1.   Explain, in words, why the energy of an ideal gas depends only on the temperature.

2.   a) C_{Vm} for He, Ne, Ar, Kr, Hg and other monatomic ideal gases is $3R/2$. Why?

      b) C_{Vm} for O_2, N_2, CO_2, CH_4 and other polyatomic ideal gases is larger than $3R/2$ and increases as the temperature is raised. Why?

3.   The van der Waals a coefficient (representing attractive forces) for NO molecules might be expected to be approximately equal to the average of the van der Waals a coefficients for N_2 and O_2 molecules. In fact, in units of L^2 bar mol^{-2}, the a coefficients for the molecules are:

$$a(N_2) = 1.37$$
$$a(O_2) = 1.38$$
$$a(NO) = 1.67$$

      Why is a for NO significantly larger than a for N_2 and O_2?

4.   5.00 moles of helium at 300 K and 50.0 bar expands to a final pressure of 1.00 bar. Assuming helium is an ideal gas, calculate q, w, ΔU and ΔH if the expansion is

      a) reversible and isothermal

      b) irreversible ($p_{external}$ = 1.00 bar) and isothermal

      c) reversible and adiabatic

      d) irreversible ($p_{external}$ = 1.00 bar) and adiabatic.

5.   Calculate q, w, ΔU and ΔH for the reaction

$$CH_4(g) \; + \; 2\,O_2(g) \; \rightarrow \; CO_2(g) \; + \; 2\,H_2O(l)$$

at 25 °C and 1.00 bar:

      Data: $\Delta H_f^\circ(CH_4, g)$ = -74.6 kJ mol^{-1}
             $\Delta H_f^\circ(O_2, g)$ =   0 (*why?*)
             $\Delta H_f^\circ(CO_2, g)$ = -110.5 kJ mol^{-1}
             $\Delta H_f^\circ(H_2O, l)$ = -285.8 kJ mol^{-1}

      density of liquid water = 0.9971 g cm^{-3} (= 997.1 kg m^{-3} in SI units)

Why can the volume of liquid water be omitted from the work calculation without serious error?

6. Determining the units of a physical quantity (**dimensional analysis**) can be useful.

a) Show that $-pdV$ (the differential of reversible expansion/compression work used in thermodynamics) has the same units as energy.

b) Use dimensional analysis to convert 55.0 L bar to units of Joules.

c) The pressure exerted by a gas is well known to be the force exerted per unit area, but the pressure can also be interpreted as the energy per unit volume. Use dimensional analysis to show that pressure in SI units of Pa has the same units as $J\ m^{-3}$.

d) An equation is wrong if the units of the left side do not equal the units of the right side. Use dimensional analysis to show the equation $(\partial U/\partial V)_T = T(\partial T/\partial p)_V$ cannot be correct.

7.   **a)** For any substance, prove

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

Application: Use calorimetry to measure C_V at one temperate and volume, then calculate C_V at other volumes (and pressures) *without calorimetry.*

b) Use the result from part a to show

$$\left(\frac{\partial^2 C_V}{\partial V}\right)_T = 0$$

for an ideal gas. (*Hint:* The order of partial differentiation "doesn't matter".)

8. Liquid-in-glass thermometers are widely used: the different thermal expansion of the liquid and the glass capillary tube causes the meniscus to move if the temperature is changed. Many other kinds of thermometers have been developed, especially for scientific and technical applications. Briefly describe how each of the following thermometers are used to measure the temperature. (*Suggestion:* Use Wiki, and a sketch if helpful.)

       a) bi-metallic strip

       b) thermocouple

       c) electrical resistance thermometer

       d) infrared thermometer

9. For an ideal gas that dimerizes to a small extent, show that the second virial coefficient is

$$B(T) = RTK_p$$

where K_p is the equilibrium constant

$$K_p(T) = \frac{p_{A2}}{p_A^2}$$

for the dimerization reaction

$$A(\text{monomer}) + A(\text{monomer}) = A_2(\text{dimer})$$
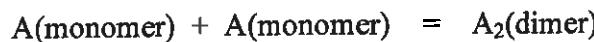
This result illustrates that the second virial coefficient is sensitive to the interaction of pairs of gas molecules (in this case, the formation of an A-A bond).

10. Use the following data for ammonia at 473 K to calculate the second and third virial coefficients ($B(T)$ and $C(T)$, respectively) at this temperature. Show that the fourth virial coefficient can be omitted from the calculations.

p / atm	V_m / (L mol^{-1})	$Z = pV_m/RT$
10.0	3.8056	0.9805
20.0	1.8651	0.9611
30.0	1.2184	0.9418
40.0	0.8945	0.9219
60.0	0.5706	0.8821
80.0	0.4081	0.8411
100.0	0.3108	0.8008

Suggestion: The virial equation

$$Z = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \cdots$$

rearranges to

$$(Z - 1)V_m = B(T) + \frac{C(T)}{V_m} + \frac{D(T)}{V_m^2} + \cdots$$

If the fourth virial coefficient $D(T)$ is negligibly small, a plot of $(Z-1)V_m$ against $1/V_m$ is a straight line with intercept $B(T)$ and slope $C(T)$.

3

(1.) No interactions between ideal gas molecules.

At a given temperature, ideal gas molecules have the same translational kinetic energy and the same rotational and vibrational energies whether they are far apart (low pressure, large volume) or packed closely together (high pressure, small volume)
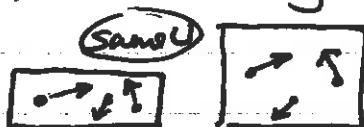
Ideal gases have no potential energy of interaction that depends on the distance between molecules.

(2.) a) Monatomic ideal gases (e.g. He) have translational kinetic energy (on average, RT/2 for each of the $x, y,$ and z kinetic energies), but no internal vibrations or rotations, for a total molar energy equal to 3RT/2.

$$C_{vm} = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{3RT}{2}\right)_V = \frac{3R}{2}$$

b) In addition to three translational modes $\left[3(RT/2)\right]^{energy}$ linear polyatomic molecules (e.g., O_2, N_2, $O=C=O$, ...) have 2 axes of rotation $\left[2(RT/2)\right]^{energy}$

In addition to three translation modes, nonlinear polyatomic (e.g., H_2O, NH_3, CH_4, ...) have 3 axes of rotation and energy (trans. + rot.) = 3(RT/2) + 3(RT/2)

$$C_{vm} \text{ (trans. + rot.)} = \frac{5}{2}R \quad linear \qquad \left(\begin{array}{c}larger\ than \\ \frac{3}{2}R \\ for\ monatomics\end{array}\right)$$

$$= 3R \quad nonlinear$$

(2 b cont.) Polyatomics, in addition to translational and rotational energies, also have vibrational energies that become more active as T increases, which absorbs more heat, causing C_{Vm} to increase as the temperature rises

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③

electric dipole forces
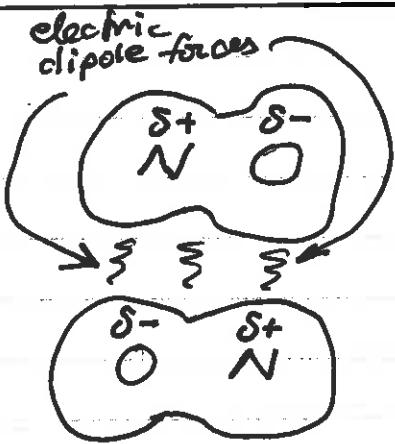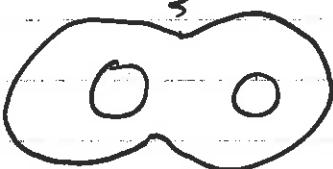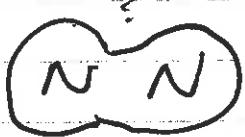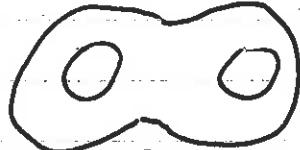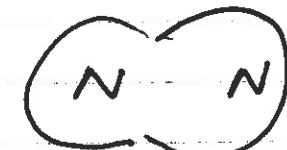
N_2 and O_2 are "homonuclear" diatomics
→ no permanent electric dipole moment

NO has a permanent electric dipole moment (one end of the molecule is slightly positive, the other end is slightly negative, due to the different electronegativities of N and O atoms), leading to stronger interactions for NO-NO than the average of the N_2-N_2 and O_2-O_2 interactions

the stronger NO-NO interactions cause the van der Waals a coefficient (representing attractive forces) to be larger for NO molecules than suggested by simply taking the average of a values for N_2 and O_2

4.) a) reversible isothermal expansion of 5.00 mol He from 50.0 bar to 1.00 bar at 300 K

isothermal ideal gas: U and H depend only on T
(constant T) $\therefore \quad \Delta U = 0 \qquad \Delta H = 0$

reversible ($P_{ext} = P$) work:

$$w = -\int P_{ext}\, dV = -\int p\, dV = -\int \frac{nRT}{V} dV$$

$$w = -nRT \int_{V_i}^{V_F} \frac{dV}{V} = -nRT \ln\left(\frac{V_F}{V_i}\right)$$

$$= -nRT \ln\left(\frac{\frac{nRT}{P_f}}{\frac{nRT}{P_i}}\right) = -nRT \ln\left(\frac{P_i}{P_f}\right)$$

$$= -(5.00 \text{ mol})(8.314 \text{ J K}^{-1}\text{mol}^{-1})(300 K) \ln\left(\frac{50.0}{1.00}\right)$$

$w = 48.8 \text{ kJ}$ $\Delta U = 0 = q + w \qquad q = -w$

$q = -48.8 \text{ kJ}$

b) irreversible isothermal expansion of 5.00 mol He
   $\overset{\displaystyle P_{ext} = 1.00 \text{ bar}}{}$
   from 50.0 bar to 1.00 bar at 300 K

isothermal ideal gas $\Delta U = 0$

$$\Delta H = 0$$

(4 b cont.) $\qquad w = -\int P_{ext}\,dV \qquad$ $P_{ext} = 1.00\ bar$
(constant)

$$w = -P_{ext}\int_{V_i}^{V_f} dV = -P_{ext}(V_f - V_i)$$

$$= -P_{ext}\left(\frac{nRT}{P_f} - \frac{nRT}{P_i}\right) = nRT\left(\frac{P_{ext}}{P_i} - \frac{P_{ext}}{P_f}\right)$$

$$= (5.00\ mol)(8.314\ J\ K^{-1}\ mol^{-1})(300\ K)\left(\frac{1.00\ bar}{50.0\ bar} - \frac{1.00\ bar}{1.00\ bar}\right)$$

$\underline{w = -12.2\ kJ} \qquad\qquad \Delta U = 0 = q + w \qquad q = -w$

$q = 12.2\ kJ \qquad$ Notice: Less work is done on the
surroundings if the expansion
is irreversible (12.2 kJ versus
48.8 kJ in part a (reversible))

$\qquad\qquad\qquad$ ✓ tricky: P, V, T all changing!

c) reversible adiabatic expansion of 5.00 mol He
from 300. K and 50.0 bar to a final pressure
of 1.00 bar

reversible: $P_{ext} = P = \dfrac{nRT}{V}$ $\qquad$ adiabatic
$\qquad\qquad\qquad\qquad\qquad$ $\therefore q = 0$

$dU = dw + \cancel{dq}^{\ P\,(adiabatic)}$ $\quad$ (1ST Law)

$C_V\,dT = -P_{ext}\,dV \qquad$ (for an ideal gas, U depends
only on T and $(\partial U/\partial T)_V = C_V$)

$nC_{Vm}\,dT = -P\,dV \qquad$ (reversible: $P_{ext} = P$)
$\qquad\qquad\qquad\qquad\qquad$ $P = nRT/V$

(4c cont.)   for He, $C_{vm} = \dfrac{3R}{2}$ see Q1.

$$n \frac{3}{2} R dT = - \frac{nRT}{V} dV$$

$$\frac{3}{2} \frac{dT}{T} = - \frac{dV}{V} \implies \frac{3}{2} \int_{T_i}^{T_f} \frac{dT}{T} = - \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\frac{3}{2} \ln\left(\frac{T_f}{T_i}\right) = - \ln\left(\frac{V_f}{V_i}\right) \quad \underline{problem} \quad \text{don't know } V_f \text{ or } T_f \text{ yet!}$$

Suggestion use $pV = nRT$ to get

$$\ln(pV) = \ln(nRT)$$
$$\ln p + \ln V = \ln(nR) + \ln T$$
$$d\ln p + d\ln V = \underset{0 \,(nR\ constant)}{d\ln(nR)} + d\ln T$$

$$d\ln p - d\ln T = - d\ln V \implies \boxed{\frac{dp}{p} - \frac{dT}{T} = - \frac{dV}{V}}$$

substitute for $-\frac{dV}{V}$

$$\frac{3}{2} \frac{dT}{T} = - \frac{dV}{V} = \frac{dp}{p} - \frac{dT}{T}$$

$$\left(1 + \frac{3}{2}\right) \frac{dT}{T} = \frac{dp}{p} \qquad \frac{5}{2} \frac{dT}{T} = \frac{dp}{p} \qquad \frac{dT}{T} = \frac{2}{5} \frac{dp}{p}$$

finally:

$$\int_{T_i}^{T_f} \frac{dT}{T} = \frac{2}{5} \int_{P_i}^{P_f} \frac{dp}{p} \qquad \ln\left(\frac{T_f}{T_i}\right) = \frac{2}{5} \ln\left(\frac{P_f}{P_i}\right)$$

(4 c cont.)

$$\ln\left(\frac{T_f}{T_i}\right) = \ln\left(\frac{T_f}{300K}\right) = \frac{2}{5}\ln\left(\frac{1.00\,bar}{50.0\,bar}\right) = -1.565$$

$$\frac{T_f}{T_i} = e^{-1.565} \qquad T_f = 0.2091\,T_i = 0.2091\,(300\,K)$$

$$T_f = 62.7\ K$$

$$\Delta U = \int C_V\,dT = \int nC_{Vm}\,dT = n\frac{3}{2}R\int_{T_i}^{T_f}dT$$

$$\Delta U = n\frac{3}{2}R\left(T_f - T_i\right) = (5.00\,mol)\frac{3}{2}\left(8.314\,\frac{J}{K\,mol}\right)(62.7-300.)K$$

$$\Delta U = -14.8\ kJ \qquad\qquad \Delta U = \cancel{q}^0 + w$$
$$w = -14.8\,kJ$$

$$\Delta H = \int C_p\,dT = \int n\,C_{pm}\,dT = \int n\left(C_{Vm}+R\right)dT$$

$$= n\left(\frac{3}{2}R + R\right)\int_{T_i}^{T_f}dT$$

$$\Delta H = n\frac{5}{2}R\left(T_f - T_i\right)$$

$$\Delta H = -24.7\ kJ$$

d) irreversible $(P_{ext} = 1.00\,bar)$ adiabatic expansion
$$\hookrightarrow q = 0$$

$$dU = dw + \cancel{dq}^{\,0}$$

$$C_V\,dT = -P_{ext}\,dV \qquad\qquad n\int C_{Vm}\,dT = -\int P_{ext}\,dV$$
$$\overset{(3/2)R}{\curvearrowleft} \qquad\qquad \overset{1.00\,bar}{\curvearrowleft}$$

$$n\frac{3}{2}R\int_{T_i}^{T_f}dT = -P_{ext}\int_{V_i}^{V_f}dV$$

(4 d cont.)

$$n \frac{3}{2} R (T_f - T_i) = -P_{ext}(V_f - V_i)$$

but... $n \frac{3}{2} R (T_f - T_i) = -P_{ext} \left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i} \right)$

once again,
2 unknowns
T_f, V_f

$$\frac{3}{2}(T_f - T_i) = -\frac{P_{ext}}{P_f} T_f + \frac{P_{ext}}{P_i} T_i$$

$$\left(\frac{3}{2} + \frac{P_{ext}}{P_f} \right) T_f = \left(\frac{3}{2} + \frac{P_{ext}}{P_i} \right) T_i$$

$$T_f = \frac{\frac{3}{2} + \frac{P_{ext}}{P_i}}{\frac{3}{2} + \frac{P_{ext}}{P_f}} T_i = \frac{1.5 + \frac{1.00 \text{ bar}}{50.0 \text{ bar}}}{1.5 + \frac{1.00 \text{ bar}}{1.00 \text{ bar}}} (300 \text{ K})$$

$$T_f = \frac{1.52}{2.50} 300 \text{ K} = 182.4 \text{ K}$$

$$\Delta U = \int n C_{vm} \, dT = (5.00 \text{ mol}) \frac{3}{2} 8.314 \frac{J}{K \text{ mol}} (182.4 - 300) K$$

$$\Delta U = -7.33 \text{ kJ} = \cancel{q}^{0} + w$$

$$w = -7.33 \text{ kJ}$$

$$C_{pm} = C_{vm} + R = \frac{5}{2} R$$

$$\Delta H = \int n C_{pm} \, dT = (5.00 \text{ mol}) \frac{5}{2} (8.314)(182.4 - 300.)$$

$$\Delta H = -12.2 \text{ kJ}$$

5.
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$
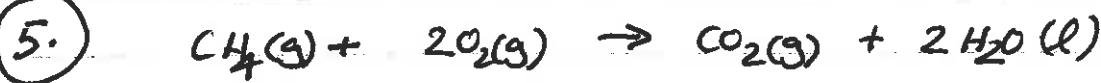
$$\Delta H = \Delta H_f(products) - \Delta H_f(reactants)$$

$$= \Delta H_{fm}(CO_2,g) + 2\Delta H_{fm}(H_2O,l) - \Delta H_{fm}(CH_4,g) - 2\Delta H_{fm}(O_2,g)$$

$$= -110.5 + 2(-285.8) - (-74.6) - 2(0)$$

$$\Delta H = -607.5 \text{ kJ}$$

O_2 is a pure element in its standard state

constant pressure, only p-V work

so $\quad \Delta H = q = -607.5$ kJ

$$w = -\int P_{ext}\, dV$$

$$= -p\int dV \qquad \text{(p constant)}$$

$\dfrac{M_{H_2O}}{V_{m\,H_2O(l)}} = $ density of $H_2O(l)$

$$V_{m\,H_2O(l)} = \dfrac{M_{H_2O}}{\text{density}_{H_2O(l)}}$$

$$= -p(V_{products} - V_{reactants})$$

$$= -p\left(V_{m\,CO_2 g} + 2V_{m\,H_2O\,l} - V_{m\,CH_4 g} - 2V_{m\,O_2 g}\right)$$

$$= -p\left(\frac{RT}{p} + \frac{M_{H_2O}}{\text{density }H_2O(l)} - \frac{RT}{p} - \frac{2RT}{p}\right)$$

$$= -2RT \quad \frac{p M_{H_2O}}{\text{density }H_2O(l)}$$

SI units:
$M_{H_2O} = 0.018\ \frac{kg}{mol}$
$\text{density}_{H_2O(l)} = 997.1\ \frac{kg}{m^3}$
$p = 10^5\ Pa$

$$= 2\left(8.314\frac{J}{K\,mol}\right)(298.15K) - \frac{10^5\,Pa(0.018\frac{kg}{mol})}{997.1\ \frac{kg}{m^3}}$$

$$= 4958\ J\,mol^{-1} - 1.8\ J\,mol^{-1}$$

very small

$$w = 4956\ \frac{J}{mol}$$

(5 cont.)

$$\Delta U = q + w = -607.5 \frac{kJ}{mol} + 5.0 \frac{kJ}{mol}$$

$$\Delta U = -602.5 \frac{kJ}{mol}$$

In the work calculation, $w = -P\Delta V$, the volume change caused by the formation of $CO_2(g)$ and the loss of $CH_4(g) + 2O_2(g)$ reactants is

$$-2\frac{RT}{P} = -2\frac{8.314 \frac{J}{mol\,K} \; 298.15K}{10^5 \, Pa} = -2(0.0248)m^3$$

$$\Delta V_{gas} = -49.6 \; L$$

The volume change due to the formation of 2 mol liquid H_2O is

$$2V_{m\,H_2O(\ell)} = \frac{2 M_{H_2O}}{density \; H_2O(\ell)} = \frac{2(0.0180 \; kg/mol)}{997.1 \; kg \; m^{-3}} =$$

$$= 0.0000361 \; m^3 = 0.0361 \; L = 36.1 \; cm^3$$
$$= 36.1 \; mL$$

The liquid volume change $(0.0361 \; L)$ is negligible compared to the gas volume change $(-49.6 L)$

So the work due to the formation of the product $2H_2O(\ell)$ can be safely neglected   only $1.8 \; J$

(6.) a) energy = force × distance

= mass × acceleration × distance

$$= kg \times \frac{m}{s^2} \times m \qquad \left(\begin{array}{c}SI \\ units\end{array}\right)$$

$$1\,J = 1\,\frac{kg\,m^2}{s^2}$$

acceleration
$$= \frac{d(velocity)}{dt} \sim \frac{m\,s^{-1}}{s}$$
$$\sim \frac{m}{s^2}$$

pdV has pV units

$$pressure \times volume = \frac{force}{area} \times volume$$

$$= \frac{mass \times acceleration}{area} \times volume$$

$$= \frac{kg\,m\,s^{-2}}{m^2}\,m^3$$

$$= \frac{kg\,m^2}{s^2} \qquad \left(\begin{array}{c}same\ units\ as \\ energy\ in\ Joules\end{array}\right)$$

b) 55.0 L bar ·

$$\left(\begin{array}{c}1\,m^3 = 1000\,L \\ 1\,bar = 10^5\,Pa\end{array}\right)$$

$$= \left(55.0 \, L \, bar\right)\left(\frac{10^{-3}\,m^3}{L}\right)\left(\frac{10^5\,Pa}{bar}\right)$$

$$= 5500\,m^3\,Pa \qquad (SI\ units)$$

$$= 5500\,J$$

(6 cont.)

c)

$$\text{pressure} = \frac{\text{force}}{\text{area}} = \frac{\text{mass} \times \text{acceleration}}{\text{area}}$$

$$= \frac{kg \frac{m}{s^2} (\times m)}{m^2 (\times m)} = \frac{kg \frac{m^2}{s^2}}{m^3} \xleftarrow{\quad} J \text{ (energy)}$$

$$\xleftarrow{\quad} \text{(volume)}$$

$$= \frac{J}{m^3} = \frac{\text{energy}}{\text{volume}}$$

d) left side has units of $\frac{\Delta U}{\Delta V} \sim \frac{J}{m^3}$

right side has units of $T \frac{\Delta T}{P} \sim \frac{K^2}{J\, m^{-3}} \xleftarrow{} \text{from part c}$

left units $\neq$ right units

---

7 a) recall $C_v = \left(\frac{\partial U}{\partial T}\right)_V$ and $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

$$\left(\frac{\partial C_v}{\partial V}\right)_T = \left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right]_T$$

use chain rule
$$\frac{\partial (fg)}{\partial T} = f\frac{\partial g}{\partial T} + g\frac{\partial f}{\partial T}$$

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

$$= T\left[\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial T}\right)_V\right]_V + \left(\frac{\partial P}{\partial T}\right)_V \cancelto{1}{\left(\frac{\partial T}{\partial T}\right)_V} - \left(\frac{\partial P}{\partial T}\right)_V$$

$$= T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

(7 cont.)

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

b) $\left(\dfrac{\partial C_v}{\partial V}\right)_T = \left(\dfrac{\partial^2 p}{\partial T^2}\right)_V = \left(\dfrac{\partial}{\partial T}\dfrac{\partial p}{\partial T}\right)_V$

$$= \left[\frac{\partial}{\partial T}\frac{\partial}{\partial T}\left(\frac{nRT}{V}\right)\right]_V = \frac{nR}{V}\left(\frac{\partial}{\partial T}\frac{\partial T}{\partial T}\right)_V$$

$$= \frac{nR}{V}\left(\frac{\partial}{\partial T}1\right)_V = \frac{nR}{V}(0) = 0$$

(8.) a) Weld together flat strips of two different
metals (e.g., brass and steel) of equal length

(or rivet or glue)

temperature T

as the **bi-metallic strip** is heated, the metal strip
with the larger thermal expansion will stretch
in length more than the other metal, forming a
curved strip (or spiral), with the former metal on
the concave side (larger radius of curvature)

$T + \Delta T$
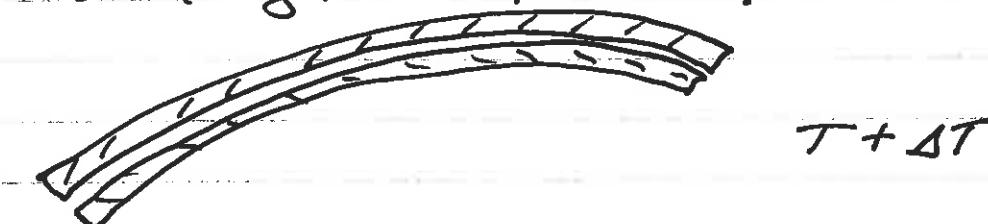
Similarly,
upon cooling, the metal strip with the larger thermal
expansivity is on the concave side (it shrinks in length more,
shorter radius of curvature)

A **mechanical thermometer**:
The bi-metallic
strip can move a
needle on a temperature
gauge or close an electrical switch in a thermostat

$T - \Delta T$

(8 cont.)

$\rightarrow$ ⟨T difference produces a voltage difference⟩

b) <u>thermocouple</u> constructed from metal wires of two different chemical compositions, such as iron and copper

voltage difference $\Delta\phi$ is proportional to $T_{unknown} - T_{ref.}$

measure voltage difference $\Delta\phi$

metal wire B

metal wire A
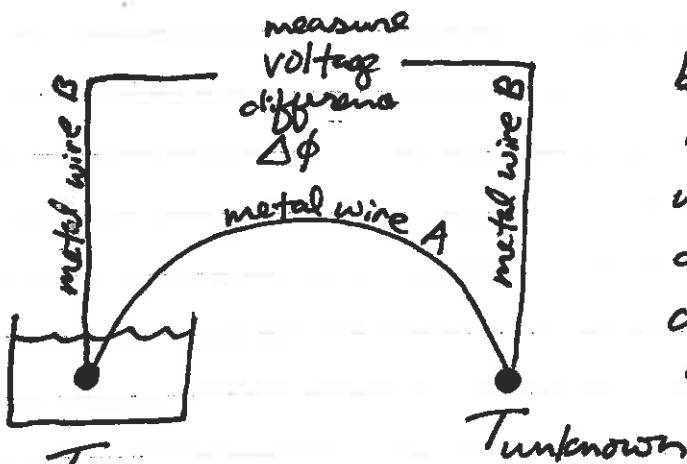
metal wire B

$T_{reference}$
e.g. $0°C$ using ice water

$T_{unknown}$

If the junctions between the two kinds of metal wires are at different temperatures, a voltage $\Delta\phi$ is generated, which can be measured

$$\Delta\phi = \text{constant} \times (T_{unknown} - T_{ref.})$$

$\nearrow$ determined by calibration

c) resistance thermometer

The resistance of an electrical conductor to the passage of electric current depends on the temperature

resistance $R(T) = \dfrac{\text{voltage}}{\text{current}} = \dfrac{\Delta\phi}{I}$

⟨platinum resistance thermometer⟩ — uses a thin <u>Platinum wire</u> as the temperature sensor

$\rightarrow$ very stable (little or no corrosion) and reproducible resistance measurements R increases with T

(8 c cont.)

(thermistor) uses a semiconductor as the temperature sensor

as the semiconductor is heated, electrons are promoted into the conduction band, decreasing the resistance

the resistance depends exponentially on the temperature, making thermistors very sensitive thermometers

d) all objects emit thermal radiation
   (mostly infrared near room temperature)

the intensity of the emitted radiation increases with temperature and shifts to higher frequencies

an (infrared thermometer) uses the measured intensity of radiation emitted by an object to determine its temperature

Important: Bi-metallic strips, thermocouples, resistance thermometers, and infrared thermometers provide mechanical or electrical outputs suitable for automated temperature measurement and computer control

9.

EVALUATE THE SECOND AND THIRD

VIRIAL COEFFICIENTS OF AMMONIA

AT 473 K

DATA: CALCULATE:

p/atm	Z	V_m/dm^3 mol^{-1}	$\frac{1}{V_m}$/mol dm^{-3}
10	0.9805	3.8056	0.2628
20	0.9611	1.8651	0.5362
30	0.9418	1.2184	0.8207
40	0.9219	0.8945	1.1179
60	0.8821	0.5706	1.7525
80	0.8411	0.4081	2.4506
100	0.8008	0.3108	3.2174

$$V_m = \frac{Z\,RT}{P}$$

$$= \frac{Z\left(0.082056\,\frac{dm^3\,atm}{K\,mol}\right)473\ K}{P}$$

(9 cont.)   **SUGGESTION:**

FIRST, IT'S A GOOD IDEA TO PLOT

THE DATA : * IS IT REASONABLE?

     * ANY TABULATION ERRORS?

     * BAD POINTS ?

z vs p/atm scatter plot. Vertical axis z with marks at 0.8, 0.9, 1.0; horizontal axis p/atm from 0 to 120. Data points decrease smoothly from about $z=0.98$ at low p to about $z=0.81$ near $p=100$.

p/atm
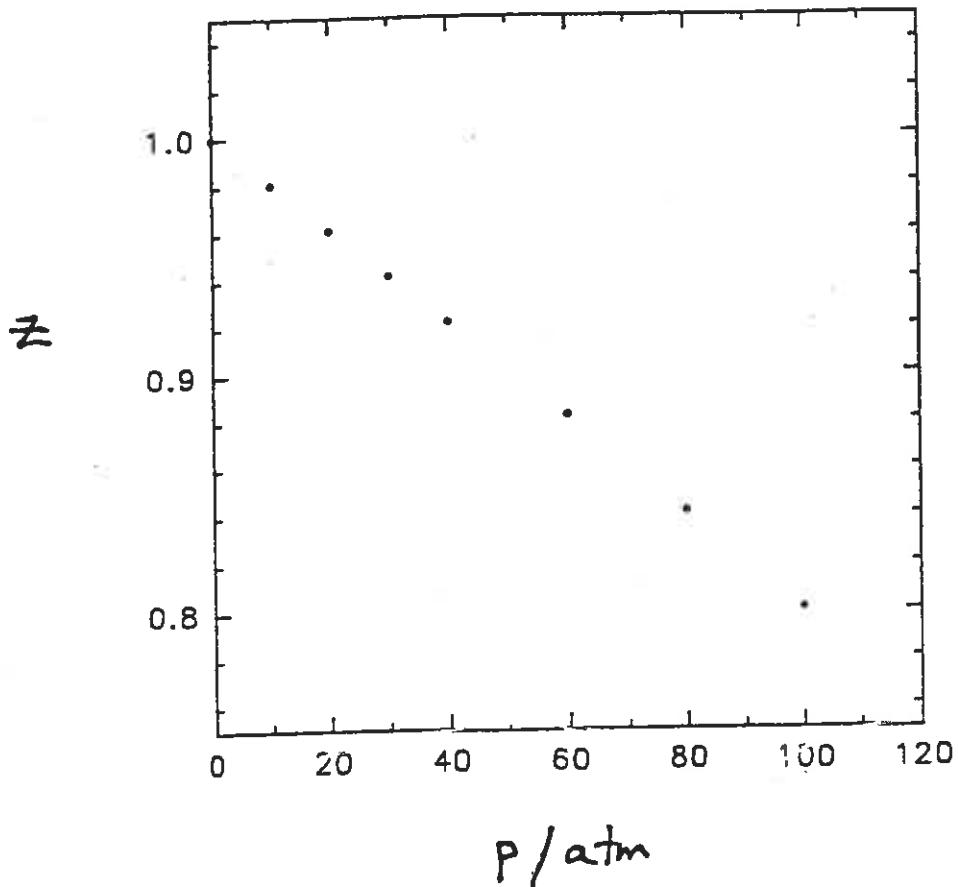
DATA LOOKS O.K: "SMOOTH" $\left(\begin{array}{c}\text{no obvious}\\ \text{"bad"}\\ \text{points}\end{array}\right)$

and $z \to 1$ AS $p \to 0$

(9. cont.)

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots$$

$$\therefore \quad (Z-1)V_m = B + \frac{C}{V_m} + \cdots$$

IF $D, E, \ldots$ COEFFICIENTS
ARE NEGLIGIBLE $\implies$ $\boxed{(Z-1)V_m = B + \frac{C}{V_m}}$

SLOPE $= C$
$= 0.00404 \frac{dm^6}{mol^2}$

$(Z-1)V_m / dm^3\ mol^{-1}$

INTERCEPT
$B = -0.0746 \frac{dm^3}{mol}$

$\frac{1}{V_m} / mol\ dm^{-3}$
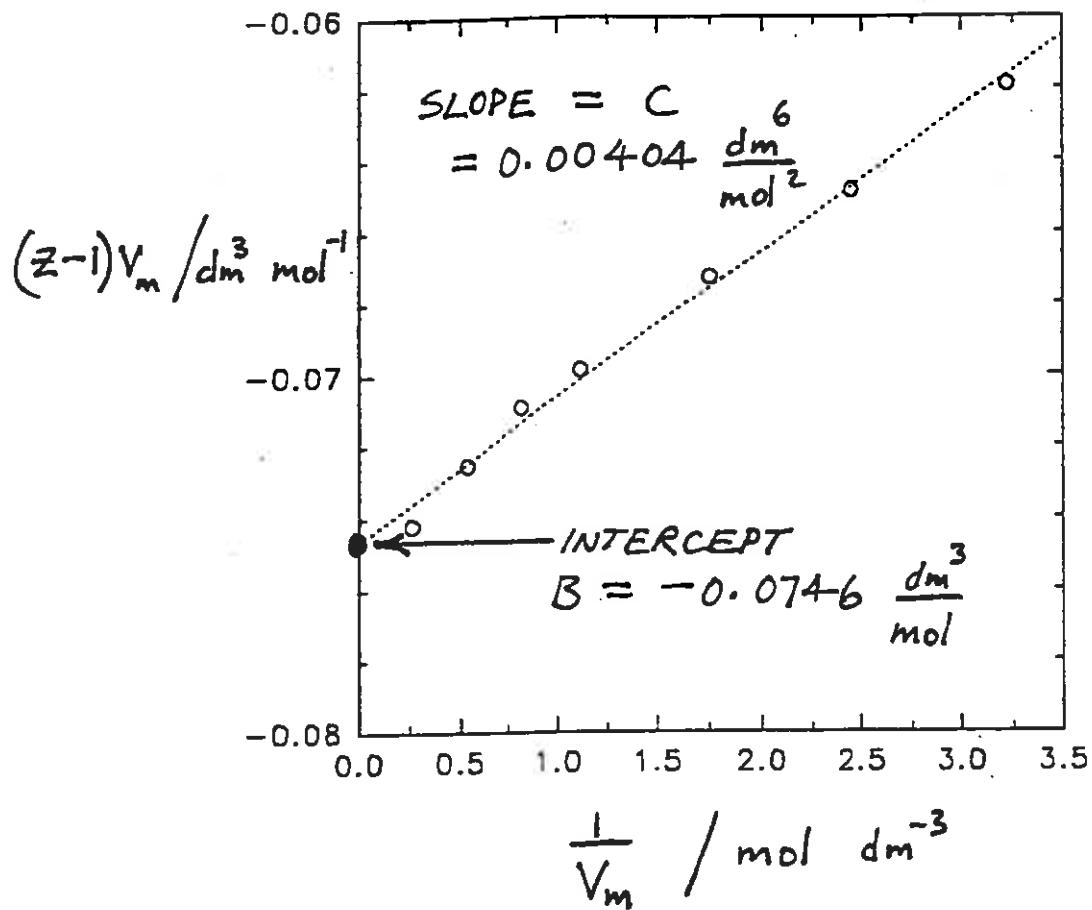
NO SIGNIFICANT CURVATURE IN THE
PLOT OF $(Z-1)V_m$ AGAINST $\frac{1}{V_m}$.

SUGGESTS HIGHER-ORDER $\frac{D}{V_m^3}, \frac{E}{V_m^4}, \ldots$ TERMS
ARE UNIMPORTANT

(10.)

Derive an expression for the 2ND Virial B coefficient of an ideal gas that dimerizes to a small extents (*ILLUSTRATES THAT B MEASURES PAIR-WISE INTERACTIONS; DIMERIZATION EQUILIBRIUM $A + A \rightleftharpoons A_2$

EQUILIBRIUM CONSTANT $K = \dfrac{P_{A_2}}{P_A^2}$

Place n moles of gas A in a container of volume V. Let ϵ be the fraction of the total A molecules that dimerize

$$2A \rightleftharpoons A_2$$

moles present: $(1-\epsilon)n \qquad \dfrac{\epsilon}{2}n$
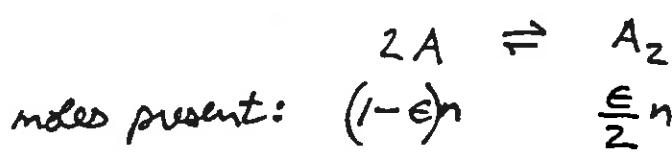
$\left(\begin{array}{l} * \ \epsilon n \text{ moles of } A \\ \text{molecules dimerize} \\ \text{to form } \frac{\epsilon}{2} n \text{ moles } A_2 \end{array}\right)$

total pressure $P = P_A + P_{A_2}$

$$P = n_A \frac{RT}{V} + n_{A_2}\frac{RT}{V} = (1-\epsilon)n\frac{RT}{V} + \frac{\epsilon}{2}n\frac{RT}{V}$$

$$P = \left(1 - \epsilon + \frac{\epsilon}{2}\right)\frac{RTn}{V} \qquad \boxed{Z = \frac{pV}{nRT} = 1 - \frac{\epsilon}{2}}$$

$$K = \frac{P_{A_2}}{P_A^2} = \frac{n_{A_2}\frac{RT}{V}}{\left(n_A\frac{RT}{V}\right)^2} = \frac{\frac{\epsilon}{2}n\frac{RT}{V}}{\left((1-\epsilon)n\frac{RT}{V}\right)^2} = \frac{V}{nRT}\frac{\epsilon/2}{(1-\epsilon)^2}$$

$$\frac{\epsilon}{2} = \frac{nRT}{V}K(1-\epsilon)^2$$

$$Z = 1 - \frac{\epsilon}{2} = 1 - \frac{nRT}{V}K(1-\epsilon)^2$$

$$Z = 1 - \frac{RTK(1-\epsilon)^2}{V_m} \cong 1 - \frac{RTK}{V_m} \quad \left(\begin{array}{l} \text{FOR SMALL DEGREES} \\ \text{OF DIMERIZATION} \\ \epsilon \ll 1 \end{array}\right)$$

COMPARE: $Z = 1 + \dfrac{B}{V_m}$ $\qquad \boxed{\text{2ND VIRIAL COEFF. } B = -RTK}$