrow \boxed{m \simeq 9.86\ kg}$$

c) THE # MOLES AND VOLUME IS UNCHANGED AFTER HEATING

$$\Rightarrow P = nRT/V$$

$$\simeq (308\ mol)(8.315\ \tfrac{J}{mol \cdot K})(\underbrace{773.15\ K}_{273.15+500})/(0.5\ m^3)$$

$$\Rightarrow \boxed{P \simeq 3.96 \times 10^6\ Pa}$$

d) AFTER REMOVAL THE FINAL PRESSURE IS

$$P' = 0.9\ P_0 \quad (\simeq 1.35 \times 10^6\ Pa)$$

THE TEMPERATURE AND VOLUME ARE FIXED. SO FINAL # MOLES IS

$$n' = P'V/(RT)$$

$$= (0.9P_0)V/(RT) = 0.9\,(P_0V/(RT)) = 0.9\,n \quad (\simeq 277\ mol)$$

SO FINAL MASS IS

$$m' = 0.9\,m \quad (\simeq 8.87\ kg)$$

THE MASS REMOVED IS $m - m' = 0.1\,m = \boxed{0.986\ kg}$

2) AT THE CRITICAL POINT $\frac{dP}{dV} = 0$ AND $\frac{d^2P}{dV^2} = 0$ ON ISOTHERM $T = T_c$

HERE THE CRITICAL VOLUME, TEMPERATURE AND PRESSURE ARE V_c, T_c AND P_c.

$$0 = \frac{dP}{dV}\Big|_{V_c} = \left[-\frac{RT}{(V-b)^2} e^{-\frac{a}{RT_cV}} + \frac{RT}{V-b}\frac{a}{RT_cV^2} e^{-\frac{a}{RT_cV}}\right]\Big|_{V=V_c}$$

THIS SIMPLIFIES TO GIVE

$$0 = \left[-1 + (V-b)\frac{a}{RT_cV^2}\right]\Big|_{V=V_c}$$

$$\Rightarrow V_c - b = \frac{RT_c}{a} V_c^2 \qquad (*)$$

$$0 = \frac{d^2P}{dV^2}\Big|_{V_c} = \Big[2\frac{RT_c}{(V-b)^3} e^{-\frac{a}{RT_cV}} - \frac{RT_c}{(V-b)^2}\frac{a}{RT_cV^2} e^{-\frac{a}{RT_cV}} - \frac{RT_c}{(V-b)^2}\frac{a}{RT_cV} e^{-\frac{a}{RT_cV}} + \frac{RT_c}{(V-b)}\left(-2\frac{a}{RT_cV^3}\right) e^{-\frac{a}{RT_cV}} + \frac{RT_c}{(V-b)}\left(\frac{a}{RT_cV^2}\right)^2 e^{-\frac{a}{RT_cV}}\Big]\Big|_{V=V_c}$$

CAN SIMPLIFY BY CANCELLING EXPONENTIALS.

ALSO USE $(*)$ TO REPLACE ALL OCCURRENCES OF $V_c - b$ WITH $\frac{RT_c}{a}V_c^2$

$$\Rightarrow 0 = 2\frac{a^3}{(RT_c)^2}\frac{1}{V_c^6} - \frac{a^2}{RT_c}\frac{1}{V_c^4}\left(\frac{a}{RT_cV_c^2}\right) - \frac{a^2}{RT_c}\frac{1}{V_c^4}\left(\frac{a}{RT_cV_c}\right) + a\frac{1}{V_c^2}\left(-2\frac{a}{RT_cV_c^3}\right) + a\frac{1}{V_c^2}\left(\frac{a}{RT_cV_c^2}\right)^2$$

$$\times \frac{(RT_c)^2}{a^3}V_c^6$$

$$\Rightarrow 0 = 2 - 1 - 1 - 2\frac{RT_c}{a}V_c + 1 = -2\frac{RT_c}{a}V_c + 1$$

$$\Rightarrow \frac{RT_c}{a} = \frac{1}{2V_c}$$

PUT THIS IN $(*)$ $\Rightarrow$ $V_c - b = \left(\frac{1}{2V_c}\right)V_c^2 = \frac{1}{2}V_c$

$$\Rightarrow \boxed{V_c = 2b}$$

3a) $\rho = \rho_0 [1 - \alpha_T (T - T_0) + \alpha_S (S - S_0)]$

$\simeq \rho_0 [1 - (2.1 \times 10^{-4}\ K^{-1})((25 - 20) K) + (6.7 \times 10^{-4}\ ppt^{-1})((35 - 38.5)\ ppt)]$

(DIFFERENCE IN °C EQUALS DIFFERENCE IN K)

$\simeq \rho_0 [1 - 1.05 \times 10^{-3} - 2.345 \times 10^{-3}]$

$\simeq \rho_0\ 0.9966$ WITH $\rho_0 = 1025\ kg/m^3$

$\simeq \boxed{1021.5\ kg/m^3}$

b) THE INITIAL VOLUME IN THE BOX IS $V_0 = h_0 A$.

IF THE INITIAL DENSITY IS ρ_0, THE MASS IS $M_0 = \rho_0 V_0 = \rho_0 h_0 A$.

IF THE TEMPERATURE CHANGES, THE MASS IS THE SAME. BUT THE DENSITY CHANGES TO $\rho = \rho_0 [1 - \alpha_T \Delta T]$. *

SO THE NEW VOLUME IS $V = M_0 / \rho = \frac{1}{\rho} (\rho_0 h_0 A)$

BECAUSE THE AREA IS THE SAME, THE NEW HEIGHT IS

$$h = \frac{V}{A} = \frac{1}{\rho} \rho_0 h_0$$

USE (*) $\Rightarrow$ $h = \frac{1}{\rho_0 (1 - \alpha_T \Delta T)} \rho_0 h_0 = \frac{1}{1 - \alpha_T \Delta T} h_0$

THE INCREASE IN DEPTH IS $\Delta h = h - h_0 = \left(\frac{1}{1 - \alpha_T \Delta T} - 1 \right) h_0$.

NOW, IF $|\alpha_T \Delta T| \ll 1$, WE CAN APPROXIMATE $\frac{1}{1 - \alpha_T \Delta T} \simeq 1 + \alpha_T \Delta T$

$$\Rightarrow \Delta h \simeq (1 + \alpha_T \Delta T - 1) h_0 = \boxed{\alpha_T \Delta T h_0}$$

c) WHEN THE TOP km OF SEA WATER WARMS, IT CAN ONLY EXPAND VERTICALLY, NOT LATERALLY (CONSTRAINED BY CONTINENTS)

SO THIS IS LIKE OUR WATER IN A BOX WITH $\Delta T = 1°C = 1 K$, $h_0 = 1 km$

$$\Delta h \simeq (2.1 \times 10^{-4}\ K^{-1})(1 K)(1000 m)$$

$$= 0.21\ m$$

$$\Rightarrow \boxed{\Delta h = 20 cm}$$

4) BY DEFINITION, EXPANSIVITY IS

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$$, WHERE V IS VOLUME AND $v = \frac{V}{M} = \frac{1}{\rho}$ SPECIFIC VOLUME

ISOTHERMAL COMPRESSIBILITY IS

$$\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

IN WHICH WE ASSUME $v = v(T, P)$

GIVEN $\beta = b\frac{T}{v} \Rightarrow \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = b\frac{T}{v}$

$\Rightarrow \left(\frac{\partial v}{\partial T}\right)_P = bT$

SOME FUNCTION OF PRESSURE

$\Rightarrow v = \frac{1}{2}bT^2 + f(P) \qquad (*)$

GIVEN $\kappa = a\frac{1}{v} \Rightarrow -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = a\frac{1}{v}$

$\Rightarrow \left(\frac{\partial v}{\partial P}\right)_T = -a$

USE $(*)$ $\Rightarrow \left(\frac{\partial}{\partial P}\left(\frac{1}{2}bT^2 + f(P)\right)\right)_T = -a$

$\Rightarrow f'(P) = -a$

CONSTANT

$\Rightarrow f(P) = -aP + C$

PUT IN $(*)$ $\Rightarrow v = \frac{1}{2}bT^2 - aP + C$

$$\Rightarrow \boxed{v - \frac{1}{2}bT^2 + aP = C}$$