

Note: in general there is no condition on the path of a gas in a piston say f the curve drawn in the (V, p) plane. What I mean is w/o any other information the path in (V, p) is arbitrary & f simply represents the points in (V, p) where the piston traveled. At every (V, p) point one could use the EOS $f(p, V, T) = 0$ to solve for the temperature in the gas at every point along its path.

If we are told more information like the path in (V, p) is along an isobar or an isotherm then the path in (V, p) is specified.

M = molecular weight $\left\{ \begin{array}{l} \text{mass of 1 molecule} \cdot \text{Avogadro's constant} \\ \text{weight of 1 mole of these molecules} \end{array} \right.$

$$N_A = 6.02 \cdot 10^{23} \text{ mol}^{-1}$$

$$PV = \left(\frac{m}{M} \right) RT$$

$$R = 8.314 \cdot 10^7 \text{ erg/degree}$$

$$= 1.986 \text{ cal/degree}$$

M = molecular weight = mass of 1 mole of molecules,

$$p = \frac{m}{V} = \frac{mP}{RT} \quad \text{eq 3}$$

$$p = \frac{mRT (\text{mass of air gas})}{M V}$$

consted temp $PV = \text{const}$

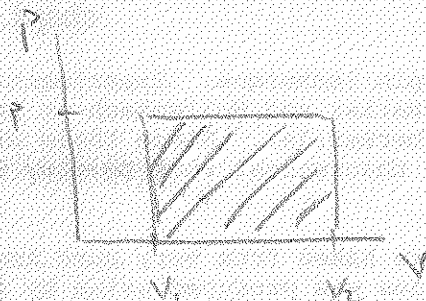
$$L = \int_{V_1}^{V_2} p dV = \frac{m}{M} RT \int_{V_1}^{V_2} \frac{dV}{V} = \frac{mRT}{M} \ln\left(\frac{V_2}{V_1}\right) = \frac{mRT}{M} \ln\left(\frac{P_1}{P_2}\right) \quad \text{eq (9)}$$

$$P_1 V_1 = \frac{m}{M} RT$$

$$P_2 V_2 = \frac{m}{M} RT$$

$$\Rightarrow \frac{P_1 V_1}{P_2 V_2} = 1 \quad \Rightarrow \quad \frac{V_1}{V_2} = \frac{P_2}{P_1}$$

① Assume constant pressure



$$dL = p dV$$

$$L = \int_{V_1}^{V_2} p dV = p(V_2 - V_1)$$

$$= (2.34 \text{ atm})(4.01 - 3.12) \text{ liters} = 2.0826 \text{ atm liters}$$

Units of work are the Nm or dyne cm.

$$1 \text{ atm} = 1.01 \cdot 10^5 \text{ Pa} = 1.01 \cdot 10^5 \text{ N/m}^2$$

$$1 \text{ liter} = 10^{-3} \text{ m}^3$$

$$\therefore 1 \text{ atm} \cdot \text{liter} = 1.01 \cdot 10^5 \frac{\text{N}}{\text{m}^2} \cdot 10^{-3} \text{ m}^3 = 1.01 \cdot 10^2 \text{ Nm}$$

$$= 1.01 \cdot 10^5 \cdot 10^{+2} \text{ dyne cm}$$

$$= 1.01 \cdot 10^7 \text{ dyne cm}$$

Thus

$$L = 2.103 \cdot 10^2 \text{ Nm} = 210.3 \text{ Nm}$$

$$= 2.103 \cdot 10^7 \text{ dyne cm}$$

② $m = 30 \text{ g}$

$M = 2 \text{ g/mole}$ $T = 18^\circ\text{C}$ $V = 1 \text{ m}^3$

$T = 18^\circ\text{C} + 273,15$

$= 291,15 \text{ K}$

$R = 8,314 \text{ (J/mole K)}$

$PV = \left(\frac{m}{M}\right)RT$

$P(1 \text{ m}^3) = \left(\frac{30 \text{ g}}{2 \text{ g/mole}}\right)(8,314 \text{ J/mole K})(291,15 \text{ K})$

$P = 3,63 \cdot 10^4 \text{ J/m}^3 = 3,63 \cdot 10^4 \frac{\text{N} \cdot \text{m}}{\text{m}^3} = 3,63 \cdot 10^4 \frac{\text{N}}{\text{m}^2}$

$= 3,63 \cdot 10^4 \text{ Pa} =$

$1 \text{ Pa} = \frac{1}{1,01 \cdot 10^5} \text{ atm} = 9,9 \cdot 10^{-6} \text{ atm}$

$\Rightarrow P = 3,63 \cdot 10^4 (9,9 \cdot 10^{-6}) \text{ atm} = 3,59 \cdot 10^{-1} \text{ atm}$

③ $T = 0^\circ\text{C} \rightarrow T = 273,15 \text{ K}$ From F

$PV = \left(\frac{m}{M}\right)RT$

$P = \frac{m}{V} = \frac{PM}{RT}$

- ③ Nitrogen exists as a diatomic molecule N_2
 & thus has molecular weight $M = 14 \text{ grams/mole} = 28 \text{ grams/mole}$

$$P = \frac{MP}{RT} \quad \text{By eq (8)}$$

$$T = 0^\circ\text{C} = 273.15^\circ\text{K}$$

$$R = 8.314 \text{ J/mol K}$$

$$V = P^{-1} = \frac{RT}{MP}$$

Assume pressure = 1 atm = $1.01 \cdot 10^5 \text{ Pa}$

Then
$$P = \frac{(14 \text{ grams/mole})(1.01 \cdot 10^5 \text{ Pa})}{8.314 (273.15) (\text{J/mole})}$$

$$= 6.22 \cdot 10^2 \frac{\text{grams Pa}}{\text{J}}$$

$$= 6.22 \cdot 10^2 \cdot 10^{-3} \frac{\text{kg} (\cancel{\text{N} \cdot \text{m}})}{(\cancel{\text{N} \cdot \text{m}}/\cancel{\text{J}})}$$

$$= 6.22 \cdot 10^{-1} \frac{\text{kg}}{\text{m}^3} = 6.22 \cdot 10^{-1} \cdot \frac{10^3}{(10^2)^3} \text{ g/cm}^3 = 6.22 \cdot 10^{-3} \text{ g/cm}^3$$

$$V = 1.6 \frac{\text{m}^3}{\text{kg}} = 1.6 \cdot \frac{10^6}{10^3} \frac{\text{cm}^3}{\text{g}} = 1.6 \cdot 10^3 \text{ cm}^3/\text{g}$$

$$\text{Pa} = \frac{\text{N}}{\text{m}^2} = \frac{\text{kg m}}{\text{m}^2 \text{ s}^2} = \frac{\text{kg}}{\text{m s}^2}$$

$$\text{J} = \text{N} \cdot \text{m} = \frac{\text{kg m}}{\text{s}^2} \cdot \text{m} = \frac{\text{kg m}^2}{\text{s}^2}$$

(4)

$$L = \frac{m}{M} RT \log\left(\frac{V_2}{V_1}\right) = \frac{m}{M} RT \log\left(\frac{P_1}{P_2}\right)$$

$$M = 32.0 \text{ g/mol} \quad R = 8.314 \text{ J/mol K}$$

$$m = 10 \text{ g}$$

$$T = 20^\circ\text{C} \Rightarrow T = 293.15 \text{ K}$$

$$L = \frac{m}{M} RT \log\left(\frac{P_1}{P_2}\right) = \left(\frac{10 \text{ g}}{32 \text{ g/mol}}\right) (8.314 \text{ J/mol K}) (293.15 \text{ K}) \log\left(\frac{1}{.3}\right)$$

$$= 916.9 \text{ J} = 916.9 \text{ N/m}$$

$$dU = \left(\frac{\partial U}{\partial p}\right)_T dp + \left(\frac{\partial U}{\partial T}\right)_p dT \quad (p, T) \quad \text{Then } U \text{ must be a fn of } T \text{ \& } p$$

$$dU + p dV = dQ$$

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT$$

$$\left(\frac{\partial U}{\partial p}\right)_T dp + \left(\frac{\partial U}{\partial T}\right)_p dT + p \left[\left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp \right] = dQ$$

$$\left[\left(\frac{\partial U}{\partial p}\right)_T + p \left(\frac{\partial V}{\partial p}\right)_T \right] dp + \left[\left(\frac{\partial U}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p \right] dT = dQ \quad \text{eq (23)}$$

eq (30)

$$C_v dT + p dV = dQ$$

eq (31)

$$p dV + V dp = R dT$$

Subtract (31) from (30)

$$C_v dT - V dp = dQ - R dT$$

$$(C_v + R) dT - V dp = dQ \quad \text{eq (32)}$$

$$dp = 0 \quad C_p \equiv \left. \frac{dQ}{dT} \right|_p = C_v + R$$

eq (26)

$$C_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p$$

$$U = C_v T$$

$$pV = RT$$

$$V = \frac{RT}{p}$$

 $C_p(T, p)$

$$U = U(T)$$

$$\left(\frac{\partial U}{\partial T} \right)_p = \left. \frac{dU}{dT} \right|_p = C_v$$

Assuming C_v is a constant,

$$C_p = C_v + p \left. \frac{\partial}{\partial T} \left(\frac{RT}{p} \right) \right|_p$$

$$= C_v + p \frac{R}{p} = C_v + R$$

$$C_p = \frac{5}{2}R + R = \frac{7}{2}R \quad \text{monatomic gas}$$

$$= \frac{5}{2}R + R = \frac{7}{2}R \quad \text{diatomic gas}$$

eq (35)

$$P \cdot \frac{V}{T} = C_4 T$$

$$T = \frac{T}{P \frac{V}{T}} = C_5 \quad \text{eq (10)}$$

on (V, P) diagram $P = \frac{C_1}{V}$ for isothermal transformation

+ on (V, P) diagram $P = \frac{C_2}{V^{\gamma}}$ for adiabatic transformation

$$\left. \frac{dP}{dV} \right|_{\text{isotherm}} = -\frac{C_1}{V^2}$$

$$\left. \frac{dP}{dV} \right|_{\text{adiabatic}} = -\frac{C_2}{V^{\gamma+1}} \quad \gamma > 1$$

$$\text{If } C_1 \approx C_2 \quad V^2 > V^{\gamma+1} \quad V < 1$$

$$\frac{1}{V^{\gamma+1}} > \frac{1}{V^2}$$

$$-\frac{1}{V^2} > -\frac{1}{V^{\gamma+1}}$$

Slope of isothermal curve is steeper?

$$k = 1 + \frac{R}{C_v}$$

$$k = 1 + \frac{\frac{3}{2}R}{\frac{3}{2}R} = 1 + \frac{2}{3} = \frac{5}{3} \quad \text{monatomic gas}$$

$$k = 1 + \frac{\frac{1}{2}R}{\frac{5}{2}R} = 1 + \frac{2}{5} = \frac{7}{5} \quad \text{diatomic gas} \quad \text{eq (37)}$$

$$C_v dT + p dV = 0$$

$$pV = RT$$

$$C_v dT + \frac{RT}{V} dV = 0$$

$$\frac{dT}{T} + \frac{R}{C_v} \frac{dV}{V} = 0$$

$$\ln T + \frac{R}{C_v} \ln V = \text{const}$$

$$TV^{\frac{R}{C_v}} = \text{const}$$

$$\frac{R}{C_v} = k-1$$

$$TV^{k-1} = \text{const}$$

$$\text{diatomic gas} \quad k = \frac{7}{5} \quad k-1 = \frac{2}{5} = .4$$

$$T_0 V_0^{k-1} = T V^{k-1} = T_1 (2V_0)^{k-1}$$

initially

$$\Rightarrow T_1 = \frac{T_0}{2^{k-1}}$$

$$1 : 2^{-(.4)} = 1 : .75$$

$$TV^{k-1} = \text{const}$$

$$PV = RT \quad \Rightarrow \quad T = \frac{PV}{R}$$

$$\frac{PV V^{k-1}}{R} = \text{const}$$

$$PV^k = \text{const} \quad \text{eq (39)} \quad \text{eq in terms of } p \text{ + } V \text{ variables.}$$

in terms of p + T it looks like

$$\frac{T(RT)^{k-1}}{p^k} = \text{const} \quad \text{from } V = \frac{RT}{p}$$

$$\Rightarrow \frac{T^k}{p^{k-1}} = \text{const.} \quad \text{one expression}$$

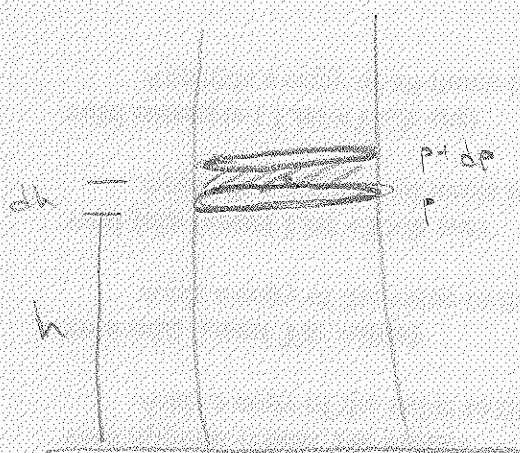
Another can be obtained by solving for V from $TV^{k-1} = C_1$

$$V = \frac{C_2}{T^{\frac{1}{k-1}}}$$

put this into ideal gas law $PV = RT$

$$P \frac{C_2}{T^{\frac{1}{k-1}}} = RT$$

$$P = C_3 T^{1 + \frac{1}{k-1}} = C_3 T^{\frac{k}{k-1}}$$



weight of fluid in cylindrical slab

$$= \underbrace{\rho g A dh}_{\text{mass}}$$

$$p + dp - p = dp = \underbrace{-}_{\substack{\text{exact} \\ \text{pressure} \\ \text{to be} \\ \text{less as} \\ \text{we move upwards} \\ \text{in the atmosphere}}} \rho g A dh = -\rho g dh \text{ if } A=1$$

$$p = \frac{M_p}{RT}$$

$$dp = - \frac{g M_p}{RT} dh$$

 N_2

Air is about 70% nitrogen, 20% O_2 + 10% other molecules (I think)

→ molecular weight of

$$M_{N_2} = 2(14) = 28$$

$$2(16) = 32$$

Average molecular weight of Air is then

$$.7(28) + .2(32) + .1(?)$$

$$= 26 \text{ what's wrong?}$$

Assume negligible

$$\text{eq (40)} \quad T P^{-\left(\frac{k-1}{k}\right)} = C$$

Assuming the gas to be expanding adiabatically

$$\log \rightarrow$$

$$\log T - \left(\frac{k-1}{k}\right) \log P = \log C$$

$$d \rightarrow$$

$$\frac{dT}{T} - \left(\frac{k-1}{k}\right) \frac{dP}{P} = 0$$

$$\frac{dT}{T} = \frac{k-1}{k} \frac{dP}{P}$$

From before

$$\frac{dP}{P} = - \frac{gM}{RT} dh$$

or

$$\left(\frac{k-1}{k}\right)^{-1} \frac{dT}{T} = - \frac{gM}{RT} dh$$

$$+ \frac{dT}{dh} = - \left(\frac{k-1}{k}\right) \frac{gM}{R} \quad \text{eq (42) use } k \text{ for a diatomic gas}$$

$$k = \frac{7}{5}$$

$$g = 980 \text{ cm/s}^2 \quad R = 8.314 \text{ J/mol K}$$

$$1J = 1 \left(\frac{\text{kg}}{\text{s}^2} \right) \text{m} = (10^3)^2 \cdot 10^3 \frac{\text{cm}}{\text{s}^2} = 10^7 \text{ dynes} \cdot \text{cm}$$

$$R = 8.314 \cdot 10^7 \frac{\text{dynes} \cdot \text{cm}}{\text{mol K}}$$

why does he use $R = 8,214$?

$$\frac{dT}{dh} = -9.8 \cdot 10^{-5} \text{ deg/cm} = -9.8 \cdot 10^{-5} \frac{\text{deg}}{10^{-5} \text{ km}}$$

units

$$= -9.8 \text{ deg/kilometer}$$

$$\left[\frac{gM}{R} \right] = \frac{\frac{L}{T^2} \cdot \frac{M}{\text{mol}}}{\left(\frac{L^2 M}{T^2} \right) \frac{1}{\text{mol} \cdot K}} = \frac{K}{L} \quad \checkmark$$

① $dU = dQ - dW$

$$1 \text{ cal} = 4.185 \cdot 10^7 \text{ ergs}$$

$$dW = 3.4 \cdot 10^8 \text{ ergs}$$

$$dQ = 32 \text{ cal} = 32 \cdot (4.185 \cdot 10^7 \text{ ergs}) = 1.339 \cdot 10^9 \text{ ergs}$$

$$\therefore dU = 1.339 \cdot 10^9 - 3.4 \cdot 10^8 = 9.9 \cdot 10^8 \text{ ergs} = 23.8 \text{ cal}$$

② Work done by isothermal expansion is given by eq (9)

$$L = \left(\frac{m}{M}\right) RT \log\left(\frac{P_1}{P_2}\right) = \left(\frac{m}{M}\right) RT \log\left(\frac{V_2}{V_1}\right)$$

$$\frac{m}{M} = \frac{\text{mass of gas}}{\text{mass per mole of gas}} = \# \text{ of moles of gas.}$$

Then
$$L = (3 \text{ moles}) (8.314 \text{ J/mole} \cdot \text{K}) (0 + 273.15 \text{ K}) \log\left(\frac{5 \text{ atm}}{3 \text{ atm}}\right)$$

$$= 3.48 \cdot 10^3 \text{ J}$$

$$dU = dQ - dW$$

As we are considering an ideal gas $U = U(T)$ as expansion is isothermal

$$dU = dU(T) = 0$$

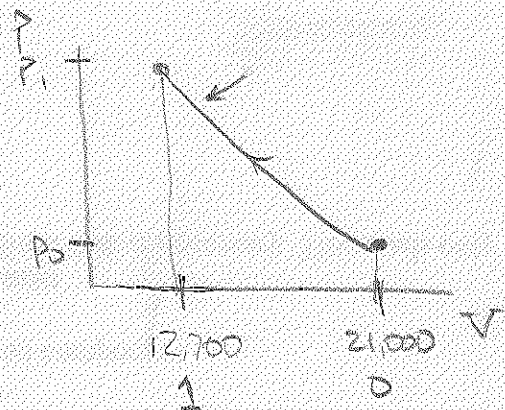
$$\therefore dQ = dW$$

$$Q = W = L \text{ from above}$$

③

$T_0 = 291^\circ\text{K}$
 $V_0 = 21,000 \text{ cc}$
 $= 2.1 \cdot 10^{-2} \text{ m}^3$

$T_1 = 305^\circ\text{K}$
 $V_1 = 12,700 \text{ cc}$
 $= 1.27 \cdot 10^{-2} \text{ m}^3$



$dW = p dV$ for mechanical expansion.

$$pV = RT \Rightarrow p = \frac{RT}{V}$$

$1 \text{ cc} = 1 \text{ cm}^3 = 1(10^{-2})^3 \text{ m}^3$
 $= 10^{-6} \text{ m}^3$

$$P_0 = \frac{(8.314 \text{ J/mol}\cdot\text{K})(291^\circ\text{K})(1 \text{ mole})}{(2.1 \cdot 10^{-2} \text{ m}^3)}$$

$$= 1.15 \cdot 10^5 \frac{\text{J}}{\text{m}^3} = 1.15 \cdot 10^5 \text{ Pa}$$

Now:

$$W = L = \int p dV$$

$$1 \text{ J} = \text{N}\cdot\text{m} = \frac{\text{m}}{\text{s}^2} \text{ kg}\cdot\text{m}$$

$$\frac{\text{J}}{\text{m}^3} = \frac{\text{N}}{\text{m}^2} = \text{unit of pressure. } \checkmark$$

eq for a line in V, P plane is

$$\frac{p(V) - P_0}{V - V_0} = \frac{P_1 - P_0}{V_1 - V_0}$$

$$P_1 = \frac{(8.314 \text{ J/mol}\cdot\text{K})(305^\circ\text{K})(1 \text{ mole})}{1.27 \cdot 10^{-2} \text{ m}^3}$$

$$= 1.99 \cdot 10^5 \frac{\text{J}}{\text{m}^3} = 1.99 \cdot 10^5 \text{ Pa}$$

$$P = P_0 + \left(\frac{P_1 - P_0}{V_1 - V_0} \right) (V - V_0)$$

Then

$$L = \int_{V_0}^{V_1} \left[P_0 + \left(\frac{P_1 - P_0}{V_1 - V_0} \right) (V - V_0) \right] dV$$

$$L = P_0(V_1 - V_0) + \left(\frac{P_1 - P_0}{V_1 - V_0} \right) \frac{(V_1 - V_0)^2}{2} \bigg|_{V_0}^{V_1}$$

$$= P_0(V_1 - V_0) + \left(\frac{P_1 - P_0}{V_1 - V_0} \right) \frac{(V_1 - V_0)^2}{2}$$

$$= P_0(V_1 - V_0) + \frac{(P_1 - P_0)(V_1 - V_0)}{2}$$

$$= (V_1 - V_0) \left[P_0 + \frac{P_1}{2} - \frac{P_0}{2} \right] = \frac{(V_1 - V_0)(P_1 - P_0)}{2} \quad \begin{matrix} < 0 & > 0 \\ \text{eq for area} \\ \text{of triangle} \end{matrix}$$

$$L = \frac{1}{2} (1.27 - 2.1) \cdot 10^{-2} \text{ m}^3 (1.99 - 1.15) \cdot 10^5 \text{ Pa}$$

$$= -3.48 \cdot 10^2 \text{ m}^3 \text{ Pa} \quad \begin{matrix} \text{negative sign means environment performs work} \\ \text{on system} \end{matrix}$$

$$U(T) = C_V T \quad \text{For diatomic gas} \quad C_V = \frac{5}{2} R$$

$$\Delta U = C_V \Delta T = C_V (T_1 - T_0) = C_V (305 - 291) = C_V (14^\circ \text{K})$$

$$= \frac{5}{2} (8.314 \text{ J/mol}^\circ \text{K}) (14^\circ \text{K}) (1 \text{ mol}) = 2.9 \cdot 10^2 \text{ J}$$

$$\left\{ \text{m}^3 \text{ Pa} = \text{m}^3 \frac{\text{N}}{\text{m}^2} = \text{m N} = \text{J} \right\}$$

$$dU = dQ - dW$$

$$\text{Then } dQ = dU + dW$$

$$\Delta Q = \Delta U + \Delta W$$

$$\therefore \Delta Q = 2.9 \cdot 10^2 \text{ J} + (-3.48 \cdot 10^2 \text{ J})$$

$$= -5.8 \cdot 10^1 \text{ J}$$

$$= -5.8 \cdot 10^8 \text{ ergs}$$

$$\left\{ \begin{array}{l} 1 \text{ J} = 10^7 \text{ ergs} \\ 1 \text{ J} = 1 \text{ Nm} = 1 \frac{\text{m}^2}{\text{s}^2} \text{ kg} \\ = (10^{+2})^2 (10^{+3}) \frac{\text{cm}^2}{\text{s}^2} \text{ g} \end{array} \right.$$

$$= 10^{+4} 10^{+3} \frac{\text{cm}^2}{\text{s}^2} \text{ g}$$

$$= 10^{+7} \text{ ergs} \quad \checkmark$$

④ diatomic gas

Inside

$$V_0 \rightarrow V_0(1.35)$$

adi

$$PV = RT$$

$$T_0 = 18^\circ\text{C}$$

$$pV^k = \text{constant}$$

$$= 18 + 273.15$$

$$TV^{k-1} = \text{constant}$$

$$= 291.15^\circ\text{K}$$

$$T_0 V_0^{k-1} = T_1 V_1^{k-1}$$

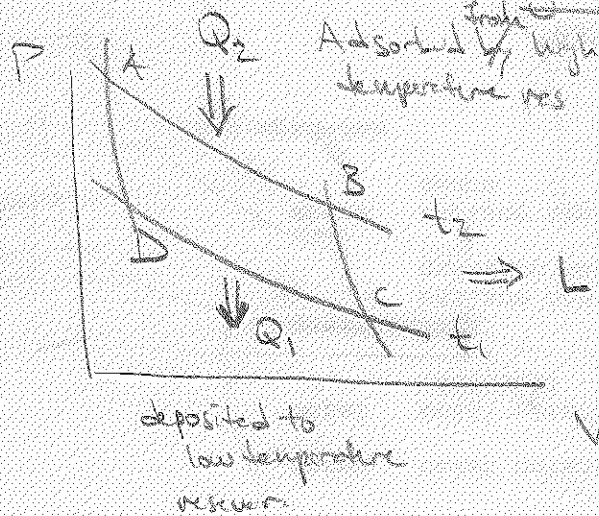
$$T_1 = T_0 \left(\frac{V_0}{V_1} \right)^{k-1}$$

for diatomic gas $k = 7/5$

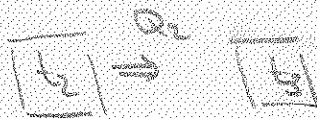
$$\frac{V_0}{V_1} = \frac{1}{1.35}$$

$$\left(\frac{V_0}{V_1} \right)^{7/5-1} = \left(\frac{V_0}{V_1} \right)^{2/5} = .507$$

$$T_1 = (291.15^\circ\text{K})(.507) = 147.6^\circ\text{K}$$



I don't follow the argument



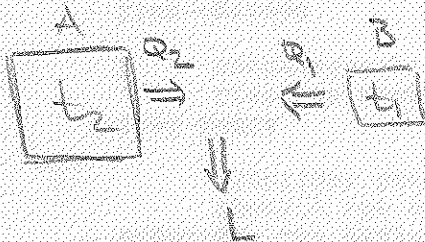
if

$$L > 0 \quad Q_2 > 0 \quad \text{and} \quad Q_1 > 0$$

if

$$Q_1 \leq 0$$

one cycle performs this. Then "Body" B has lost an amount of heat Q_1



put Bodies in contact & let A replenish the heat lost B lost.

$$L_{\text{total}} = N' L' - N L$$

$\uparrow$
 work done by us work done by heat

Adsorbed from T_2

$$Q_{2, \text{total}} = N' Q_2' - N Q_2$$

Given up to temp t_1

$$Q_{1, \text{total}} = + N' Q_1' - N Q_1$$

$$L_{\text{total}} = N'L' - NL$$

$$= N'(Q_2' - Q_1') - N(Q_2 - Q_1)$$

$$= \underbrace{N'Q_2' - NQ_2} - N'Q_1' + NQ_1$$

$$= Q_{2,\text{total}} - Q_{1,\text{total}}$$

$$Q_{2,\text{total}} = 0$$

$$L_{\text{total}} = -Q_{1,\text{total}}$$

eq (51)

$$L_{\text{total}} \leq 0$$

=

$$Q_{1,\text{total}} \geq 0$$

$$N'Q_1' \geq NQ_1$$

$$\frac{N'}{N}Q_1' \geq Q_1$$

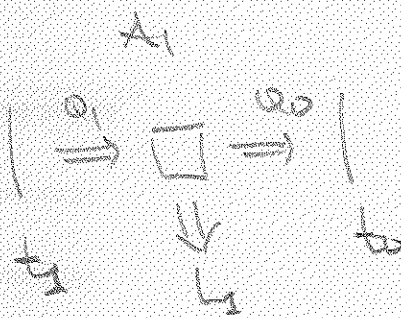
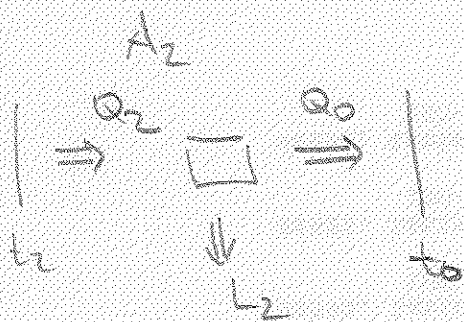
$$\frac{Q_2}{Q_2'}Q_1' \geq Q_1 \quad \text{from eq (49)}$$

$$Q_2Q_1' \geq Q_1Q_2'$$

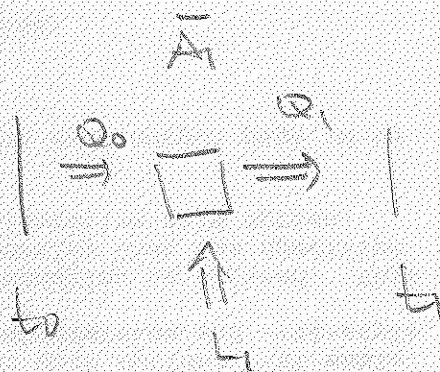
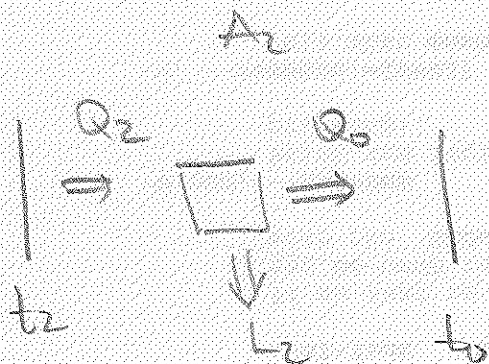
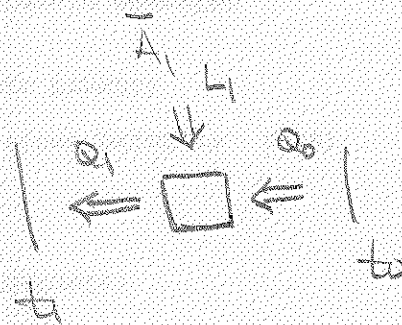
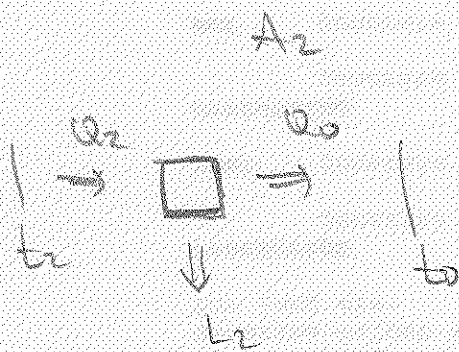
$$\frac{Q_2}{Q_1} \geq \frac{Q_2'}{Q_1'} \Rightarrow \frac{Q_1}{Q_2} \leq \frac{Q_1'}{Q_2'}$$

$$1 - \frac{Q_1}{Q_2} \geq 1 - \frac{Q_1'}{Q_2'}$$

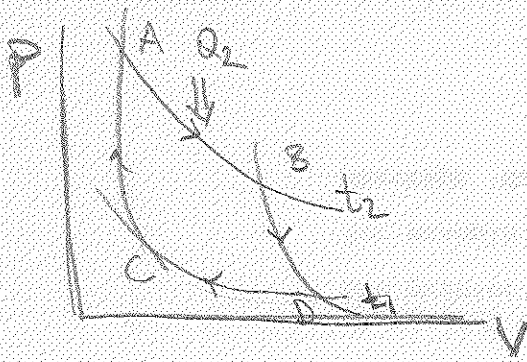
$$\gamma_{\text{rev.}} \geq \gamma_{\text{non-rev}}$$



Direct cycle of engine A_2 + reverse cycle of engine A_1



Example of combined process.



$$U_B - U_A + L_{AB} = Q_2$$

$$L_{AB} = RT_2 \log\left(\frac{V_B}{V_A}\right)$$

$$U_C - U_D + L_{DC} = Q_{DC}$$

||

$$RT_1 \log\left(\frac{V_D}{V_C}\right) = Q_{DC}$$

AC lie on Adiabatic curve $T_1 V_C^{k-1} = T_2 V_A^{k-1}$

BD " " " " $T_2 V_B^{k-1} = T_1 V_D^{k-1}$

$$\left(\frac{V_C}{V_D}\right)^{k-1} = \left(\frac{V_A}{V_B}\right)^{k-1} \Rightarrow \frac{V_C}{V_D} = \frac{V_A}{V_B}$$

Thus

$$\frac{Q_2}{Q_1} = \frac{RT_2 \log\left(\frac{V_B}{V_A}\right)}{RT_1 \log\left(\frac{V_D}{V_C}\right)} = \frac{T_2}{T_1}$$

eq (43) $L = Q_2 - Q_1$

$$Q_1 = Q_2 - L$$

$$1 = \frac{Q_2}{Q_1} - \frac{L}{Q_1} \Rightarrow 1 = \frac{T_2}{T_1} - \frac{L}{Q_1}$$

$$\frac{L}{Q_1} = \frac{T_2}{T_1} - 1$$

$$Q_1 = \frac{L}{\frac{T_2}{T_1} - 1} = \frac{L T_1}{T_2 - T_1} = L \frac{T_1}{T_2 - T_1} \quad \text{eq (60)}$$

$$\Rightarrow L = \left(\frac{T_2 - T_1}{T_1} \right) Q_1 = Q_1 \left(\frac{T_2}{T_1} - 1 \right) \quad \text{For refrigeration}$$

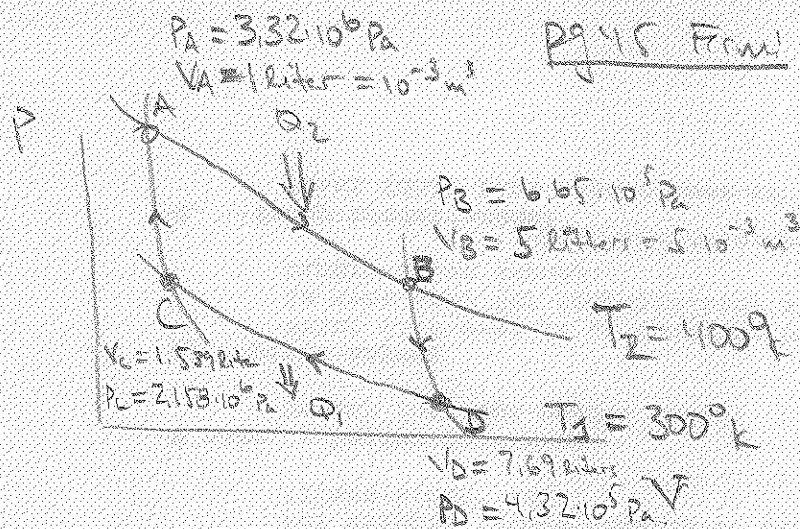
T_2 is atmosphere

T_1 is cooled temperature

$$T_1 < T_2 \quad \frac{T_2}{T_1} > 1$$

$$T_1 \rightarrow 0 \Rightarrow \frac{T_2}{T_1} \rightarrow +\infty \Rightarrow L \rightarrow +\infty$$

①



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$$PV = RT$$

$$P = \frac{RT}{V}$$

Paths BD + CA are adiabatic $\therefore$ not heat flow through them

Along AB + DC the temperature does not change & since $U = U(T)$ for an ideal gas $\Delta U = \Delta Q - \Delta W$

Along AB + DC $\Delta U = 0$ $\Delta Q = \Delta W$ $\therefore Q = W$

$$W_{\text{isothermal}} = RT \log\left(\frac{V_2}{V_1}\right) = RT_2 \log\left(\frac{V_B}{V_A}\right)$$

$$= (8.314 \text{ J/mol K})(400^\circ \text{K}) \log\left(\frac{5}{1}\right) = 5352.3 \text{ J along AB}$$

$$= Q_2$$

Along BD adiabatic $TV^{k-1} = \text{constant}$

$$1 \text{ liter} = 1000 \text{ cc}$$

$$= 0.001 \text{ m}^3$$

$$\Rightarrow T_2 V_B^{k-1} = T_1 V_D^{k-1}$$

$$\Rightarrow V_D = \left(\frac{T_2}{T_1} V_B^{k-1}\right)^{\frac{1}{k-1}} = V_B \left(\frac{T_2}{T_1}\right)^{\frac{1}{k-1}}$$

$$V_D = 5 \text{ liters} \left(\frac{400}{300}\right)^{\frac{1}{k-1}}$$

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$$k \text{ for monatomic gas} = \frac{5}{3}$$

$$\gamma - 1 = \frac{2}{3} \Rightarrow \frac{1}{\gamma - 1} = \frac{3}{2}$$

$$V_D = 7.69 \text{ liters}$$

Along isothermal DC $PV = \text{constant}$

$$\Rightarrow P_D V_D = P_C V_C \Rightarrow P_C = P_D \left(\frac{V_D}{V_C} \right) = 4.32 \cdot 10^5 \text{ Pa}$$

Also along CA adiabatic

$$T_2 V_A^{\gamma-1} = T_1 V_C^{\gamma-1}$$

$$V_C = \left(\frac{T_2}{T_1} \right)^{\frac{1}{\gamma-1}} V_A$$

$$\left(\frac{7.69}{1.539} \right) = 2.158 \cdot 10^6 \text{ Pa}$$

$$V_C = 1 \text{ liter} \left(\frac{4}{3} \right)^{\frac{1}{\gamma-1}} = 1.539 \text{ liters}$$

Then

$$W_{\text{isothermal}} = Q_1 = RT_1 \log \left(\frac{V_D}{V_C} \right) = (8.314 \text{ J/mol K}) (300 \text{ K}) \log \left(\frac{7.69}{1.539} \right) = 4.01 \cdot 10^3 \text{ J}$$

Total work performed during cycle

$$L_{\text{total}} = L_{AB} + L_{BD} + L_{DC} + L_{CA}$$

adiabatic

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work performed during isothermal expansion gives

$$L_{12} = \int_{V_1}^{V_2} P dV = \frac{P_1}{V_1^{-k}} \int_{V_1}^{V_2} V^{-k} dV = \frac{P_1}{V_1^{-k}(-k+1)} \left| V^{-k+1} \right|_{V_1}^{V_2}$$

$$PV^k = \text{constant}$$

$$PV^k = P_1 V_1^k$$

$$P = P_1 \left(\frac{V_1}{V} \right)^k = P_1 \left(\frac{V}{V_1} \right)^{-k}$$

$$= \frac{P_1}{V_1^{-k}(-k+1)} (V_2^{-k+1} - V_1^{-k+1})$$

$$= \frac{P_1 V_1^k}{1-k} (V_2^{-k+1} - V_1^{-k+1})$$

$$\text{Then } L_{BD} = \frac{(6.65 \cdot 10^5 \text{ Pa})(5 \cdot 10^{-3} \text{ m}^3)^{\frac{5}{3}}}{(1 - \frac{5}{3})} \left((7.69 \cdot 10^{-3} \text{ m}^3)^{1-\frac{5}{3}} - (5 \cdot 10^{-3} \text{ m}^3)^{1-\frac{5}{3}} \right)$$

$$= 1.24 \cdot 10^3 \text{ J}$$

units $\text{Pa} \cdot \text{m}^5 \cdot (\text{m}^3)^{-\frac{2}{3}}$

$$\text{Pa} \cdot \text{m}^5 \cdot \text{m}^{-2} = \text{Pa} \cdot \text{m}^3$$

$$= \frac{\text{N}}{\text{m}^2} \cdot \text{m}^3 = \text{N} \cdot \text{m} = \text{J}$$

$$\downarrow L_{CA} = \frac{(2158 \cdot 10^6 \text{ Pa})(1.539 \cdot 10^{-3} \text{ m}^3)^{\frac{5}{3}}}{-\frac{2}{3}} \left((10^{-3})^{-\frac{2}{3}} - (1.539 \cdot 10^{-3} \text{ m}^3)^{-\frac{2}{3}} \right)$$

$$= -1.658 \cdot 10^3 \text{ J}$$

Then

$$\begin{aligned}
 W_{\text{tot}} &= 5.3523 \cdot 10^3 \text{ J} + 1.24 \cdot 10^3 \text{ J} - 4.01 \cdot 10^3 \text{ J} - 1.658 \cdot 10^3 \text{ J} \\
 &= 9.27 \cdot 10^2 \text{ J}
 \end{aligned}$$

②

$$T_2 = 400^\circ\text{C} = 673.15^\circ\text{K}$$

$$T_1 = 13^\circ\text{C} = 291.15^\circ\text{K}$$

$$\eta_{\text{max}} = 1 - \frac{T_1}{T_2} = 1 - \frac{291.15}{673.15} = .567$$

③

$$0^\circ\text{F} = 255.92^\circ\text{K} = T_1$$

$$100^\circ\text{F} = 310.927^\circ\text{K} = T_2$$



Minimum work required when cycle is reversible.

eq (60)

$$L = \left(\frac{T_2 - T_1}{T_1} \right) Q_1$$

$$Q_1 = 1 \text{ cal}$$

$$L = .2149 Q_1$$

$$= .2149 \text{ cal} = .2149 \cdot 4.185 \cdot 10^7 \text{ ergs}$$

$$= 8.99 \cdot 10^6 \text{ ergs}$$

$$\left\{ 1 \text{ ergs} = 10^{-7} \text{ J} \right\}$$

$$= .899 \text{ J}$$

$$\frac{T_2}{A_2} \Rightarrow \frac{T_1}{A_1}$$

$$T_2 > T_1$$

$$\Delta S_1 = \frac{Q}{T_1} \quad \Delta S_2 = -\frac{Q}{T_2}$$

$$\Delta S_1 + \Delta S_2 = \frac{Q}{T_1} - \frac{Q}{T_2} = Q \frac{(T_2 - T_1)}{T_1 T_2} > 0$$

$$I1 \quad f(xy) = f(x) + f(y)$$

$$f(x(1+\epsilon)) = f(x + \epsilon x) = f(x) + f(1+\epsilon)$$

$$f(x) + \epsilon f'(x) + \frac{\epsilon^2}{2} f''(x) + O(\epsilon^3) = f(x) + f(1) + f'(1)\epsilon + \frac{f''(1)}{2}\epsilon^2 + O(\epsilon^3)$$

$$\epsilon f'(x) + O(\epsilon^2) = f(1) + f'(1)\epsilon + O(\epsilon^2)$$

$O(1)$

$$f(1) = 0$$

$O(\epsilon)$

$$\epsilon f'(x) = f'(1) = k$$

$$f'(x) = \frac{k}{x}$$

$$f(x) = k \log x + \text{const}$$

$$S = k \log \pi + \text{const}$$

$$dQ = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\left(\frac{\partial U}{\partial V} \right)_T + p \right) dV$$

eq (72) $dS = \frac{dQ}{T}$ reversible quasi-static only

$$dS = \frac{dQ}{T} = \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V dT + \frac{1}{T} \left(\left(\frac{\partial U}{\partial V} \right)_T + p \right) dV$$

$$dU = dQ - p dV$$

$$dQ = C_V dT + p dV \quad p = \frac{RT}{V}$$

$$C_V dT + \frac{RT}{V} dV \quad \text{eq (34)}$$

$$C_V \equiv \left(\frac{\partial Q}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_V = \frac{dU}{dT} \equiv \frac{dU}{dT} \quad \uparrow \text{ideal gas}$$

Is dQ a perfect diff?

$$\frac{\partial}{\partial T} \left(\frac{RT}{V} \right) \stackrel{?}{=} \frac{\partial}{\partial V} C_V$$

$$\frac{R}{V} \stackrel{?}{=} 0 \quad \text{since } C_V = \frac{dU}{dT} \text{ For ideal gas.}$$

No Not exact differential

$$dS = \frac{dQ}{T} = \frac{C_V}{T} dT + \frac{R}{V} dV \quad \text{eq (35)}$$

Exact differential?

$$\frac{\partial}{\partial T} \left(\frac{R}{V} \right) \stackrel{?}{=} \frac{\partial}{\partial V} \left(\frac{C_V}{T} \right)$$

$$0 = 0 \quad \checkmark \quad \text{Yes}$$

$$S = C_v \ln T + R \ln v + a \quad \text{eq (86)} \quad \text{assuming } C_v \text{ a constant}$$

$$v = \frac{RT}{P}$$

which is true for ideal gas.

$$S(P, T) = C_v \ln T + R \ln \left(\frac{RT}{P} \right) + a$$

$$R \ln R + R \ln T - R \ln P$$

$$S(P, T) = (C_v + R) \ln T - R \ln P + a + R \ln R$$

$$C_p \ln T - R \ln P + a + R \ln R \quad \text{eq (87)}$$

General case $U = U(T, V)$ Then (80) requires as S is an exact differential

$$\frac{\partial}{\partial V} \left(\frac{1}{T} \frac{\partial U}{\partial T} \right)_V = \frac{\partial}{\partial T} \left(\frac{1}{T} \left(\frac{\partial U}{\partial V} \Big|_T + P \right) \right)$$

$$\frac{1}{T} \frac{\partial^2 U}{\partial V \partial T} = \left(\frac{\partial U}{\partial V} + P \right) \left(-\frac{1}{T^2} \right) + \frac{1}{T} \left(\frac{\partial^2 U}{\partial T \partial V} + \frac{\partial P}{\partial T} \right)$$

$$\frac{\partial U}{\partial V} + P = T \frac{\partial P}{\partial T} \Big|_V$$

$$\frac{\partial U}{\partial V} \Big|_T = T \frac{\partial P}{\partial T} \Big|_V - P \quad \text{eq (88)}$$

(88) has been independent of equation of state to this point

If $P = n \frac{RT}{V}$ $n = \# \text{ of moles}$

$$\left. \frac{\partial U}{\partial V} \right|_T = T \left(\frac{nR}{V} \right) - n \frac{RT}{V} = 0$$

Using (T, P) as state variables eq (23) gives for da

$$da = \left(\left. \frac{\partial U}{\partial T} \right|_P + P \left. \frac{\partial V}{\partial T} \right|_P \right) dT + \left(\left. \frac{\partial U}{\partial P} \right|_T + P \left. \frac{\partial V}{\partial P} \right|_T \right) dP$$

reversible path

$$dS = \frac{da}{T} = \frac{1}{T} \left(\left. \frac{\partial U}{\partial T} \right|_P + P \left. \frac{\partial V}{\partial T} \right|_P \right) dT + \frac{1}{T} \left(\left. \frac{\partial U}{\partial P} \right|_T + P \left. \frac{\partial V}{\partial P} \right|_T \right) dP$$

$$\frac{\partial}{\partial P} \left(\frac{1}{T} \left(\left. \frac{\partial U}{\partial T} \right|_P + P \left. \frac{\partial V}{\partial T} \right|_P \right) \right) = \frac{\partial}{\partial T} \left(\frac{1}{T} \left(\left. \frac{\partial U}{\partial P} \right|_T + P \left. \frac{\partial V}{\partial P} \right|_T \right) \right)$$

$$\Rightarrow \frac{1}{T} \left(\cancel{\frac{\partial^2 U}{\partial P \partial T}} + \frac{\partial V}{\partial T} + P \cancel{\frac{\partial^2 V}{\partial T \partial P}} \right) = \left(\left. \frac{\partial U}{\partial P} \right|_T + P \left. \frac{\partial V}{\partial P} \right|_T \right) \left(-\frac{1}{T^2} \right)$$

$$+ \frac{1}{T} \left(\cancel{\frac{\partial^2 U}{\partial P \partial T}} + P \cancel{\frac{\partial^2 V}{\partial T \partial P}} \right)$$

$$\Rightarrow \left. \frac{\partial U}{\partial P} \right|_T = -P \left. \frac{\partial V}{\partial P} \right|_T - T \left. \frac{\partial V}{\partial T} \right|_P \quad \text{eq (89)}$$

w/ p & v as independent variables

$$\left. \frac{\partial U}{\partial p} \right|_v dp + \left(\left. \frac{\partial U}{\partial v} \right|_p + p \right) dv = dQ$$

reversible path

$$dS = \frac{dQ}{T} = \frac{1}{T} \left. \frac{\partial U}{\partial p} \right|_v dp + \frac{1}{T} \left(\left. \frac{\partial U}{\partial v} \right|_p + p \right) dv$$

$$\frac{\partial}{\partial v} \left(\frac{1}{T} \left. \frac{\partial U}{\partial p} \right|_v \right) = \frac{\partial}{\partial p} \left(\frac{1}{T} \left(\left. \frac{\partial U}{\partial v} \right|_p + p \right) \right)$$

$$\frac{\partial}{\partial v} \left(\frac{1}{T} \right) \frac{\partial U}{\partial p} + \frac{1}{T} \frac{\partial^2 U}{\partial p \partial v} = \frac{\partial}{\partial p} \left(\frac{1}{T} \right) \left(\left. \frac{\partial U}{\partial v} \right|_p + p \right) + \frac{1}{T} \left(\frac{\partial^2 U}{\partial p \partial v} + 1 \right)$$

$$-\frac{1}{T^2} \frac{\partial T}{\partial v} \frac{\partial U}{\partial p} = -\frac{1}{T^2} \frac{\partial T}{\partial p} \left(\left. \frac{\partial U}{\partial v} \right|_p + p \right) + \frac{1}{T}$$

$$T = - \frac{\partial T}{\partial v} \frac{\partial U}{\partial p} + \frac{\partial T}{\partial p} \left(\left. \frac{\partial U}{\partial v} \right|_p + p \right)$$

$$T = \left(\left. \frac{\partial U}{\partial v} \right|_p + p \right) \frac{\partial T}{\partial p} \bigg|_v - \frac{\partial U}{\partial p} \bigg|_v \left(\frac{\partial T}{\partial v} \right)_p \quad \text{eq (90)}$$

Note: two unknowns exp determine $\left. \frac{\partial T}{\partial p} \right|_v$ $\frac{\partial T}{\partial v} \bigg|_p$ etc

Solve this non-linear eq for determine $\frac{\partial U}{\partial v} \bigg|_p$ & $\frac{\partial U}{\partial p} \bigg|_v$

to determine $U = U(v, p)$

$$dV = \{v_2(T) - v_1(T)\} dm$$

$$dU = \{u_2(T) - u_1(T)\} dm$$

$$\left. \frac{dU}{dV} \right|_T = \frac{u_2(T) - u_1(T)}{v_2(T) - v_1(T)} = \frac{1 - p(v_2(T) - v_1(T))}{v_2(T) - v_1(T)}$$

$$= \frac{1}{v_2 - v_1} - p \quad \square$$

eq (93) $\left. \frac{\partial U}{\partial V} \right|_T = T \left. \frac{\partial p}{\partial T} \right|_V - p$ set eq

$$T \left. \frac{\partial p}{\partial T} \right|_V = \frac{1}{v_2 - v_1} \quad \text{eq (94)}$$

$$\Delta = 540 \text{ cal/gm} = 540 \cdot (4.185 \cdot 10^7 \text{ ergs})/\text{gm}$$

$$= 2259 \cdot 10^7 \text{ ergs/gm}$$

$$T = 100 + 273.15 = 373.15^\circ \text{K}$$

$$\frac{dp}{dT} = \frac{(2259 \cdot 10^7 \text{ erg/gm})}{(373.15^\circ \text{K})(1677 - 1.043) \text{ cm}^3/\text{gm}} = 3.61 \cdot 10^4 \frac{\text{ergs}}{\text{cm}^3 \cdot \text{K}}$$

$$\left\{ [v] = \left[\frac{1}{\rho} \right] = \frac{1}{\text{gm/cm}^3} = \frac{\text{cm}^3}{\text{gm}} \right\} \quad \left\{ 1 \text{ dyne} = \frac{\text{ergs}}{\text{cm}} \right\}$$

$$\frac{dp}{dT} = 3.61 \cdot 10^4 \frac{\text{dyne}}{\text{cm}^2 \cdot \text{K}}$$

$\frac{\text{dyne}}{\text{cm}^2}$ unit of pressure.

$$1 \frac{\text{erg}}{\text{cm}^2} = 7.5 \cdot 10^{-5} \text{ cm} \cdot \text{Hg}$$

$$\therefore \frac{dp}{dT} = 2.7 \text{ cm} \cdot \text{Hg}/^\circ\text{C}$$

Normally for a gas-liquid or a gas-solid interface

$$V \ll V_2$$

↑ ↑
liquid gas/vapor

For 1 gram eq (6) gives

$$pV = \frac{1}{M} RT \quad \text{Then } V \text{ is Volume per gram (wt) also}$$

$$pV_2 = \frac{1}{M} RT$$

$$V_2 = \frac{RT}{Mp}$$

$$\frac{dp}{dT} \approx \frac{1}{TV_2} = \frac{1}{T \left(\frac{RT}{Mp} \right)}$$

$$= \frac{\Delta MP}{RT^2} \quad \text{eq (7b)}$$

For H_2O vapor over liquid at temperature of Boiling we put

$$M = 2(1) + 16 = 18 \text{ gm/mole}$$

$$\frac{dp}{dT} = \frac{(2260 \cdot 10^7 \text{ ergs/gm})(18 \text{ gm/mole})(1 \text{ atm})}{(8.314 \text{ J/mol}^\circ\text{K})(373.1^\circ\text{K})^2}$$

$$1 \text{ atm} = 1.01 \cdot 10^5 \text{ Pa}$$

$$1 \text{ erg} = 10^{-7} \text{ J}$$

$$\frac{dp}{dT} = \frac{(2260 \text{ J/gm})(18 \text{ gm/mole})(1.01 \cdot 10^5 \text{ Pa})}{(8.314 \text{ J/mol}^\circ\text{K})(373.1^\circ\text{K})^2}$$

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$$\frac{dp}{dT} = 3,55 \cdot 10^3 \left(\frac{\text{Pa}}{^\circ\text{C}} \right) = 3,55 \cdot 10^4 \frac{\text{dynes}}{\text{cm}^2 \cdot ^\circ\text{C}}$$

$$\left\{ 1 \text{ Pa} = 7,5 \cdot 10^{-3} \text{ mm Hg} = 7,5 \cdot 10^{-2} \text{ cm Hg} \right.$$

$$1 \text{ Pa} = \frac{\text{N}}{\text{m}^2} = \frac{\frac{\text{kg}}{\text{s}^2} \text{m}}{\text{m}^2} = \frac{10^3 \cdot 10^3 \frac{\text{cm}}{\text{s}^2} \text{gm}}{(10^2)^2 \text{cm}^2} = 10 \frac{\text{dynes}}{\text{cm}^2}$$

$$\frac{dp}{p} = \frac{\Delta M}{RT^2}$$

$$\ln p = \frac{\Delta M}{R} \left(-\frac{1}{T} \right) + \text{constant}$$

$$p = C e^{-\frac{\Delta M}{RT}} \quad \text{eq (98)}$$

Note: we can evaluate the constant for H_2O using known values

Now vap pressure = 1 atm at boiling

$$1 \text{ atm} = C \exp\left(\frac{\Delta M}{RT}\right) \quad \text{Then}$$

$$\Delta = 540 \text{ cal/gm}$$

$$\frac{\Delta M}{RT} = 1.311 \cdot 10^1$$

$$M = 18 \text{ gm/mol}$$

$$\Rightarrow C = 2.01 \cdot 10^{-6} \text{ atm}$$

$$R = 1.986 \text{ cal/mol}^\circ K$$

$$T = 100^\circ C = 373.15$$

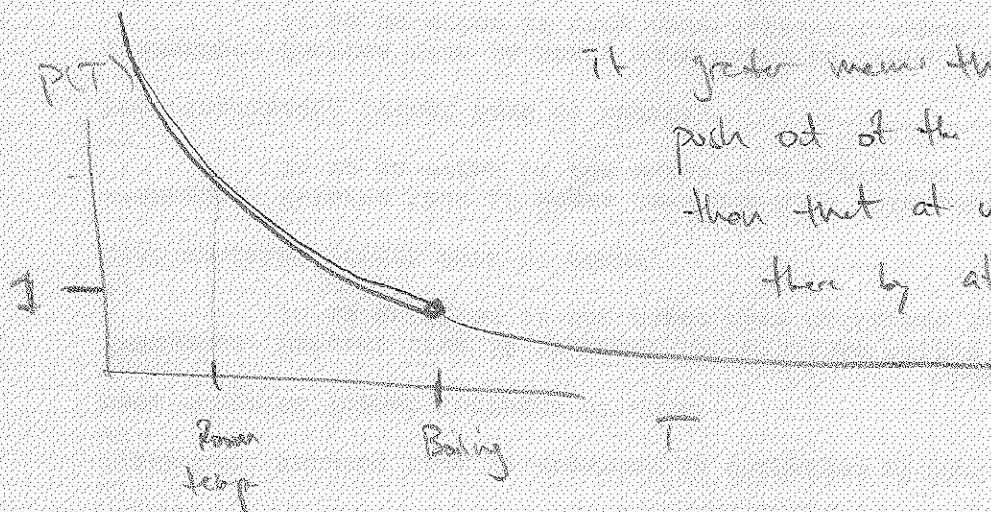
$$P_{H_2O}(T) = 2.01 \cdot 10^{-6} \text{ atm} \exp\left[\frac{\Delta M}{RT}\right]$$

vap
pressure

At room temp this is $P(18^\circ) = 40.0 \text{ atm}$?

I would think that it would be less than atmospheric because having

it greater means that the force atoms push out of the surface w/ is greater than that at which they are held there by atmospheric pressure.



Where is the contradiction?

$$\Delta = 80 \text{ cal/gm} = (80 \cdot 4.185) \frac{10^7 \text{ ergs}}{\text{gm}} = 334.8 \cdot 10^7 \frac{\text{ergs}}{\text{gm}}$$

$$\begin{aligned} \frac{dp}{dT} &= \frac{\Delta}{T(v_2 - v_1)} = \frac{(335 \cdot 10^7 \text{ ergs/gm})}{(273.15^\circ \text{K})(1.00013 - 1.0907) \text{ cm}^3/\text{gm}} \\ &= -1.35 \cdot 10^8 \frac{\text{ergs}}{\text{cm}^3 \cdot ^\circ \text{K}} \\ &\quad \parallel \\ &\quad \frac{\text{dyne}}{\text{cm}^2} \cdot ^\circ \text{K} \end{aligned}$$

$$1 \frac{\text{dyne}}{\text{cm}^2} = 9.86 \cdot 10^{-7} \text{ atm}$$

$$\therefore \frac{dp}{dT} = -1.33 \cdot 10^2 \text{ atm/}^\circ \text{K} = -133 \text{ atm/}^\circ \text{K}$$

Thus increase in pressure by 134 atmospheres lowers melting point by 1°K

∴ More pressure ice is under the ~~harder~~ easier it is to ~~break~~ melt it.

$$(P + \frac{a}{V^2})(V - b) = RT \quad \text{given } T + P$$

$$(V^2 P + a)(V - b) = V^2 RT$$

$$V^3 P - bV^2 P + aV - ab = V^2 RT$$

$$PV^3 + (-bP - RT)V^2 + aV - ab = 0 \quad \text{cubic eq for } V$$

$$\text{evaluating at } P = P_c \quad T = T_c$$

$$P_c V^3 - (bP_c + RT_c)V^2 + aV - ab = 0$$

$$P_c(V - V_c)^3 = 0 \quad \text{if } V_c \text{ is a triple root}$$

$$P_c(V^3 - 3V^2 V_c + 3V V_c^2 - V_c^3) = 0$$

comparing with

$$\Rightarrow -3P_c V_c = -(bP_c + RT_c) + 3V_c^2 P_c = a + -P_c V_c^3 = -ab$$

$$\Downarrow$$

$$3V_c = \frac{bP_c + RT_c}{P_c}$$

$$\Downarrow$$

$$3V_c^2 = \frac{a}{P_c}$$

$$\Downarrow$$

$$V_c^3 = \frac{ab}{P_c}$$

3 eqs + 3 unknowns (V_c, P_c, T_c) solving from eq (2) + (3)

$$\frac{\div \text{ two}}{\text{eq 1}} \Rightarrow \frac{V_c^3}{3V_c^2} = \frac{ab/P_c}{a/P_c} \Rightarrow V_c = 3b$$

$$\text{Then } p_c = \frac{a}{3V_c^2} \Rightarrow p_c = \frac{a}{3(9b^2)} = \frac{a}{27b^2}$$

$$\downarrow T_c = \frac{3V_c p_c - b p_c}{R} = \frac{3(3b)\left(\frac{a}{27b^2}\right) - b\left(\frac{a}{27b^2}\right)}{R}$$

$$= \frac{\frac{a}{b}\left(\frac{1}{3} - \frac{1}{27}\right)}{R} = \frac{a}{bR} \frac{8}{27} = \frac{8}{27} \frac{a}{Rb} \quad \text{eq (100)}$$

From remark on page 72 if T_c, V_c, p_c are a point of 3rd order contact at $V = V_c$ the $p = p(V)$ should have a

$$p' = p'(V)_1 = 0$$

$$V = V_c$$

$$p'' = p''(V)_1 = 0$$

$$V = V_c$$

} is this correct? If so why?

$$\text{From } \frac{dp}{dV} V^3 + p 3V^2 - \frac{dp}{dV} bV^2 - pb 2V + 2RTV + a = 0$$

$$\frac{dp}{dV} (V^3 - bV^2) + 3pV^2 + 2(2T - pb)V + a = 0$$

$$\frac{dp}{dV} = \frac{3pV^2 + 2(2T - pb)V + a}{bV^2 - V^3}$$

$$P = \frac{P}{P_c} ; V = \frac{V}{V_c} ; T = \frac{T}{T_c}$$

$$P = P P_c ; V = V_c V ; T = T T_c \quad \text{put into eq (99)}$$

$$(P + \frac{a}{V^2})(V - b) = RT$$

$$(P P_c + \frac{a}{V_c^2 V^2})(V_c V - b) = R T T_c$$

$$(P + \frac{a}{P_c V_c^2 V^2})(V - \frac{b}{V_c}) = \frac{R T_c}{V_c P_c} T$$

$$\text{Now } \frac{a}{P_c V_c^2} = \frac{6}{(\frac{a}{27 P_c})(9 V_c^2)} = \frac{1}{3} = 3$$

$$\frac{b}{V_c} = \frac{b}{3b} = \frac{1}{3}$$

$$\frac{R T_c}{V_c P_c} = \frac{R(\frac{8}{27} \frac{K}{P_c})}{(3P_c)(\frac{A}{27 V_c^2})} = \frac{\frac{8}{27}}{\frac{3}{27}} = \frac{8}{3}$$

∴ we get

$$(P + \frac{3}{V^2})(V - \frac{1}{3}) = \frac{8}{3} T \quad \text{eq (101)}$$

$$P = -\frac{a}{V^2} + \frac{RT}{(V-b)} \quad \text{eq (102)}$$

$$(88) \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{R}{V-b} + \frac{a}{V^2} - \frac{RT}{(V-b)} = \frac{a}{V^2}$$

$$U = -\frac{a}{V} + f(T) \quad \text{eq (103)}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = f'(T)$$

$$dU = dQ - PdV$$

Assumed constant

$$f(T) = C_V T + w$$

$$U = -\frac{a}{V} + C_V T + w$$

$$dS = \frac{dQ}{T} = \frac{1}{T} (dU + PdV)$$

reversible
path

$$= \frac{1}{T} (C_V dT + \frac{a}{V^2} dV) + \frac{1}{T} \left(-\frac{a}{V^2} + \frac{RT}{(V-b)} \right) dV$$

$$= C_V \frac{dT}{T} + \frac{a}{V^2} dV - \frac{a}{V^2} dV + \frac{R}{V-b} dV$$

$$= C_V \frac{dT}{T} + \frac{R dV}{V-b}$$

$$S = C_v \ln T + R \ln(V-b) + \text{const.} \quad \text{eq 105}$$

eq (86) for ideal gas $S = C_v \ln T + R \ln V + a$

$$dQ = 0 \quad dS = 0 \Rightarrow S = \text{constant}$$

$$C_v \ln T + R \ln(V-b) = \text{const.}$$

$$\ln T + \frac{R}{C_v} \ln(V-b) = w$$

$$T(V-b)^{R/C_v} = \text{const} \quad \text{eq 106}$$

① $1 \text{ kg } H_2O = 1000 \text{ gm } H_2O$

From $T_1 = 0 + 273.15^\circ K = 273.15^\circ K$

to $T_2 = 100 + 273.15 = 373.15^\circ K$

For liquid I'll assume that $C_p \approx C_v = 1 \text{ cal/gm}^\circ K$ is constant

Then From $dU = dQ - p dV$

at constant volume $dU = dQ$

$$\frac{dQ}{dT}|_V = C_v$$

$$\therefore S(B) - S(A) = \int_A^B \frac{dQ}{T}$$

$$\Rightarrow Q(T) = C_v T + f_1(V)$$

$$dQ = C_v dT + f_1'(V) dV$$

integrate along a constant volume transformation?

$$\Delta S = \int_{273.15^\circ K}^{373.15^\circ K} \frac{C_v dT}{T} = C_v \ln\left(\frac{T_2}{T_1}\right) \quad \text{per unit mass}$$

$$\Delta S = (1000 \text{ gm}) (1 \text{ cal/gm}^\circ K) \ln\left(\frac{373.15}{273.15}\right)$$

$$= 311.9 \text{ cal/}^\circ K = 311.9 (4.185 \cdot 10^7) \text{ ergs/}^\circ K$$

$$= 1.305 \cdot 10^{10} \text{ ergs/}^\circ K$$

② $PV^{1.2} = 10^9 T^{1.1}$ eq of state

let $PV^a = dT^b$ $a=1.2, d=10^9, b=1.1$
 a & b are unitless

$[V] = \text{liters}$. If I was told the units of P, V & T, d , I could get a relationship between a, b , & d .

Assume all units will work out (since I'm not given them see below)

We are told the value of C_v given in units of cal/deg

why is this not in units per mole or per gm?

Given $U = U(V, T)$ one can show for a system doing only $p-V$ work that

$$\left. \begin{aligned} \frac{\partial U}{\partial V} \Big|_T &= T \frac{\partial P}{\partial T} \Big|_V - P \end{aligned} \right\} \begin{array}{l} \text{Nice because } U \text{ on EOS} \\ \text{is determined explicitly} \\ \text{just } \frac{\partial U}{\partial V} \Big|_T \end{array}$$

In our case $P = \frac{dT^b}{V^a}$

$$\frac{\partial P}{\partial T} \Big|_V = \frac{dbT^{b-1}}{V^a}$$

$$\therefore \frac{\partial U}{\partial V} \Big|_T = \frac{dbT^b}{V^a} - \frac{dT^b}{V^a} = (b-1) \frac{dT^b}{V^a} = (b-1)P$$

$\therefore$ integrating U holding T fixed gives

$$(b-1)dT^b V^{-a}$$

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$$U(V, T) = (b-1)dT \frac{V^b}{1-a} + Q_1(T) \quad \checkmark$$

We are given C_V in terms of T only, units

for C_V since $dU = dQ - p dV$

$$C_V \equiv \left. \frac{\partial Q}{\partial T} \right|_V = \left. \frac{\partial U}{\partial T} \right|_V = (b-1)d \frac{V^b}{1-a} + Q'_1(T) = C_V$$

↑
constant

at $V = V_0 = 100 \text{ l.itres}$

Ask what for if I can't put V_0 in
eqn $\rightarrow$ as $Q_1(T)$ Not a fn of
 T only $\rightarrow$.

$$\Rightarrow Q'_1(T) = C_V - (b-1)d \frac{V_0^b}{1-a} \quad \checkmark$$

$$Q(T) = C_V T - (b-1)d \frac{V_0^b}{1-a} + C_2 \quad C_2 \text{ constant}$$

$$Q(T) = C_V T - (b-1)d \frac{V_0^b}{1-a} + C_2$$

Think Ask

$$U(V, T) = (b-1)dT \frac{V^b}{1-a} + C_V T - (b-1)d \frac{V_0^b}{1-a} + C_2$$

$$= C_V T + \frac{(b-1)d}{1-a} (V^b - V_0^b) + C_2 \quad \checkmark$$

entropy $dS = \frac{dQ}{T} = \frac{dU + PdV}{T}$
 reversible process

$$dU = \frac{1}{T} dU + \frac{1}{T} PdV$$

$$\left\{ dU = \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial V} dV \right\}$$

$$= \frac{1}{T} \left[\left(C_v + (b-1) \frac{db T^{b-1}}{1-a} (V^{1-a} - V_0^{1-a}) \right) dT + (b-1) dT^b V^{-a} dV \right]$$

$$+ \frac{1}{T} \frac{dT^b}{V^a} dV \quad \checkmark$$

$$= \frac{C_v}{T} dT + \frac{(b-1)db T^{b-2}}{1-a} (V^{1-a} - V_0^{1-a}) dT + \frac{(b-1) T^b V^{-a}}{T} dV$$

$$+ \frac{dT^b}{T V^a} dV$$

$$= C_v \frac{dT}{T} + \frac{b dT^b V^{-a}}{T} dV + b \frac{(b-1) T^{b-2}}{1-a} d \frac{V^{1-a}}{1-a} dT$$

$$- \frac{(b-1)db V_0^{1-a} T^{b-2}}{1-a} dT \quad \checkmark$$

$$= C_v \frac{dT}{T} - \frac{(b-1)db V_0^{1-a} T^{b-2}}{1-a} dT + \underbrace{b dT^{b-1-a}}_{\frac{dT^b}{dT} V^{-a} dV} dV + \frac{dT^b}{dT^2} \frac{dV^{1-a}}{1-a} dT$$

$$\frac{dT^b}{dT} V^{-a} dV$$

$$dS = C_V \frac{dT}{T} - \frac{b(b-1)}{1-a} \frac{dV_0^{1-a}}{V_0^{1-a}} T^{b-2} dT + \frac{dT^2}{dT^2} \frac{dV^{1-a}}{1-a} dT$$

$$+ d \left[\frac{dT^b}{dT} \right] V^{-a} dV$$

check if this is exact differential

$$\frac{\partial}{\partial V} \left[\frac{C_V}{T} - \frac{b(b-1)}{1-a} \frac{dV_0^{1-a}}{V_0^{1-a}} T^{b-2} + \frac{dT^2}{dT^2} \frac{dV^{1-a}}{1-a} \right] =$$

$$\frac{\partial}{\partial T} \left[d \left[\frac{dT^b}{dT} \right] V^{-a} \right]$$

$$\Rightarrow d \left[\frac{dT^2}{dT^2} \right] V^{-a} = d \left[\frac{dT^b}{dT^2} \right] V^{-a} \quad \text{yes!!}$$

$\therefore$ we can integrate dS if I can find an integrating factor?

$\Rightarrow \exists f(T, V) \rightarrow$

$$\frac{\partial S}{\partial T} \Big|_V = d \left[\frac{dT^2}{dT^2} \right] \frac{V^{1-a}}{1-a} + \frac{\partial S}{\partial V} \Big|_T = d \left[\frac{dT^b}{dT} \right] V^{-a}$$

$$+ \frac{C_V}{T} - \frac{b(b-1)}{1-a} \frac{dV_0^{1-a}}{V_0^{1-a}} T^{b-2} \Rightarrow S = d \left[\frac{dT^b}{dT} \right] \frac{V^{1-a}}{1-a} + F(T)$$

taking $\frac{\partial S}{\partial T} \Big|_V = d \left[\frac{dT^b}{dT^2} \right] \frac{V^{1-a}}{1-a} + F'(T) = d \left[\frac{dT^b}{dT^2} \right] \frac{V^{1-a}}{1-a}$

$$+ \frac{C_V}{T} - \frac{b(b-1)}{1-a} \frac{dV_0^{1-a}}{V_0^{1-a}} T^{b-2}$$

$$\rightarrow F'(T) = \frac{C_V}{T} - b(b-1)T^{b-2} \frac{V_0^{1-a}}{1-a} d$$

$$F(T) = C_V \ln T - bT^{b-1} \frac{V_0^{1-a}}{1-a} d + S_0$$

$$S(T, V) = dbT^{b-1} \frac{V^{1-a}}{1-a} + C_V \ln T - dbT^{b-1} \frac{V_0^{1-a}}{1-a} + S_0$$

$$= C_V \ln T + \frac{dbT^{b-1}}{1-a} (V - V_0) + S_0$$

③ From the Clapeyron's eq

$$\frac{dp}{dT} = \frac{\lambda}{T(v_2 - v_1)}$$

v_2 specific volume of gas

v_1 specific volume of liquid

Assuming 1) $v_1 \ll v_2$

+ 2) that $v_1 \approx$ same for $H_2O = 1677 \text{ cm}^3/\text{gm}$ How do this problem w/o this info?

$$T = 351.45^\circ\text{K}$$

could look up v_2 & v_1 for that water in a CRC.

To Do 1) look up values in CRC.

2) can one calculate v_1 &

v_2 from 1st principles

like knowing atomic

sizes of Carbon C

atoms etc?

$$\frac{dp}{dT} = \frac{855 \text{ J/gm}}{(351.45^\circ\text{K})(1677 \cdot 10^{-6} \text{ m}^3/\text{gm})}$$

$$= 1.45 \cdot 10^3 \text{ J/m}^3\text{K}$$

$$1 \text{ J} = \text{Nm}$$

$$\text{J/m}^3 = \frac{\text{Nm}}{\text{m}^3} = \text{Pa}$$

$$= 1.45 \cdot 10^3 \text{ Pa/K}$$