

Q1. (20 Points)

A 1.0 liter glass bulb contains  $1.0 \times 10^{23}$   $H_2$  molecules. If the pressure exerted by the gas is 100 kPa (kilo-Pascals) what is: (i) the temperature of the gas, and (ii) the root mean square velocity of the gas molecules?

$$P = 100 \text{ kPa} = 100,000 \text{ Pa} = 10^5 \text{ Pa} \quad (\text{or } 1 \text{ atm})$$

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

$$N = \# H_2 \text{ molecules} = 10^{23}$$

$$i) \quad PV = nRT$$

$$n = \frac{10^{23}}{6.022 \times 10^{23}} = \frac{N}{N_A} = 0.166 \text{ moles of } H_2$$

$$T = \frac{PV}{nR}$$

$$R = 8.315 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = \frac{10^5 \text{ Pa} \times 10^{-3} \text{ m}^3}{0.166 \text{ moles} \times 8.315 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$= \underline{\underline{72.5 \text{ K}}}$$

$$ii) \quad v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

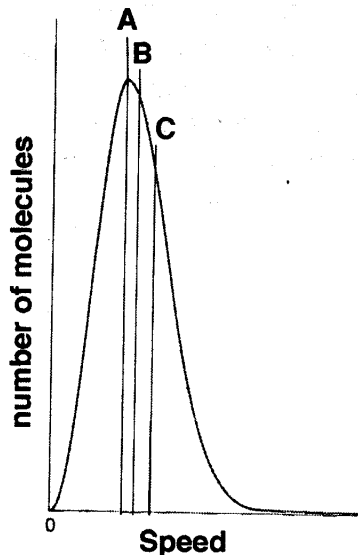
$$M = \text{mass of 1 mole of } H_2 \text{ (molar mass)}$$

$$M = 2 \text{ g} = 2 \times 10^{-3} \text{ kg}$$

$$v_{\text{rms}} = \sqrt{\frac{3 \times 8.315 \times 72.5}{2 \times 10^{-3}}}$$

$$= \underline{\underline{95 \text{ m s}^{-1}}}$$

Q2. (20 Points)



Shown above is the distribution of speeds for gas molecules. Three values of the speeds, A, B and C are indicated.

- (i) Which is the root mean square speed (A, B or C)? (4 Points)

$$C \quad c_{rms} > \bar{c} > c_{mp}$$

- (ii) Which is the mean speed (A, B or C)? (4 Points)

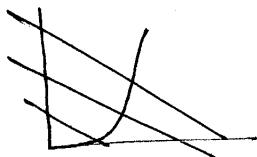
B

- (iii) Which is the most probable speed (A, B or C)? (4 Points)

A

- (iv) Suppose we already know the most probable speed of a collection of gas molecules. Explain what additional information we gain if we are also told what the mean and root mean square speeds are for the same distribution. (8 Points)

Knowing the  $c_{rms}$  and  $\bar{c}$  we can calculate the standard deviation of the speeds. This gives us an idea of the width or spread of the distribution.



Q 3. (20 points)

A 5.0 g block of solid carbon dioxide is allowed to evaporate in a vessel with a movable piston, of initial volume 100 cm<sup>3</sup>, maintained at 25°C (defined as the system). Ignore the volume of the solid carbon dioxide.

(i) The system is allowed to expand isothermally against a constant external pressure of 1.0 atm. The volume of the vessel will expand until it comes to a stop at equilibrium. Calculate the total work done by the system in this case. (10 points)

$$n = \frac{5.0 \text{ g}}{44 \frac{\text{g}}{\text{mol}}} = .114 \text{ mol}$$

$$V_2 = \frac{nRT}{p} = \frac{.114 \text{ mol} (8.314 \frac{\text{J}}{\text{K mol}}) (298 \text{ K})}{10^5 \frac{\text{Pa}}{\text{kg}} \frac{\text{N}}{\text{m}^2}}$$

$$\approx 0.0028 \frac{\text{Nm}}{\frac{\text{N}}{\text{m}^2}} = \text{m}^3$$

$$= 2.8 \text{ L}$$

$$W = -P_{\text{ext}} \Delta V$$

$$= -(1.0 \text{ atm}) \left( 10^5 \frac{\text{Pa}}{\text{atm}} \right) (2.78 \text{ L})$$

$$= -278000 \frac{\text{kg m}^2}{\text{s}^2} \text{ L}$$

$$= -278 \frac{\text{kg m}}{\text{s}^2} \text{ m}^3$$

$$= -278 \text{ J}$$

## QUESTION 3, CONTINUED

(ii) Now consider a process that starts from the same initial conditions as in (i). Now consider that the system expands isothermally and reversibly to the same final volume as in (i). Is the work done by the system in Process A greater than or less than the work done by the system in Process B? Will this always be the case? Explain your answer. You do not need to calculate the work done. (10 points).

both derive from  $w = - \int_{V_1}^{V_2} P dV$

for ~~non~~ irreversible  $P = P_{EXT}$  is constant

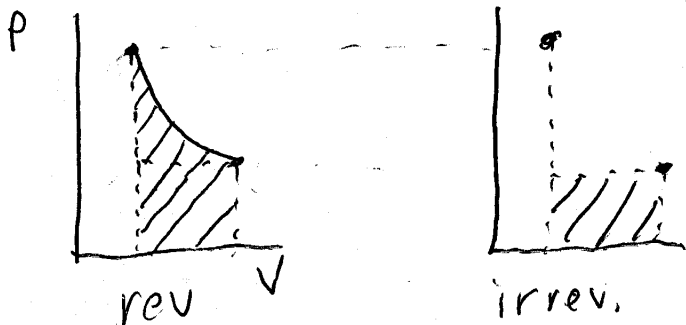
$$\text{so } w = -P_{EXT} \Delta V$$

for reversible

$$w = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \frac{V_2}{V_1}$$

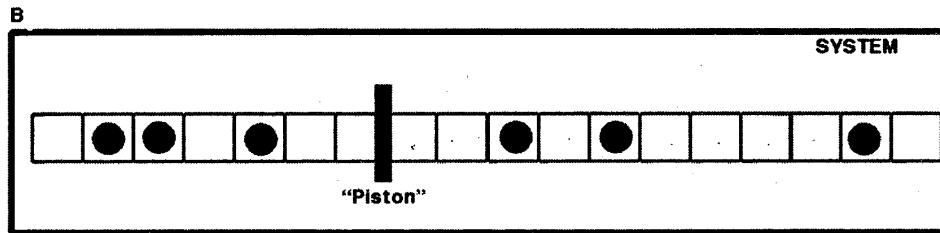
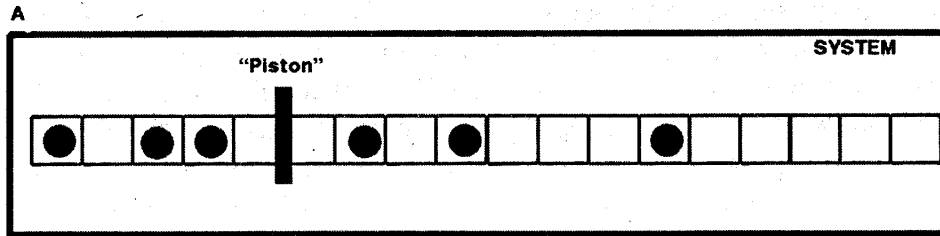
because the reversible process takes infinitesimal steps remaining at equilibrium the entire way it ~~has~~ ~~the~~ does the most work

Graphically



Q4. (20 points)

Consider the following very simple model for gas expansion:



The grids represent positions that the gas molecules (represented by circles) can occupy, while the vertical bar represents a movable barrier or piston through which the gas molecules cannot pass. In other words gas molecules on the left of the piston can occupy any of the grids on the left of the piston, but cannot pass to the right. Likewise, gas molecules on the right cannot pass to the left of the piston, but can occupy any grid points on the right.

Note: Use entropy,  $S = k \ln W$ , where  $k = 1.0$

$W$ , the multiplicity, is given by:

$W = M! / [N!(M-N)!]$ , where  $M$  is the number of grid points and  $N$  is the number of molecules.

- (i) Calculate the entropy of the system for case A (top) and for case B (bottom). (10 points)

For each case  $S_{\text{total}} = S_{\text{left}} + S_{\text{right}}$

$$= k \ln W_{\text{left}} + k \ln W_{\text{right}}$$

$$= k \ln (W_{\text{left}} W_{\text{right}})$$

$$\underline{\underline{k = 1.0 \text{ J/K}}}$$

CASE A

left

$$W = \frac{5!}{3!(5-3)!} = 10$$

Right

$$W = \frac{13!}{3!(13-3)!} = 286$$

$$\therefore S = (1.0) \ln (286 \cdot 10) = \underline{\underline{7.958 \text{ J/K}}}$$

## QUESTION 4, CONTINUED

CASE B

left

Right

$$W = \frac{7!}{3!(7-3)!} = 35$$

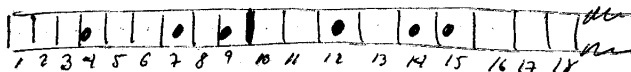
$$W = \frac{11!}{3!(11-3)!} = 165$$

$$S = (1.0) \ln(35 \cdot 165) = 8.661 \text{ J/K}$$

- (ii) What will be the position of the piston at equilibrium? Explain your answer.  
(10 points)

We know that at equilibrium the  $S$  of the system will be at its maximum or  $S_{\text{left}} = S_{\text{right}}$ .

The position of the piston will be the center of the system



left

Right

$$W = \frac{9!}{3!(9-3)!} = 84$$

$$W = \frac{9!}{3!(9-3)!} = 84$$

$$S = (1.0) \ln(84 \cdot 84) = 8.8616$$

5. (20 Points)

At 25°C the standard enthalpy of combustion of sucrose is -5797 kJ/mol and the standard Gibbs energy of the reaction is -6333 kJ/mol. Estimate the additional non-expansion work that may be obtained by raising the temperature to blood temperature, 37°C.

@ 25°C

$$\Delta H_r^\circ = -5797 \text{ kJ mol}^{-1}$$

$$\Delta G_r^\circ = -6333 \text{ kJ mol}^{-1}$$

$$T = 273.15 + 25 = 298.15 \text{ K}$$

$$\Delta G_r^\circ = \Delta H_r^\circ - T \Delta S_r^\circ$$

$$6333 = 5797 + 298.15 \Delta S_r^\circ$$

$$\Delta S_r^\circ = 1.797 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

@ 37°C

$$\Delta G_r = \Delta H_r^\circ - T \Delta S_r^\circ$$

$$T = 273.15 + 37 = 310.15 \text{ K}$$

$$\Delta G_r = -5797 - 310.15 \times 1.797$$

$$\Delta G_r = -6354.34 \text{ kJ mol}^{-1}$$

CHANGE IN GIBBS FREE ENERGY = MAXIMUM NON-EXPANSION WORK

$$\Delta \Delta G = \Delta G_{37^\circ\text{C}} - \Delta G_{25^\circ\text{C}}$$

$$= -6354.34 + 6333$$

$$\Delta \Delta G = -21.339 \text{ kJ mol}^{-1}$$

= maximum non-expansion work.

-END OF EXAM-