

Study of the diffusion in gaseous state and molecular speeds

Introduction

Were established following inequalities (see Ex.23 in [1]):

$$\hat{\varepsilon} = \frac{J-2}{2} \cdot k_B T \leq \frac{m\hat{s}^2}{2} = \frac{J-1}{2} \cdot k_B T \leq \frac{m\bar{s}^2}{2} = \left(\frac{\Gamma\left(\frac{J+1}{2}\right)}{\Gamma\left(\frac{J}{2}\right)} \right)^2 \cdot k_B T \leq \bar{\varepsilon} = \frac{J}{2} \cdot k_B T$$

in which the energy at mode is smaller than the energy of the molecules with the mode speed, which is smaller than the energy of the molecules with average speed, which is smaller than the energy of the molecules with the speed equal with average of squared speed.

Expressing the relationships on $R \cdot T$ ($R = k_B \cdot N_A$; $m \cdot N_A = M$):

$$RT = \frac{Ms_{\hat{\varepsilon}}^2}{J-2} = \frac{Ms_{\bar{s}}^2}{J-1} = \frac{Ms_{\bar{s}}^2}{2\left(\frac{\Gamma((J+1)/2)}{\Gamma(J/2)}\right)^2} = \frac{Ms_{\bar{\varepsilon}}^2}{J}$$

For two gases at the same temperature the $k_B \cdot T$ term is the same, allowing the obtaining of a relationship between the masses and the speeds. This law can be easily verified experimentally with a simple experiment of diffusion in gaseous state. Are phrased thus the hypothesis that the diffusion speed is proportional with the speed of the molecules. For the speed of the molecules we have, as was shown above, more than one statistic: real speeds (when the number of the energy components J , is always 3) and virtual speeds (when the number of the energy components depends on the structure of the molecules).

Thus, are opened the problem to identify which is the number of the energy components which are used by the molecules in the diffusion process.

Purpose

Establishing by experimental path of the relationship linking the diffusion speeds, and on this way, of the proportionality between these and the speeds derived from molecular kinetic theory.

Material and method

It will be studied the reaction in gaseous state between ammonia and hydrochloric acid. Both these substances are solved in water, and thus following chemical reactions can be written:

No	Equilibrium chemical reaction
R1	$\text{HCl} + \text{H}_2\text{O} \leftrightarrow \text{Cl}^- + \text{H}_3\text{O}^+$
R2	$\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{HO}^-$
R3	$\text{NH}_3 + \text{HCl} \leftrightarrow \text{NH}_4\text{Cl}$
R4	$\text{NH}_4^+ + \text{Cl}^- \leftrightarrow \text{NH}_4\text{Cl}$

Supposing that at environmental temperature the number of the energy components can be approximated with the number of degrees of freedom, starting from structure of the compounds can be calculated the squares of the virtual (s) and real (v) speeds, for each reactant candidate leading to formation of ammonium chloride intended to be observed in the experiment (the reactants involved in the reactions

¹ Lorentz JÄNTSCHI, 2013. Physical chemistry: theory, applications and problems), (in Romanian), AcademicDirect, ISBN 978-973-86211-0-7 (Print) 978-606-93534-0-0 (Electronic), Cluj-Napoca, Romania, 158 p.

R3 and R4). The calculation are given in the next table (M(H) = 1.008; M(N) = 14.007; M(Cl) = 35.45 g/mol):

Specie	M	df =J	$s_{\hat{\epsilon}}^2 = \frac{s_{\hat{\epsilon}}^2}{RT} =$	$s_{\hat{s}}^2 = \frac{s_{\hat{s}}^2}{RT} =$	$s_{\bar{s}}^2 = \frac{s_{\bar{s}}^2}{RT} =$	$s_{\bar{\epsilon}}^2 = \frac{s_{\bar{\epsilon}}^2}{RT} =$	$v_{\hat{\epsilon}}^2 = \frac{v_{\hat{\epsilon}}^2}{RT} =$	$v_{\hat{s}}^2 = \frac{v_{\hat{s}}^2}{RT} =$	$v_{\bar{s}}^2 = \frac{v_{\bar{s}}^2}{RT} =$	$v_{\bar{\epsilon}}^2 = \frac{v_{\bar{\epsilon}}^2}{RT} =$
NH ₃	17.031	6	0.2349	0.2936	0.3243	0.3523	0.1174	0.1468	0.1621	0.1761
HCl	35.45	5	0.0823	0.1097	0.1242	0.1371	0.0494	0.0658	0.0745	0.0823
NH ₄ ⁺	18.039	6	0.2217	0.2772	0.3061	0.3326	0.1109	0.1386	0.1531	0.1663
Cl ⁻	36.458	3	0.0282	0.0564	0.0718	0.0846	0.0282	0.0564	0.0718	0.0846
Specie	M	df =J	$\frac{s_{\hat{\epsilon}}}{\sqrt{RT}} =$	$\frac{s_{\hat{s}}}{\sqrt{RT}} =$	$\frac{s_{\bar{s}}}{\sqrt{RT}} =$	$\frac{s_{\bar{\epsilon}}}{\sqrt{RT}} =$	$\frac{v_{\hat{\epsilon}}}{\sqrt{RT}} =$	$\frac{v_{\hat{s}}}{\sqrt{RT}} =$	$\frac{v_{\bar{s}}}{\sqrt{RT}} =$	$\frac{v_{\bar{\epsilon}}}{\sqrt{RT}} =$
NH ₃	17.031	6	0.4847	0.5418	0.5695	0.5935	0.3426	0.3831	0.4026	0.4196
HCl	35.45	5	0.2869	0.3312	0.3524	0.3703	0.2223	0.2565	0.2729	0.2869
NH ₄ ⁺	18.039	6	0.4709	0.5265	0.5533	0.5767	0.3330	0.3723	0.3913	0.4078
Cl ⁻	36.458	3	0.1679	0.2375	0.2680	0.2909	0.1679	0.2375	0.2680	0.2909
$s_{\hat{\epsilon}}^2 = \frac{J-2}{M} \cdot RT; s_{\hat{s}}^2 = \frac{J-1}{M} \cdot RT; s_{\bar{s}}^2 = \frac{2}{M} \left(\frac{\Gamma((J+1)/2)}{\Gamma(J/2)} \right)^2 \cdot RT; s_{\bar{\epsilon}}^2 = \frac{J}{M} \cdot RT; \frac{v^2}{3} = \frac{s^2}{J}$										

If the speeds given above are divided, a series of speed ratios are obtained. Thus is possible to compare these ratios with the ratio obtained from the experiment for the diffusion speeds. The outcome of this comparison is the decision of which of the molecular speeds are used by the molecules for diffusion, and respectively which chemical species diffuses, the neutral or the ionic ones. Results of the calculation are given below:

Case	Speeds ratio (v _A /v _B)
R3 (A=NH ₃ , B=HCl), mode energy ($\hat{\epsilon}$), virtual speed (s)	1.689
R3 (A=NH ₃ , B=HCl), mode speed (\hat{s}), virtual speed (s)	1.636
R3 (A=NH ₃ , B=HCl), average speed (\bar{s}), virtual speed (s)	1.616
R3 (A=NH ₃ , B=HCl), average energy ($\bar{\epsilon}$), virtual speed (s)	1.603
R3 (A=NH ₃ , B=HCl), mode energy ($\hat{\epsilon}$), real speed (v)	1.542
R3 (A=NH ₃ , B=HCl), mode speed (\hat{s}), real speed (v)	1.494
R3 (A=NH ₃ , B=HCl), average speed (\bar{s}), real speed (v)	1.475
R3 (A=NH ₄ ⁺ , B=Cl ⁻), average energy ($\bar{\epsilon}$), real speed (v)	1.463
R4 (A=NH ₄ ⁺ , B=Cl ⁻), mode energy ($\hat{\epsilon}$), virtual speed (s)	2.804
R4 (A=NH ₄ ⁺ , B=Cl ⁻), mode speed (\hat{s}), virtual speed (s)	2.217
R4 (A=NH ₄ ⁺ , B=Cl ⁻), average speed (\bar{s}), virtual speed (s)	2.065
R4 (A=NH ₄ ⁺ , B=Cl ⁻), average energy ($\bar{\epsilon}$), virtual speed (s)	1.983
R4 (A=NH ₄ ⁺ , B=Cl ⁻), mode energy ($\hat{\epsilon}$), real speed (v)	1.983
R4 (A=NH ₄ ⁺ , B=Cl ⁻), mode speed (\hat{s}), real speed (v)	1.568
R4 (A=NH ₄ ⁺ , B=Cl ⁻), average speed (\bar{s}), real speed (v)	1.460
R4 (A=NH ₄ ⁺ , B=Cl ⁻), average energy ($\bar{\epsilon}$), real speed (v)	1.402

Experimental apparatus

For the experiment of diffusion in gaseous state of the chemical species involved in formation of the ammonium chloride (HCl, Cl⁻, NH₃, NH₄⁺) are required a glass tube of (at least) 1m length and a diameter of about 2 cm. The tube must be dry. Are also required two rubber stoppers, two cotton pads, a

horizontal fixing frame of the glass tube, and a timer for measuring a straight edge distance (see Fig. E5).

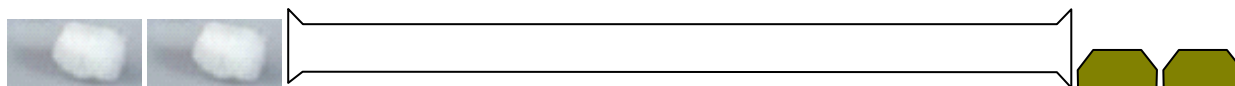


Fig. E5. Experimental apparatus for the study of diffusion in gaseous state

Working procedure

Assemble the experimental apparatus as shown in Fig. E6

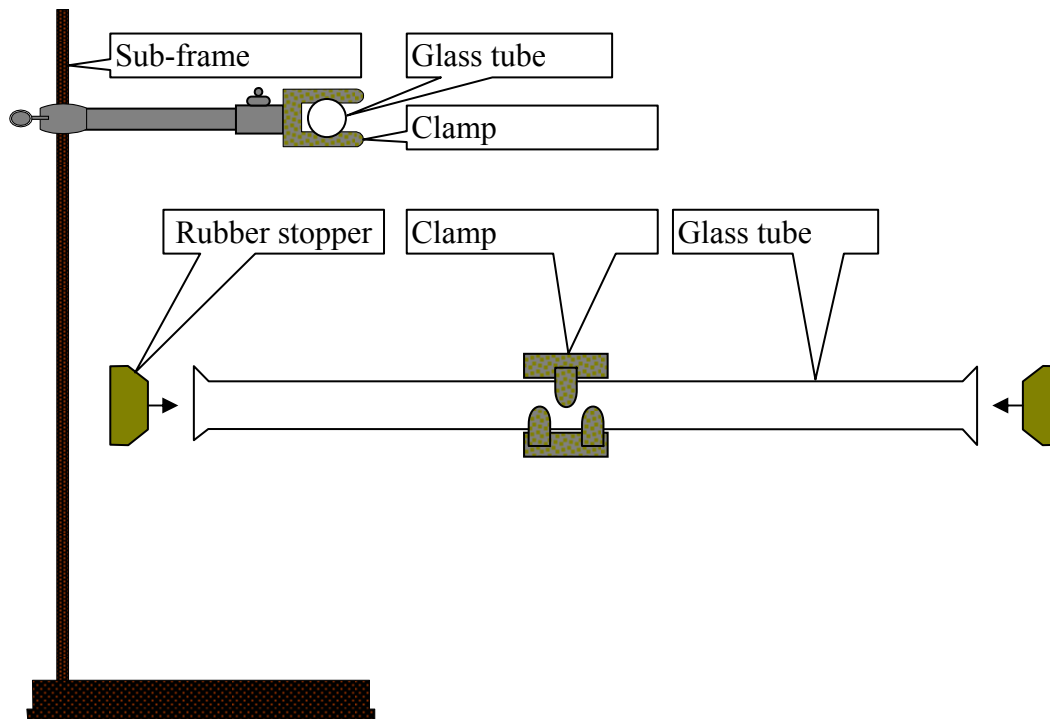


Fig. E6. The experimental setup for studying the gaseous diffusion

- ÷ The next steps are followed:
- ÷ The cotton swab is wetted in the solution of hydrochloric acid and other ammonia buffer solution;
- ÷ Are simultaneously placed on one side of the tube and the other two cotton pads, start the chronometer and put stoppers (v. Fig. E7);

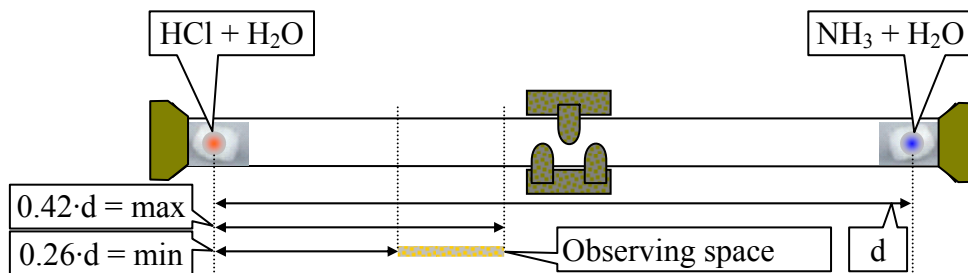


Fig. E7. Observation of the formation of ammonium chloride

- ÷ Ammonium chloride ring formation is observed; time is noted when (t_0);
- ÷ The distance from the ring to the spot of hydrochloric acid is measured; note this value (d_1);
- ÷ Measure the distance from the ring to the spot of ammonia; note this value (d_2);

Data analysis

Two parameters were identical in the experiment: temperature and the diffusion time.

÷ Is possible thus to calculate the diffusion speeds as well as their ratio. The following table is filled:

Chemical species	Distances (in m)	Time (in s)	Diffusion speeds (in m/s)	Speeds ratio
NH ₃ or NH ₄ ⁺	d ₁ =	t ₀ =	d ₁ /t ₀ = v ₁ =	v ₁ /v ₂ =
HCl or Cl ⁻	d ₂ =		d ₂ /t ₀ = v ₂ =	

÷ Are compared the value of the diffusion speeds ratio with the value of the molecular speeds ratio with the purpose to decide which of the molecular speeds is responsible for the movement of the molecules in the process of diffusion. In order to do this, the values of the molecular speeds ratios (previous table) are sorted (ascending), are calculated the differences between these values and the value of the observed ratio and a seek for the lowest (absolute) difference is conducted:

Case	$\frac{v_A}{v_B}$	$\frac{v_A}{v_B} - \frac{v_1}{v_2}$	$ \frac{v_A}{v_B} - \frac{v_1}{v_2} $	=minim
R4 (A=NH ₄ ⁺ , B=Cl ⁻), average energy ($\bar{\epsilon}$), real speed (v)	1.402			?
R4 (A=NH ₄ ⁺ , B=Cl ⁻), average speed (\bar{s}), real speed (v)	1.460			?
R3 (A=NH ₄ ⁺ , B=Cl ⁻), average energy ($\bar{\epsilon}$), real speed (v)	1.463			?
R3 (A=NH ₃ , B=HCl), average speed (\bar{s}), real speed (v)	1.475			?
R3 (A=NH ₃ , B=HCl), mode speed (\hat{s}), real speed (v)	1.494			?
R3 (A=NH ₃ , B=HCl), mode energy ($\hat{\epsilon}$), real speed (v)	1.542			?
R4 (A=NH ₄ ⁺ , B=Cl ⁻), mode speed (\hat{s}), real speed (v)	1.568			?
R3 (A=NH ₃ , B=HCl), average energy ($\bar{\epsilon}$), virtual speed (s)	1.603			?
R3 (A=NH ₃ , B=HCl), average speed (\bar{s}), virtual speed (s)	1.616			?
R3 (A=NH ₃ , B=HCl), mode speed (\hat{s}), virtual speed (s)	1.636			?
R3 (A=NH ₃ , B=HCl), mode energy ($\hat{\epsilon}$), virtual speed (s)	1.689			?
R4 (A=NH ₄ ⁺ , B=Cl ⁻), average energy ($\bar{\epsilon}$), virtual speed (s)	1.983			?
R4 (A=NH ₄ ⁺ , B=Cl ⁻), mode energy ($\hat{\epsilon}$), real speed (v)	1.983			?
R4 (A=NH ₄ ⁺ , B=Cl ⁻), average speed (\bar{s}), virtual speed (s)	2.065			?
R4 (A=NH ₄ ⁺ , B=Cl ⁻), mode speed (\hat{s}), virtual speed (s)	2.217			?
R4 (A=NH ₄ ⁺ , B=Cl ⁻), mode energy ($\hat{\epsilon}$), virtual speed (s)	2.804			?

÷ Is identified the lowest absolute difference and thus are identified the chemical species which diffuses in gaseous state as well as the link between molecular speeds and diffusion speeds.

÷ The relations which characterize the model are written. These include the reaction of the formation of the ammonium chloride (R3 or R4), determinant factors in diffusion (energy or speed; real or virtual speeds) and expressions of the molecular speeds for the identified model;

÷ The coefficients of diffusion are calculated as ratios between diffusion speeds and molecular speeds: $c_1 = c(\text{NH}_3/\text{NH}_4^+) = v_1/v_A$; $c_2 = c(\text{HCl}/\text{Cl}^-) = v_2/v_B$;

÷ Are filled the table:

Equation of the chemical reaction	F1: energy or speed	F2: real or virtual	Coefficients of diffusion
			c ₁ =
			c ₂ =