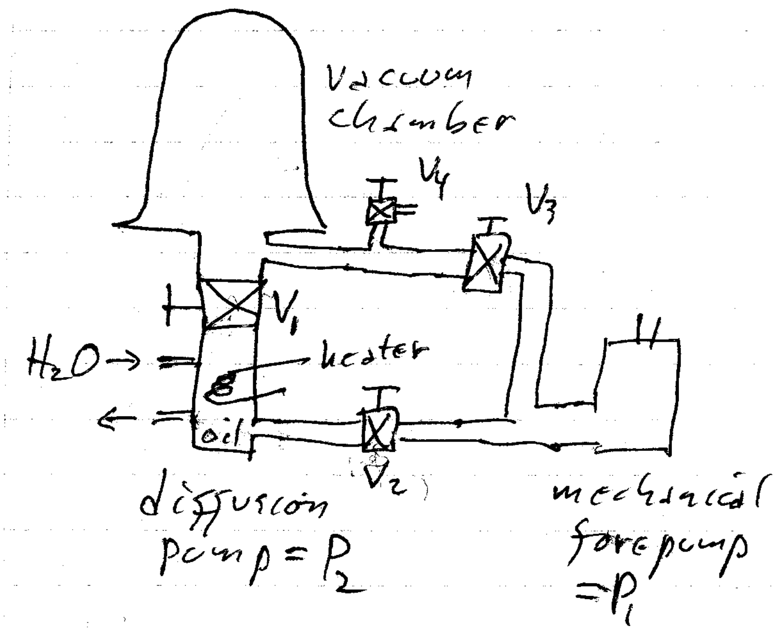
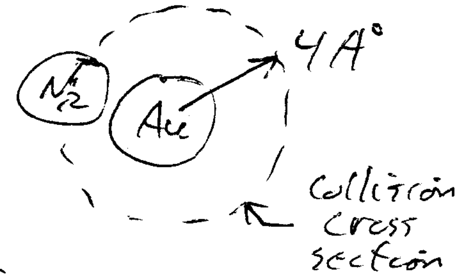
Experimental Solution



1) Close V_1. (V_3 and V_4 are already closed.)
2) Close V_2. Hot oil in diffusion pump is now protected from oxidation by air when chamber is opened. THIS IS EXTREMELY IMPORTANT!
3) Open V_4 slowly to bring chamber up to atmospheric pressure.
4) Remove bell jar, change sample, replace bell jar.
5) Close V_4, then open V_3 and wait until chamber pressure drops to ~50 milli torr. This low pressure air won't damage the oil.
6) Close V_3, then open V_2.
7) Wait a few seconds, then open V_1.
8) Wait for chamber pressure to drop to desired level, then do next experiment.

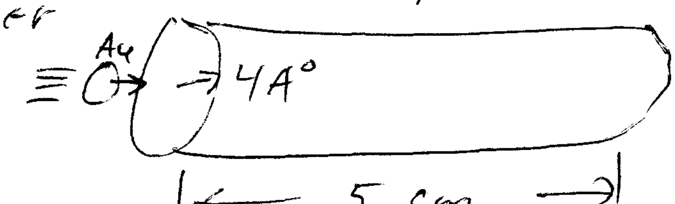
Experimental Solution

B. Estimate collision cross section as $\sim \pi \times (4 \times 10^{-10}\,m)^2 \sim 50 \times 10^{-20}\,m^2$ based on $\sim 4\,A^\circ$ atomic or small molecular diameter.



Air at STP has ~ 0.001 density of water, so molecules are around $4A^\circ \times 10 = 40A^\circ$ apart, or have number density $\left(\frac{1}{40 \times 10^{-10}\,m}\right)^3 = \frac{10^{30}}{64000\,m^3} \simeq 1.5 \times 10^{25}/m^3$

For $5\,cm = 0.05\,m$ mean free path, we want 1 molecule of N_2 (say) in cylinder



or number density $\frac{1}{50 \times 10^{-20} \times 0.05\,m^3} = 0.4 \times 10^{20}/m^3$

This corresponds to a pressure of

$$760\,\text{torr} \times \frac{0.4 \times 10^{20}}{1.5 \times 10^{25}} = 200 \times 10^{-5}\,\text{torr} = \boxed{2\ \text{millitorr}}$$

<u>Building Scientific Apparatus</u> (Moore et al., p. 72) lists 5 cm MFP for 1 millitorr.

15. List five forms of interatomic bonding found in solids. List them in order of increasing bond strength per atom. For each type of bonding give the following:

a) The characteristic range of bonding energies per atom (*e.g.* in units of eV or kcal)

b) List one material exhibiting primarily bonding of that type.

c) List one property (physical, chemical, or mechanical) of solids having that type of bonding.

Specific types of bonding:

	Type	Binding Energy (eV)	Property
weak	Van der Waals (Argon, Hydrogen)	0.01 to 0.5	low melting point insulating transparent to far uv
	Hydrogen Bond (ice, KH_2PO_4	0.5	many allotropic forms dielectric activity optically transparent
medium	Covalent (Silicon, GaAs)	1 - 5	semiconductor/insulator absorbs light of energy > threshold (gap) rigid and hard (cleave)
	Metallic Ni, Cu, Ag	1 - 5	conductor of electrons opaque (visible) and highly reflecting
strong	Ionic NaCl, KCl	5 - 20	dissociate on heating insulator at low temp. plastic.

— now discuss each type —

	p^2	M_S: 1	0	-1
	2		$(1^+ 1^-)$	
	1	$(1^+ 0^+)$	$(1^+ 0^-)$ $(1^- 0^+)$	$(1^- 0^-)$
M_L	0	$(1^+ -1^+)$	$(1^+ -1^-)$ $(1^- -1^+)$ $(0^+ 0^-)$	$(1^- -1^-)$
	-1	$(0^+ -1^+)$	$(0^+ -1^-)$ $(0^- -1^+)$	$(0^- -1^-)$
	-2		$(-1^+ -1^-)$	

$M_L = 2 \quad M_S = 0 \quad \Rightarrow \quad {}^1D \quad 5$

$M_L = 1 \quad M_S = 1, 0, -1 \quad \Rightarrow \quad {}^3P \quad 9$

$M_L = 0 \quad M_S = 0 \quad \Rightarrow \quad {}^1S \quad 1$

15

$N = 2(2l+1) = 6$

$$\binom{N}{x} = \frac{6 \cdot 5}{2} = 15$$ ✓

16. Consider a thermodynamic system consisting of a fixed number, N, of identical particles. Let P, V, S and T be the pressure, volume, entropy and temperature of this system.

a) When P and S are consider as functions of V and T, use the first law of thermodynamics to show that:

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

b) Consider the specific heats $C_x \equiv \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_x$. Show that

$$C_P = C_v - \frac{T}{N}\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T.$$

Lee Lindblom

Thermodynamics

Consider a thermodynamic system consisting of a fixed number, N, of identical particles. Let P, V, S and T be the pressure, volume, entropy and temperature of this system. When P and S are

a) considered as functions of V and T, use the first law of thermodynamics to show that:

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

b) Consider the specific heats $C_x \equiv \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_x$. Show that

$$C_P = C_V - \frac{T}{N}\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T .$$

Solution:

a) The first law of thermodynamics for a fixed number of particles is given by:

$$dU = -PdV + TdS$$

When V and T are the desired independent variables perform a Legendre transform. Let $F = U - TS$

$$dF = d(U - TS) = -PdV - SdT$$

Therefore $P = -\left(\frac{\partial F}{\partial V}\right)_T$ and $S = -\left(\frac{\partial F}{\partial T}\right)_V$. The equality of mixed partial derivatives gives:

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial T \partial V} = -\frac{\partial^2 F}{\partial V \partial T} = \left(\frac{\partial S}{\partial V}\right)_T$$

b) $c_p = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_p$

$c_V = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_V$

$$c_p = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_p$$

$$= \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_V + \frac{T}{N}\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial S}{\partial V}\right)_T$$

$$= c_V + \frac{T}{N}\left(\frac{\partial V}{\partial T}\right)_p^2\left(\frac{\partial T}{\partial V}\right)_p\left(\frac{\partial S}{\partial V}\right)_T$$

$$= c_V - \frac{T}{N}\left(\frac{\partial V}{\partial T}\right)_p^2\left(\frac{\partial T}{\partial p}\right)_V\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial S}{\partial V}\right)_T$$

$$= c_V - \frac{T}{N}\left(\frac{\partial V}{\partial T}\right)_p^2\left(\frac{\partial p}{\partial V}\right)_T$$