(2) EQUATIONS OF STATE

GENERALLY, THE EQUATION OF STATE EXPRESSES THE RELATIONSHIP BETWEEN PROPERTIES OF A SYSTEM (eg PRESSURE (P), TEMPERATURE (T), VOLUME (V) OR DENSITY (ρ), SALINITY (S), MOISTURE CONTENT, etc). THE EQUATION IS USUALLY <u>VERY</u> COMPLICATED AND DETERMINED ONLY THROUGH EMPIRICAL MEASUREMENTS. BUT IT IS STRAIGHTFORWARD FOR AN "IDEAL GAS".

I] THE IDEAL GAS

AS FIRST DETERMINED THROUGH EXPERIMENTS (BOYLE 1662: $P \propto \rho$, T-CONSTANT; CHARLES 1780: $\rho \propto \frac{1}{T}$, P-CONSTANT) THE PRESSURE, VOLUME AND TEMPERATURE OF AN "<u>IDEAL GAS</u>" (ie LOW DENSITY, NO INTERACTIONS WITH BOUNDARIES, etc) ARE RELATED BY

$$PV = nRT. \qquad (1)$$

HERE 'n' IS THE NUMBER OF MOLES OF GAS AND 'R' IS THE "<u>UNIVERSAL GAS CONSTANT</u>":

$$\boxed{R \simeq 8.315\ J/(\text{mol} \cdot K)}$$

FOR P IN $Pa \equiv N/m^2$, V IN m^3 AND T IN KELVIN (<u>NOT</u> CELSIUS)

ALTERNATELY, DEFINE "SPECIFIC VOLUME" $v = \frac{V}{n}$ (IN m^3/mol)
SO (1) BECOMES

$$Pv = RT \qquad (2)$$

PHYSICISTS OFTEN CARE MORE ABOUT THE NUMBER OF MOLECULES $N = n \times N_A$, WITH $N_A \equiv 6.02 \times 10^{23}$, AVOGADRO'S NUMBER (1811)
SO (1) BECOMES

$$PV = NkT \qquad (3)$$

IN WHICH $\boxed{k \equiv R/N_A = 1.381 \times 10^{-23}\ J/K}$ IS "BOLTZMANN'S CONSTANT"

1] (CONT'D)

ATMOSPHERIC SCIENTISTS ALWAYS WORK WITH AIR, WHICH CONTAINS 78% N_2 (MOLAR MASS $M_{N_2} \simeq 28\,g/mol$) AND 21% O_2 (MOLAR MASS $M_{O_2} \simeq 32\,g/mol$). THE MOLAR MASS OF AIR IS $M_a \simeq 0.78\,M_{N_2} + 0.21\,M_{O_2} + \ldots \simeq 28.97\,g/mol$.

So, DEFINING THE GAS CONSTANT FOR AIR AS

$$R_a \equiv \frac{1}{M_a} R = [8.31\ J/(mol\cdot K)]/(28.97\ g/mol) = \boxed{287\ J/(kg\cdot K)}$$

(1) IS REWRITTEN IN TERMS OF DENSITY:

$$P = \rho R_a T \quad \left(\text{FROM } P = \frac{1}{V} nRT = \frac{M}{V}\left(\frac{nR}{M}\right)T = \rho\left(\frac{R}{M_a}\right)T\right) \qquad (4)$$

IN PARTICULAR AT 1 ATM AND 0°C (STANDARD TEMPERATURE AND PRESSURE: STP) HAVE AIR DENSITY

$$\rho_a \simeq \overbrace{(1.251\ kg/m^3)}^{\rho_{N_2}} \times 0.78 + \overbrace{(1.429\ kg/m^3)}^{\rho_{O_2}} \times 0.21$$
$$= 1.29\ kg/m^3$$

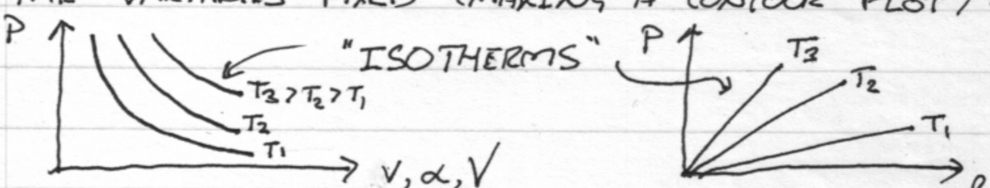
[CHECK: $P = (1.29\ kg/m^3)(287\ J/(kg\,K))(273\,K) \simeq 1.01 \times 10^5\ Pa$ ✓]

FINALLY, WE CAN REWRITE (4) IN TERMS OF SPECIFIC VOLUME $\alpha \equiv 1/\rho$ (NOTE: VOLUME/MASS, NOT LIKE v IN VOLUME/MOL):

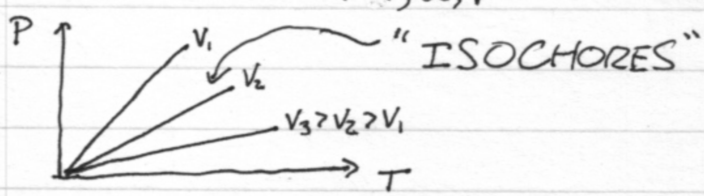
$$P\alpha = R_a T \qquad (5)$$

EQ$^{\underline{N}}$s (1) – (5) INVOLVE 3 VARIABLES. CAN PLOT THE FORMULAE KEEPING ONE OF THE VARIABLES FIXED (MAKING A CONTOUR PLOT):

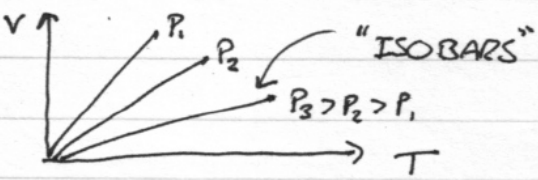
T - CONSTANT



V - CONSTANT



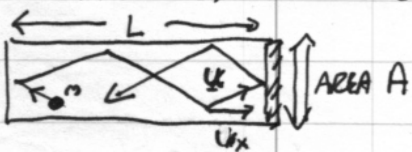
P - CONSTANT



2] THE MICROSCOPIC INTERPRETATION OF PRESSURE FOR A GAS

THE PRESSURE EXERTED BY A GAS ON A WALL IS A CONSEQUENCE OF THE CHANGE IN MOMENTUM OF GAS MOLECULES AS THEY BOUNCE OFF THE WALLS

FOR EXAMPLE, CONSIDER A CHAMBER CONTAINING A SINGLE MOLECULE.



ASSUMING NO ENERGY LOSS, THE MOLECULE WILL BOUNCE FOREVER AT SPEED $u = |\underline{u}|$ WITH KINETIC ENERGY $\frac{1}{2} m u^2 = \frac{1}{2} m (u_x^2 + u_y^2 + u_z^2)$

NOW CONSIDER FORCE/AREA OF MOLECULE THAT REPEATEDLY BOUNCES OFF THE RIGHT WALL OF AREA A. A SINGLE BOUNCE PRODUCES A LARGE IMPULSE. THE LONG TIME AVERAGE OF MANY BOUNCES GIVE THE PRESSURE

$$P = \frac{F_{x,\text{ON PISTON}}}{A} = -\frac{F_{x,\text{ON MOLECULE}}}{A} = -\frac{1}{A}\left[m\left(\frac{\overline{\Delta u_x}}{\Delta t}\right)\right],$$

IN WHICH WE TAKE $\Delta t = 2L/u_x$ AS THE TIME FOR ONE BOUNCE AND $\overline{\Delta u_x} = u_{x,\text{FINAL}} - u_{x,\text{INITIAL}} = (-u_x) - (+u_x) = -2u_x$ IS THE CHANGE OF HORIZONTAL VELOCITY IN THIS TIME.

$$\text{So} \qquad P = -\frac{m}{A}\left[\frac{-2u_x}{(2L/u_x)}\right] = \frac{m u_x^2}{AL} = \frac{m u_x^2}{V} \leftarrow V \equiv AL \text{ IS VOLUME}$$

HENCE PRESSURE IS RELATED TO THE KINETIC ENERGY DENSITY.
NOTE, P INCREASES AS u_x^2: FASTER MOLECULES EXCHANGE MORE MOMENTUM AND DO SO MORE OFTEN.

ALSO NOTE, THE RESULT DOES NOT DEPEND UPON THE ASPECT RATIO, BUT ONLY ON THE COMBINATION $AL = V$. SO THE SAME REASONING APPLIES TO ALL WALLS, WITH THE ASSUMPTION THAT, ON AVERAGE, THE VELOCITY IS ISOTROPIC: $V_x \approx V_y \approx V_z$.

2] (CONT'D)

NOW SUPPOSE WE HAVE N (eg 10^{23}) MOLECULES, BUT ASSUME THEY ARE SO SPARSE THAT MOLECULE-MOLECULE INTERACTIONS ARE SO INFREQUENT AS TO BE NEGLIGIBLE.

SO THE PRESSURE IS $\overline{P} = \frac{N}{V} m\overline{u_x^2}$ ← AVERAGE OF SQUARE, NOT SQUARE OF AVERAGE.

RECALL THAT THE IDEAL GAS LAW CAN BE WRITTEN $PV = NkT$ (k: 1.381×10^{-23} J/K)

HENCE $kT = m\overline{u_x^2}$.

LIKEWISE $kT = m\overline{u_y^2}$, $kT = m\overline{u_z^2}$.

THUS WE CAN RELATE A MOLECULE'S MEAN KINETIC ENERGY TO THE MACROSCOPICALLY OBSERVED TEMPERATURE:

$$\overline{K} = \overline{\tfrac{1}{2} m u^2} = \tfrac{1}{2} m \left(\overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}\right) = \tfrac{3}{2} kT \qquad (1)$$

FOR EXAMPLE, AT ROOM TEMPERATURE ($T \sim 300K$)

$$kT \approx (1.38 \times 10^{-23}\ \mathrm{J/K})(300K) \simeq 4.14 \times 10^{-21}\ \mathrm{J}$$
$$\simeq (4.14 \times 10^{-21}\ \mathrm{J})\left(\frac{1}{1.6 \times 10^{-19}} \frac{\mathrm{eV}}{\mathrm{J}}\right) \simeq 0.026\ \mathrm{eV}$$

SO THE KINETIC ENERGY IS SMALL RELATIVE TO TYPICAL ELECTRIC FORCES

NONETHELESS, THE MEAN SPEED OF GAS MOLECULES AT ROOM TEMPERATURE IS QUITE LARGE. AN ESTIMATE OF THIS SPEED IS GIVEN BY THE "ROOT-MEAN-SQUARE":

$$V_{rms} \equiv \sqrt{\overline{V^2}} = \sqrt{3kT/m} \qquad (2)$$

[WE WILL FIND A BETTER ESTIMATE FROM STATISTICAL MECHANICS TO BE $\sqrt{\frac{8}{\pi} kT/m}$]

FOR A MOLECULE OF NITROGEN $m_{N_2} = (28\ \mathrm{g/mol}) / (6.02 \times 10^{23} \frac{\mathrm{molecules}}{\mathrm{mol}}) \simeq 4.7 \times 10^{-23}\ \mathrm{g}$

$\Rightarrow V_{rms} \simeq \left[3(1.38 \times 10^{-23}\ \mathrm{J/K})(300K) / (4.7 \times 10^{-26}\ \mathrm{kg})\right]^{1/2} \simeq \underline{500\ \mathrm{m/s}}$!!

3] VAN DER WAAL'S EQUATION FOR A "REAL" GAS (1873)

THIS EXTENDS THE IDEAL GAS LAW TO ACCOUNT CRUDELY FOR MOLECULE-MOLECULE INTERACTIONS IN GASES CLOSE TO CONDENSATION:

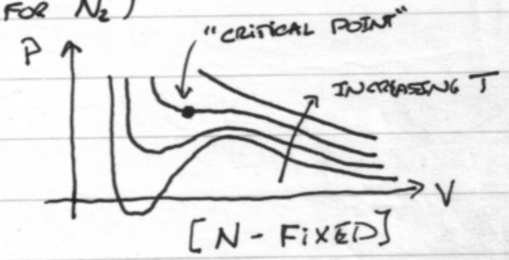
$$\boxed{\left(P + a\frac{N^2}{V^2}\right)(V - bN) = NkT} \qquad (1)$$

HERE a & b ARE EMPIRICAL CONSTANTS THAT DEPEND UPON THE GAS IN QUESTION.
IF $a = b = 0$, WE RETRIEVE THE IDEAL GAS LAW (3) ON p.7.

- bN IS A LOWER BOUND ON THE VOLUME OF N MOLECULES. SO b IS THE APPROXIMATE 'VOLUME' OF ONE MOLECULE.
  (eg $b \sim (4\text{Å})^3 \simeq 6 \times 10^{-29}\,m^3$ FOR SMALL MOLECULES LIKE N_2)
- aN^2/V^2 IS THE DECREASE IN PRESSURE DUE TO MOLECULES IN CLOSE PROXIMITY. (THE POTENTIAL ENERGY OF A MOLECULE INCREASES AS THE NUMBER DENSITY; TOTAL P.E $\propto N^2/V$; SO $p \propto -\left(\frac{\partial PE}{\partial V}\right) \propto \frac{N^2}{V^2}$)
  (eg $a \simeq 2.5\,eV \cdot \text{Å}^3 \simeq 4 \times 10^{-49}\,J \cdot m^3$ FOR N_2)

EXPLICITLY, $P = \frac{NkT}{(V - bN)} - a\frac{N^2}{V^2}$

PLOTTED USING ISOTHERMS ON A PV DIAGRAM:



FOR LARGE T, P VS V IS MONOTONIC DECREASING. FOR SMALL T, THE CURVES HAVE A DISTINCT MINIMUM. THE TRANSITION OCCURS FOR $T = T_c$, THE "CRITICAL TEMPERATURE". ALONG THIS ISOTHERM THERE IS A UNIQUE POINT $P = P_c$, $V = V_c$ WHERE THE CURVE HAS ZERO SLOPE AND CURVATURE:

$$0 = \frac{dP}{dV}\bigg|_{V_c} = -\frac{NkT_c}{(V_c - bN)^2} + 2a\frac{N^2}{V_c^3} \Rightarrow kT_c = 2aN\left[\frac{(V_c - bN)^2}{V_c^3}\right]$$

$$0 = \frac{d^2P}{dV^2}\bigg|_{V_c} = \frac{2NkT_c}{(V_c - bN)^3} - 6a\frac{N^2}{V_c^4} = \dots = \frac{2NkT_c}{(V_c - bN)^3}\left[-\frac{1}{2} + \frac{3}{2}\frac{bN}{V_c}\right]$$

$$\frac{2NkT_c}{(V_c - bN)^3}\left[1 - \frac{3aN^2}{V^4}\frac{(V - bN)}{NkT}\right]$$

SO $V_c = 3bN \Rightarrow kT_c = \frac{8}{27}\frac{a}{b} \Rightarrow P_c = \frac{1}{27}a/b^2$

$a \simeq 2.5\,eV \cdot \text{Å}^3 = 4 \times 10^{-49}\,J/m^3$, $b \sim (4\text{Å})^3 \sim 6 \times 10^{-29}\,m^3$

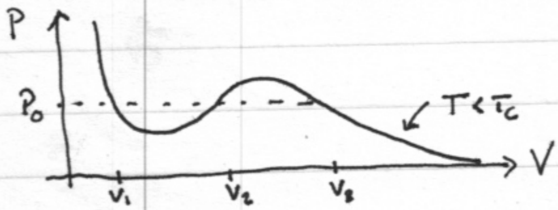
EXAMPLE: FOR N_2

$$T_c \simeq \frac{8}{27}\frac{4 \times 10^{-49}}{6 \times 10^{-29}}\frac{1}{1.38 \times 10^{-23}} \simeq 143\,K$$

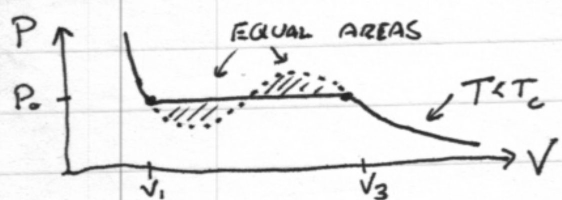
$$P_c \simeq \frac{1}{27}\frac{4 \times 10^{-49}}{(6 \times 10^{-29})^2} \simeq 4 \times 10^6\,Pa \approx 40 \text{ BARS}$$

3] (CONT'D)

IN THE SUBCRITICAL CASE, THERE APPEARS TO BE A PROBLEM: AT FIXED $T < T_c$ AND SUFFICIENTLY SMALL PRESSURE, THE SYSTEM LOOKS AS IF IT CAN HAVE ONE OF 3 POSSIBLE VOLUMES:

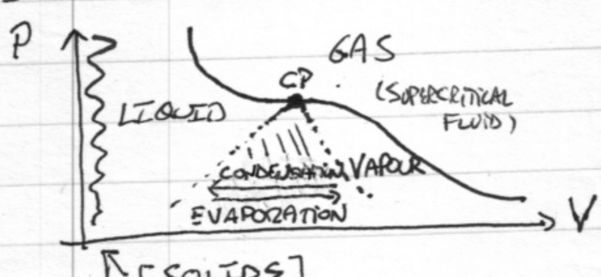


LATER IN THE COURSE WE WILL SEE ALL POINTS ON THE CURVE ARE "UNSTABLE" BETWEEN V_1 AND V_3. THE SYSTEM EVOLVES TOWARD EQUILIBRIUM IF $V_1 < V < V_3$ SO THAT THE SYSTEM AT TEMPERATURE T AND PRESSURE P_0 HAS VOLUME V_1 OR V_3. AND P_0 IS CONSTRAINED SO THE AREA BETWEEN V_1 & V_2 EQUALS THAT BETWEEN V_2 & V_3:



THE "PV" DIAGRAM DRAWN WITH MANY ISOTHERMS ACTUALLY LOOKS LIKE THIS:

IN EFFECT, THIS REVEALS THE PHASE CHANGE BETWEEN GAS AND LIQUID IF THE TEMPERATURE IS SUBCRITICAL:

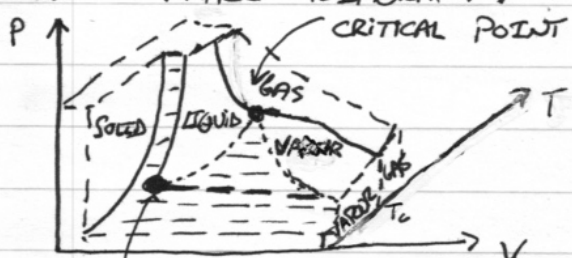


AT CRITICAL POINT, GAS & LIQUID ARE INDISTINGUISHABLE. THE GAS IS CALLED A "VAPOUR" IF $T < T_c$

4] PHASE TRANSFORMATIONS OF PURE SUBSTANCES

IF THE VOLUME OCCUPIED BY N MOLECULES IS SMALL ENOUGH (AND PRESSURE HIGH / TEMPERATURE LOW) THE SUBSTANCE SOLIDIFIES. THIS PROCESS IS NOT CAPTURED BY VAN DER WAALS EQUATION. BUT EXPERIMENTATION ON MANY SUBSTANCES REVEALS TYPICAL PHASE-CHANGE BEHAVIOUR ON A "PHASE DIAGRAM":

PVT DIAGRAM



AT CRITICAL POINT, LIQUID & GAS CO-EXIST.

A TRIPLE POINT, SOLID, LIQUID & GAS CO-EXIST

THIS MUCH EASIER TO SEE WHEN PROJECTED ONTO A P-T DIAGRAM

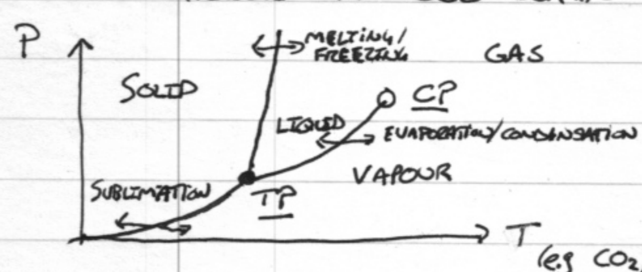
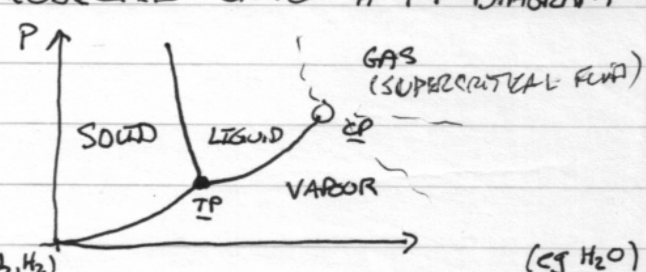


DIAGRAM FOR SUBSTANCE THAT CONTRACTS UPON FREEZING



SUBSTANCE THAT EXPANDS UPON FREEZING

SOME NUMBERS:

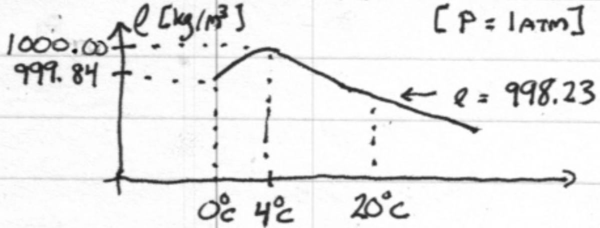
H_2O	TRIPLE POINT	$P = 0.006$ BAR	$T = 0.01°C$
	CRITICAL POINT	$P = 221$ BAR	$T = 374°C$
CO_2	TRIPLE POINT	$P = 5.2$ BAR	$T = -56.6°C$
	CRITICAL POINT	$P = 73.8$ BAR	$T = 31°C$

IT IS BECAUSE THE TRIPLE POINT PRESSURE OF CO_2 IS GREATER THAN 1 BAR THAT WE SEE FROZEN CO_2 SUBLIMATE AT ROOM TEMPERATURE (DRY ICE)

THE LINE BETWEEN VAPOUR AND LIQUID/SOLID IS THE "VAPOUR PRESSURE"
e.g. FOR WATER AT 25°C, THE VAPOUR PRESSURE IS 0.03 BAR.
SO WATER WILL BOIL IF IN A VACUUM CHAMBER BELOW 0.03 BAR

5] THE EQUATION OF STATE OF SEAWATER

BECAUSE OF THE ELBOW-SHAPE OF AN H_2O MOLECULE, ITS MACROSCOPIC PROPERTIES EXPRESSED THROUGH THE EQUATION OF STATE ARE QUITE UNUSUAL: IT IS MOST DENSE AT $4°C$, ABOVE FREEZING TEMPERATURE



[NOT LINEAR SCALE]

ACCORDING TO THE 1980 UNESCO STANDARD, AT $P = 1$ ATM DENSITY VARIES WITH TEMPERATURE ACCORDING TO [WITH T IN °C]

$$\rho_W \simeq 999.842594 + 6.793952 \times 10^{-2} T - 9.095290 \times 10^{-3} T^2 + \dots$$

[SEE SUPPLEMENTARY MATERIAL ON WEB FOR FULL EXPANSION]

IN THE OCEAN, DENSITY CHANGES WITH SALINITY AS WELL AS TEMPERATURE. DEFINE SALINITY S TO BE MASS SALT PER MASS SOLVENT. Eg IF YOU PUT 35g SALT IN 1kg H_2O, THE SALINITY IS $S = 35\,g/kg = 0.035 = 35\,ppt$ ['ppt' MEANS PARTS PER THOUSAND], SO AT 1 ATM, THE DENSITY OF SEAWATER IS $\rho(T,S) \simeq \rho_W + S(0.824493 - 4.0899 \times 10^{-3} T \dots) + S^{3/2}(-5.72466 \times 10^{-3}) \dots$

IN THE ABYSS, PRESSURES GET UP TO 500 ATM! THIS IS LARGE ENOUGH TO AFFECT DENSITY:

$$\rho(T,S,p) = \rho(T,S)\left[1 - \frac{p}{K}\right]^{-1} \text{ WITH } K \simeq (19652.21 + 148.42T) + S(54.67) + p(3.2399) \dots$$

WHERE $p = P - P_0$, $P_0 = 1$ ATM, P IN ATM

YUCK! AND IT GETS MORE COMPLICATED WHEN ADDING OTHER SALTS IN OCEAN. THE WHOLE THING WAS REVISED IN 2010 USING "GIBBS FREE ENERGY". FORTUNATELY, IN MANY CIRCUMSTANCES, A LINEAR APPROXIMATION SUFFICES:

$$\rho \sim \rho_0 \left[1 - \alpha_T (T - T_0) + \alpha_S (S - S_0) + \alpha_P (P - P_0)\right]$$

AT $T_0 = 293\,K$, $S_0 = 0\,ppt$, $P_0 = 101.3\,kPa \Rightarrow \rho_0 = 998.23\,kg/m^3$

AND $\alpha_T \simeq 2.1 \times 10^{-4}\,K^{-1}$ (THERMAL EXPANSION COEFFICIENT),

$\alpha_S \simeq 7.4 \times 10^{-4}\,ppt^{-1}$, $\alpha_P = 4.1 \times 10^{-10}\,Pa^{-1}$ (COMPRESSIBILITY)

6] EXPANSIVITY AND COMPRESSIBILITY

THE EXPRESSIONS FOR THERMAL EXPANSION AND COMPRESSIBILITY (DUE TO PRESSURE) EXTEND TO ALL SUBSTANCES IN ANY PHASE (SOLID - LIQUID - GAS). HERE, RATHER THAN DENSITY, WE CAST THE PROBLEM IN TERMS OF SPECIFIC VOLUME, V.

SUPPOSE $V \equiv V(T, P)$. (1)

A LINEAR APPROXIMATION TO V ABOUT GIVEN TEMPERATURE T_0 AND PRESSURE P_0 (HENCE GIVEN $V_0 = V(T_0, P_0)$) IS

$$V \approx V_0 \left[1 + \beta (T - T_0) - \chi (P - P_0) \right]$$

$$\Rightarrow V - V_0 \approx V_0 \beta (T - T_0) - V_0 \chi (P - P_0)$$

TAKING THE LIMIT $T \to T_0$ AND $P \to P_0$ (HENCE $V \to V_0$), WE WRITE THIS AS A DIFFERENTIAL

$$dV = V_0 \beta \, dT - V_0 \chi \, dP,$$

IN WHICH WE NOW RECOGNIZE THE COEFFICIENTS AS PARTIAL DERIVATIVES SINCE, FROM (1), $dV = \left(\frac{\partial V}{\partial T}\right) dT + \left(\frac{\partial V}{\partial P}\right) dP$.

HENCE

THERMAL EXPANSIVITY; ISOTHERMAL COMPRESSIBILITY

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{AND} \quad \chi = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad (2)$$

WHERE THE SUBSCRIPTS EMPHASIZE THAT P AND T ARE FIXED WHEN FINDING β AND χ, RESPECTIVELY. NOTE, THE DEFINITIONS IN (2) MEAN THAT V CAN BE MEASURED IN VOLUME/MOL OR VOLUME/kg (AS WITH $\alpha \equiv \frac{1}{\rho}$)

GENERALLY, β AND χ CAN THEMSELVES BE FUNCTIONS OF P AND T AND MUST BE DETERMINED EMPIRICALLY. BUT THEY CAN BE FOUND EXPLICITLY FOR AN IDEAL GAS:

$$V = RT/P \Rightarrow \beta = \frac{1}{V}\left(\frac{R}{P}\right) = \frac{1}{T} \; ; \; \chi = -\frac{1}{V}\left(-\frac{RT}{P^2}\right) = \frac{1}{P} \qquad (3)$$

[IN REVERSE: GIVEN $\beta = \frac{1}{T} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \frac{dV}{dT} = \frac{V}{T} \Rightarrow \frac{1}{V} dV = \frac{1}{T} dT \Rightarrow \ln V = \ln T + C(P) \Rightarrow V = C(P)T$; $\frac{1}{P} = \chi = -\frac{1}{V}\frac{\partial V}{\partial P} = -\frac{1}{CT}\frac{\partial TC}{\partial P}$ $\Rightarrow V = C_0 T/P$]

EXAMPLE: GIVEN $\beta \simeq 5.2 \times 10^{-5}\,K^{-1}$ AND $\chi \simeq 7.6 \times 10^{-12}\,Pa^{-1}$ FOR COPPER AROUND $130°C$, THE PRESSURE INCREASE REQUIRED TO KEEP THE VOLUME FIXED AS THE TEMPERATURE RAISES $\Delta T = 10°C$ IS $\Delta P \simeq \frac{\beta}{\chi}\Delta T \simeq 6.8 \times 10^{7}\,Pa \simeq 680$ ATM