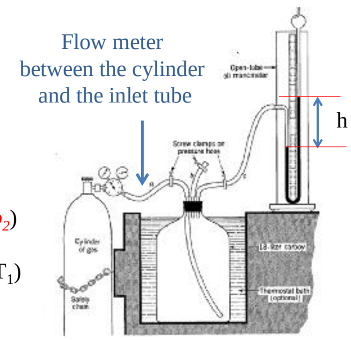
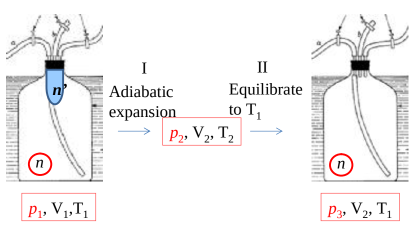
Heat Capacity Ratios of Gases

Experimental Set up

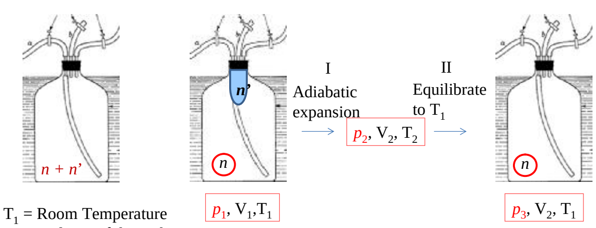
1. Fill carboy with a gas thermally equilibrate (T_1) measure p_1
2. Open/close stopper (pressure= atm. press. = p_2)
3. thermally equilibrate to (T_1) measure p_3





The gas leaving as the stopper is opened be *n'* moles and the rest of the gas moles be *n*. Consider this *n* moles here onwards.

As n' moles (p_1, V_1,T_1) leave the carboy *n* moles occupying expands into the volume of the carboy (V_2, cooled down to T_2) adiabatically.



T_1 = Room Temperature
V_2 = Volume of the carboy

<u>I. Adiabatic expansion</u> *For n moles* p_1, V_1,T_1 $\longrightarrow$ p_2, V_2, T_2

$dE = q - pdV \quad dE = -pdV$;adabatic $\quad dE = -\dfrac{nRT}{V}dV$

$\dfrac{dE}{dT} = n\widetilde{C}_v \Rightarrow dE = n\widetilde{C}_v dT \quad \widetilde{C}_v$ = molar constant volume heat capacity

Equating dE; $\quad n\widetilde{C}_v dT = -\dfrac{nRT}{\widetilde{V}}dV \quad \Rightarrow \quad \widetilde{C}_v \dfrac{dT}{T} = -R\dfrac{dV}{\widetilde{V}}$

Integrating the preceding,

$$\widetilde{C}_v \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\widetilde{C}_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} \quad \Rightarrow \ln \frac{T_2}{T_1} = -\frac{R}{\widetilde{C}_v} \ln \frac{V_2}{V_1}$$

using ideal gas for n moles $nR = \frac{p_2 V_2}{T_2} = \frac{p_1 V_1}{T_1} \Rightarrow \ln \frac{T_2}{T_1} = \ln \frac{p_2}{p_1} + \ln \frac{V_2}{V_1}$

equating $\ln \frac{T_2}{T_1}$ we get, $\ln \frac{p_2}{p_1} = -\frac{R}{\widetilde{C}_v} \ln \frac{V_2}{V_1} - \ln \frac{V_2}{V_1}$

$$\ln \frac{p_2}{p_1} = \left(-\frac{R}{\widetilde{C}_v} - 1 \right) \ln \frac{V_2}{V_1}$$

$$\ln \frac{p_2}{p_1} = -\left(\frac{R + \widetilde{C}_v}{\widetilde{C}_v} \right) \ln \frac{V_2}{V_1}$$

For an ideal gas; $\widetilde{C}_p = R + \widetilde{C}_v$

$$\ln \frac{p_2}{p_1} = -\left(\frac{\widetilde{C}_p}{\widetilde{C}_v} \right) \ln \frac{V_2}{V_1}$$

II Equilibrate to T_1 n $\boxed{p_1, V_1, T_1} \longrightarrow \boxed{p_3, V_2, T_1}$

Using IDE; $\frac{V_2}{V_1} = \frac{p_1}{p_3} \quad \Rightarrow \ln \frac{V_2}{V_1} = \ln \frac{p_1}{p_3}$

substitutefor $\ln \frac{V_2}{V_1}$ in $\ln \frac{p_2}{p_1} = -\left(\frac{\widetilde{C}_p}{\widetilde{C}_v} \right) \ln \frac{V_2}{V_1}$

$$\ln \frac{p_2}{p_1} = -\left(\frac{\widetilde{C}_p}{\widetilde{C}_v} \right) \ln \frac{p_1}{p_3}$$

C_v = Energy (heat) absorbed or released per unit temperature increase or decrease, respectively.

At low temperatures the heat exchanged is involved with translational, rotational and vibrational motions of a molecule (particle).

For a molecule with N atoms there are 3N total number of degrees of freedom. Of the N the degrees of freedom for translational motion are 3, rotational motions are 3 for nonlinear and 2 for linear molecules; for vibrational motions the # degrees of freedom are 3N-5 (for linear) and 3N-6 (for non-linear) molecules.

Each quadratic term of energy (motional and potential) contributes k_B 2per molecule or R/2 per mole of the substance.

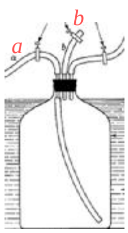
Each quadratic term in the (active) energy modes contribute $(R/2)$ J mol^{-1} K^{-1} amount of heat to the C_v of the substance.

# atoms=N	Contribution for C_v		
motion	all	linear	non-linear
translation	3(R/2)		
rotation		2(R/2)	3(R/2)
vibration		(3N-5)R	(3N-6)R

	Contribution for C_v		
motion	He(N=1)	N_2(N=2)	CO_2(N=3)
translation	3(R/2)	3(R/2)	3(R/2)
rotation		2(R/2)	2(R/2)
vibration		(6-5)R	(9-5)R
Total	1.5R	7.5R	9.5R

Note:

1. Start with He, fill the carboy with using *b* as the inlet.
2. Once He data are taken, using the tubing as shown in the figure study nitrogen and carbon dioxide in that order (inlet *a*, outlet *b*).



1 hPa = 100 Pa

pressure(mmHg)

$$= h(\text{cm}) \times \frac{\text{Density of Hg}}{\text{Density of liquid used}} + \text{atmospheric pressure(mmHg)}$$