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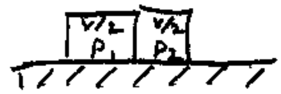
Consider an ideal gas of particles having mass m and initially confined to two isolated cells, each of volume $\frac{V}{2}$, as shown below. The cells are in contact with a heat reservoir at temperature T.



At time $t=0$ the left cell has pressure $p_1(0)$ and the right one $p_2(0)$. At this time a very small hole of area A is opened in the partition that separates the two cells and mixing occurs.

(a) calculate the pressure p_1 inside the left cell at an arbitrary time $t>0$.

One way to find an expression for the pressure at any time t is to start with the number of electrons striking/emitted a wall per second per unit area (see Reif 7.11.13)

$$\Phi_0 = \frac{\bar{p}}{\sqrt{2\pi m k T}} \qquad (1)$$

So, the number of electrons, n, is

$$n = \Phi_0 A \Delta t$$

Then we can write the number of electrons on the left (cell 1) at $t>0$ is

$$n_1 = \Phi_{0_2} A \Delta t - \Phi_{0_1} A \Delta t = A \Delta t (\Phi_{0_2} - \Phi_{0_1})$$

where

$A \Delta t \Phi_{0_1}$ is the number of electrons striking the hole from cell 1 going into cell 2

and

$A \Delta t \Phi_{0_2}$ is the number of electrons striking the hole from cell 2 going into cell 1

Why is this the whole story? See Reif section 7.12 (effusion).

If the hole is small enough then the number of molecules which emerge through the small hole is the same as the number that would strike the area occupied by the hole if the hole was closed off. Also, the equilibrium of the gas inside is disturbed to a negligible extent.

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So, if hole is small enough we can use the ideal gas law.

Now, substituting eq (1) into our expression for n_1 yields

$$n_1 = \frac{A\Delta t}{\sqrt{2\pi m k T}} \left(\bar{p}_2 - \bar{p}_1 \right) \qquad (2)$$

From the ideal gas equation, we have

$$\Delta p_i \left(\frac{V}{2} \right) = (\Delta n_i) kT \qquad , i = 1,2$$

$$\Rightarrow \Delta p_1 = \frac{2kT}{V} \Delta n_1 \underset{\substack{\uparrow \\ eq(2)}}{=} \frac{2kT}{V} A \Delta t \frac{\bar{p}_2 - \bar{p}_1}{\sqrt{2\pi m k T}}$$

$$\therefore \Delta p_1 = \sqrt{\frac{2kT}{\pi m}} \frac{A\Delta t}{V} (\bar{p}_2 - \bar{p}_1) \qquad , \frac{A}{V} = \frac{1}{L} \qquad (3)$$

Now, apply our constraint that

$$n_1 + n_2 = N = \text{constant}$$

So,

$$p_1 \frac{V}{2} + p_2 \frac{V}{2} = NkT \quad \Rightarrow \quad \bar{p}_2 = \frac{2NkT}{V} - \bar{p}_1$$

Substituting this result into eq (3) yields

$$\Delta p_1 = \sqrt{\frac{2kT}{\pi m}} \frac{A\Delta t}{V} \left[\frac{2NkT}{V} - 2\bar{p}_1 \right]$$

a bit of a sloppy rearrangment gives us

$$\frac{\Delta p_1}{\Delta t} \approx \frac{dp_1}{dt} = \sqrt{\frac{2kT}{\pi m}} \frac{2A}{V} \left[\frac{NkT}{V} - \bar{p}_1 \right]$$

$$\Rightarrow \frac{dp_1}{\left[p_1 - \frac{NKT}{V}\right]} = -\frac{2A}{V}\sqrt{\frac{2KT}{\pi m}}\,dt$$

$$\Rightarrow \ln\left[\bar{P}_1 - \frac{NKT}{V}\right] = \frac{-2At}{V}\sqrt{\frac{2KT}{\pi m}} + C$$

$$\Rightarrow \bar{P}_1 = \frac{NKT}{V} + c' e^{-\frac{2At}{V}\sqrt{\frac{2KT}{\pi m}}}$$

recall we are given that

$$\bar{P}_1(t=0) = P_1(0) = \frac{NKT}{V} + c' \Rightarrow c' = P_1(0) - \frac{NKT}{V}$$

Thus,

$$\boxed{\bar{P}_1(t) = \frac{NKT}{V} + \left[P_1(0) - \frac{NKT}{V}\right]\exp\left[-\frac{2At}{V}\sqrt{\frac{2KT}{\pi m}}\right]} \quad (4)$$

b) what should be the value of p_1 as $t \to \infty$?

if you wait long enough each cell should contain $\frac{N}{2}$ particles since the volumes are the same and they are in contact with the same reservoir. So, we expect

$$P_1\left(\frac{V}{2}\right) = \frac{N}{2}KT \Rightarrow P_1 V = NKT$$

consider eq (4) as $t \to \infty$, we get

$$\bar{p}_1(t\to\infty) = \frac{NKT}{V} + \underbrace{\left[P_1(0) - \frac{NKT}{V}\right]e^{-\infty}}_{=0}$$

$$\therefore \quad \bar{p}_1 V = NKT \checkmark$$