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Determination of the chemical activation energy, the rate constant and order of inorganic solid – solid reactions from capillary studies

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ABSTRACT

Capillary solid-solid reaction studies have been going on for many decades. These have largely been used for finding out the order of the reaction, the rate constant and for determining the activation energy. We have not come across any satisfactory justification for assigning the same meaning to these terms as in the more conventional reactions. The present work was undertaken with this in view. It is found that the terms reaction order, rate constant and the activation energy, as used and experimentally found out in capillary studies, make sense. They tell important things about a capillary reaction. However, the quantities so found out may not be directly applicable to solid-solid reactions, carried out in bulk, and more so to the same reactions occurring in solution. Capillary reactions have their own special features and are important in their own way. The above explanatory comments are based on a detailed experimental study of the two capillary reactions: CuI+$HgCl_2$ and KI+$HgCl_2$. These reactions have been studied in the past, but here the objective is different.

Key words: Reaction order, rate constant, activation energy, capillary solid-solid reactions.

INTRODUCTION

Inorganic solid – solid reactions of a wide variety have been studied by many authors over the last many decades[1-8]. Solid-solid reactions have been going on in nature for hundreds of millions of years. Much of the earlier interest was in finding out the reaction mechanism. Today, solid- solid reactions are being extensively used for producing a variety of important new materials[9]. Their advantage over solution chemistry is that one can work at much higher temperatures in the solid state. Inorganic solid – solid reactions were studied in bulk as well as in capillaries. When the reactants were used in bulk, the reactants could be taken in different molar ratios. Electrical measurements of the product were carried out over the long duration of the experiment with a view to using significant changes of the conductivity as a pointer of intermediate steps of the solid – solid reaction being studied. For reactions that proceeded at room temperature, thermal curves are also used for the same purpose. The thermal curve is a plot of the rise in temperature with respect to time. Occurrence of any additional peaks is taken as a sign of intermediate steps. Changes of colour during the reaction are also taken as a sign of intermediate steps. All the indications should be looked at X-ray diffractogram of the products for their identification is very important. However, the X-ray study usually tells about the end products and not about the intermediate products. Many a time, the intermediate products disappear at the end. However, in some cases, steps could be taken to obtain the diffractograms at intermediate

stages, but we are not aware of any such effort, in practice. The conclusions are more reliable if several approaches corroborate each other.

If a step is so fast that it is completed in a time interval much smaller than that required to carry out the electrical or thermal experimental measurements, such a step is not indicated by these data and has to be guessed and then supported by indirect evidence.

Solid-solid reactions, in the capillary, are usually carried out for determining the activation energy, the rate constant and the order of the reaction[1-8]. We carry out the capillary experiments with capillaries of different bores for two systems to find out the justification or otherwise of identifying the relevant measured quantities with the order of the reaction, the rate constant and the activation energy.

Section 2 describes the Experimental procedure; Section 3 is Results and Discussion. The last section, i.e. Section 4 is 'Identification of the Parameters'. This is followed by Conclusions.

EXPERIMENTAL

We have chosen the reaction $CuI+HgCl_2$ that has been studied earlier, carried it out at different temperatures, using a capillary of the same bore[6] and then the study has been carried out at other bore sizes. For our study, the same reaction has been carried out, at different temperatures, with four different bores and the parameters have been found in each case. The solid – solid reaction $CuI+HgCl_2$ was studied by us placing 400 mgms of CuI and the same amount of $HgCl_2$ in close contact near the middle of a Pyrex glass tube of internal diameter of about 0.5 cm and about 5 cm length, at different constant temperatures, 80°C, 90°C & 100°C. Both the reactants are 99.9% purity Merck chemicals. These reactants are tightly packed in the middle. These are kept in an air thermostat oven, controlled upto 0.5°C to 1°C, at 80°C and same was done for the 90°C, 100°C temperatures, and measurement of the product thickness, formed in the middle, at equal time intervals (15 minutes) was carried out with a traveling microscope, having a least count of 0.01 mm. The product, formed in the middle, is identified by its distinct colour. It had already been established by several other methods[1, 2] that colour change could be taken as proof of the occurrence of the reaction. So, the distinctive colour would be taken to be that of the product. In fact, capillary studies can only be carried out if the product has a colour different from that of the two reactants.

The measurement is quickly made by taking out the capillary from the thermostat after each interval of 15 minute and then it is quickly replaced in the oven, maintained at a fixed desired temperature, starting with 80°C till the experiment is completed. After completing the experiment, the capillary is cleaned, washed and dried. The experiment is repeated once again in the same way as before and the average reading is taken at the same time interval of 15 minutes. A record of the average product thickness with time, at a fixed temperature and for a given capillary bore, is obtained in this way. Then the capillary is thoroughly washed, cleaned and dried and the experiment is carried out in the same way at 90°C and then at 100°C. In each of these three experiments, the same pair of reactants and the same capillary is used.

Exactly the same procedure is followed for the solid – solid reaction system $KI+HgCl_2$. The $HgCl_2$ is the same Merck chemical as before, but KI is Qualigen chemical of 99.9% purity. The later reaction has not been studied in detail before; only some preliminary study has been carried out. Colour change, in this case is also regarded as unambiguous proof of product formation[10]. The procedure is the same as before.

The same experiment is repeated, for both the systems with bore sizes of 0.71 cm, 0.81 cm and 1.11 cm at the three different constant temperatures of 80°C, 90°C & 100°C. With the increased bores, 1 gm of both the reactants are taken. For all the capillaries the inner diameter is measured by a traveling microscope, three times for each capillary, each reading being taken in one direction and then in the perpendicular direction, at the same place. Thus there are six readings in all. The mean value is taken as the diameter of the capillary. All the above procedures are exactly

reproduced for the study of both the reaction systems.

RESULTS AND DISCUSSION

The result of the experiments, carried out here for the different bores, the different temperatures and the two chemical systems are the width of the product *x* (in cm) as a function of the time *t* (in hours), both measured from the start of the experiment. Table 1(a) gives the experimental *x* vs. *t*, for all the bores studied, in digital form, for the system CuI+$HgCl_2$, at 80°C. Table 2(a) presents the corresponding data for the same chemical system at 90°C and Table 3(a) does that for 100°C. Tables 1(b), 2(b) and 3(b) gives the experimental *x* vs. *t* for all the different bores studied at 80°C, 90°C and 100°C respectively, for the system KI+$HgCl_2$. Figures 1(a), 2(a), 3(a), 1(b), 2(b) and 3(b) give a graphical presentation of the corresponding digital data.

It has been found from long experience that the *x* vs. *t* relation may be expressed as

$$x^n = \kappa t \qquad \ldots(1)$$

where *x* is the thickness of product (in cm),

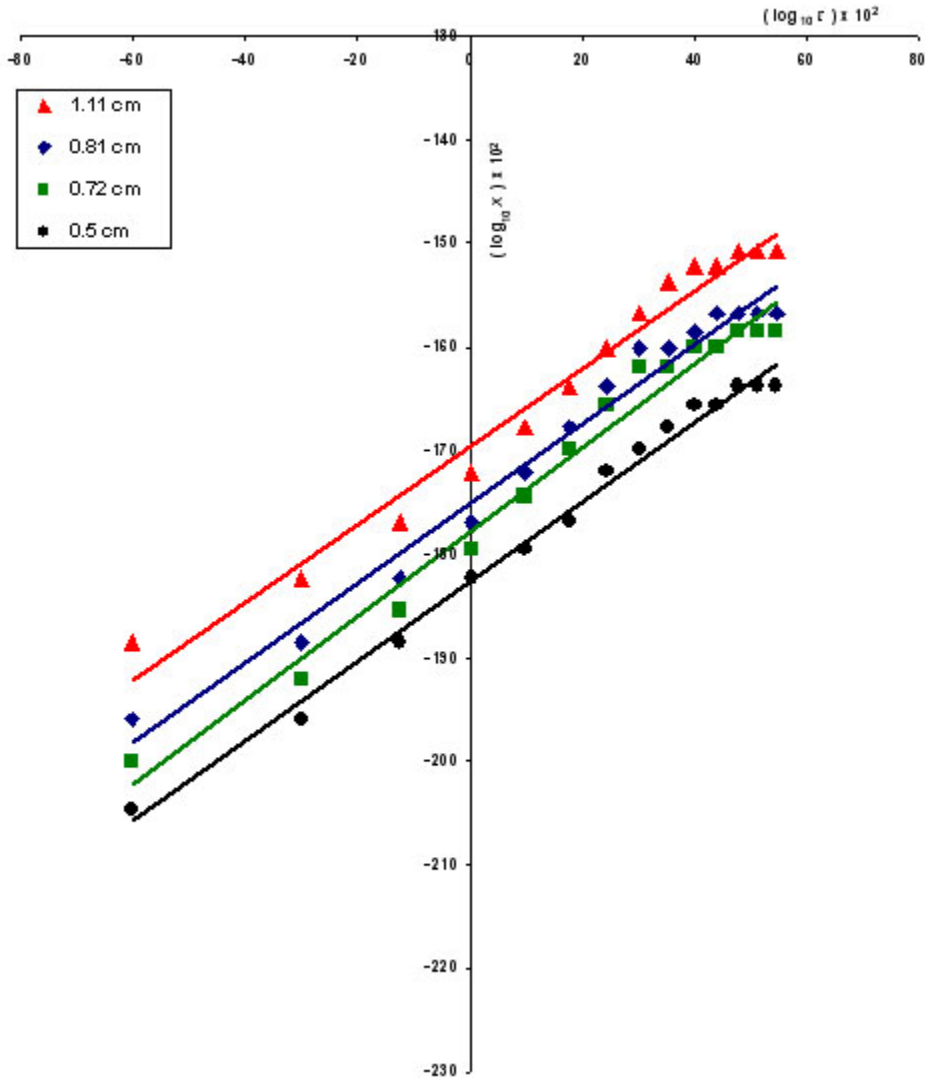

Fig. 1(a): Solid -solid reactions between (CuI+$HgCl_2$) with different bore size of capillary, at 80°C

n and are constants, *t* is the time (in hours). Taking $\log_{10}$ of both sides, we have

$$\log_{10} x = \frac{1}{n}\log_{10} K + \frac{1}{n}\log_{10} t \quad \text{R} \qquad ...(1)$$

For the convenience, we multiply both sides by 10^2 to get

$$(\log_{10} x)\times 10^2 = \frac{1}{n}(\log_{10} K)\times 10^2 + \frac{1}{n}(\log_{10} t)\times 10^2 \quad ...(3)$$

We see that the plot of $(\log_{10} x)\times 10^2$ vs. is a straight line which has the slope *1/n* and the intercept on the -axis is . Thus by plotting the data vs. , where *x* is in cm and time *t* is in hours, and by doing a least square fitting of the data of early times, we get *n*. The quantity , which is the intercept on the -axis, is taken directly from the *x* at *t*=1 hours (log *t*=0). From the latter, by multiplying with *n* and dividing by 10^2, we get and hence .

We see that, at early times, for a given temperature, the experimental curves are almost parallel straight lines. From these, the average *n* is obtained by least square fitting of the curves and the for different bores and temperatures are obtained directly from the *x* at *t*=1 hours (log *t* = 0). These are given in Tables 4(a), 4(b) for both the

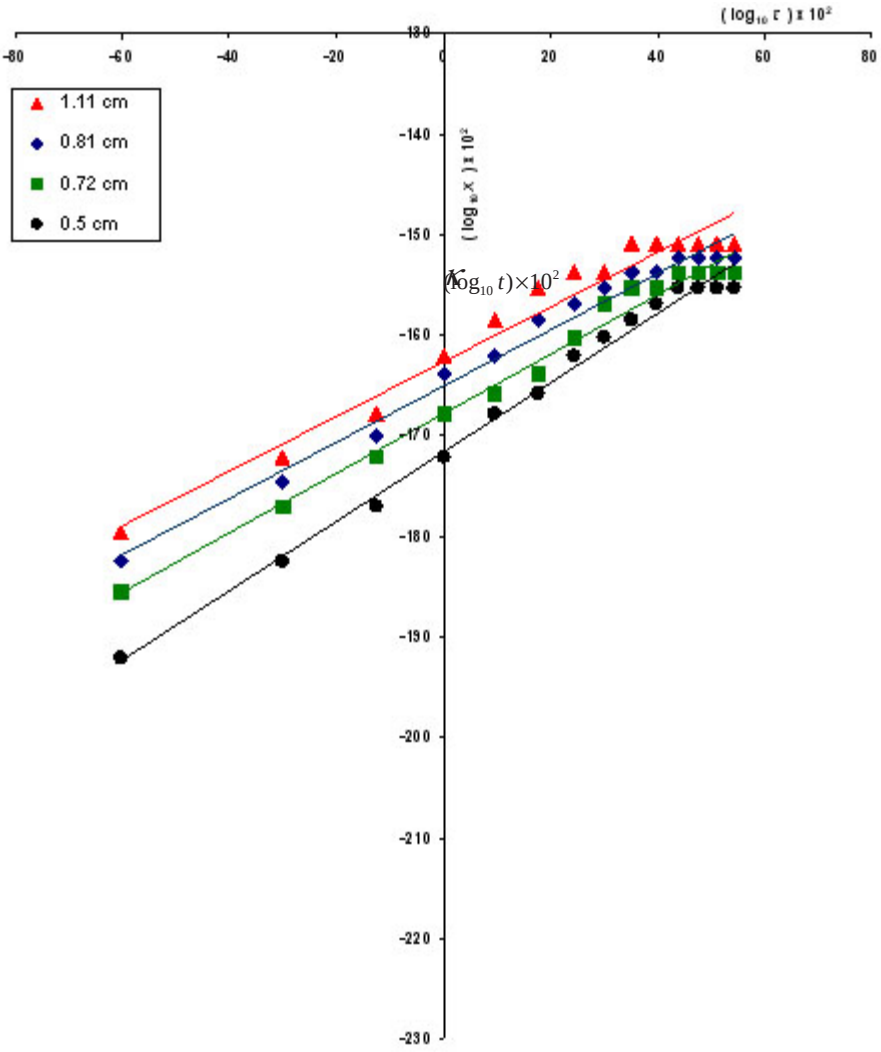

Fig. 2(a): Solid-solid reactions between (CuI+$HgCl_2$) with different bore sized capillary, at 90°C

systems.

By using the relation

$$\kappa = \kappa_o e^{-E_o/kT} \quad ...(4)$$

where and are constants, E_o is the activation energy, *k* is the Boltzmann constant and T is the temperature (in Kelvin)

We have $\ln \kappa = -\frac{E_o}{kT} + \ln \kappa_o$ ...(5)

The plot of vs. is a straight line with the slope $-E_o$. By the least square fitting to the above straight line, at different bores, we obtain E_o, given in Tables 5(a) and 5(b) for both the systems.

We may point out that only the data of early times presents a simple behaviour mathematically described above. Only these data have been used for finding out the parameters. At higher times, the interacting molecule of one species diffuses through the whole length of the product to reach the reactant on the other side. As the product thickness increases with time, the molecule has to travel an increasingly longer distance to interact with the other species. That slows down the reaction rate with time, as can be seen from equation (1). The reaction generally

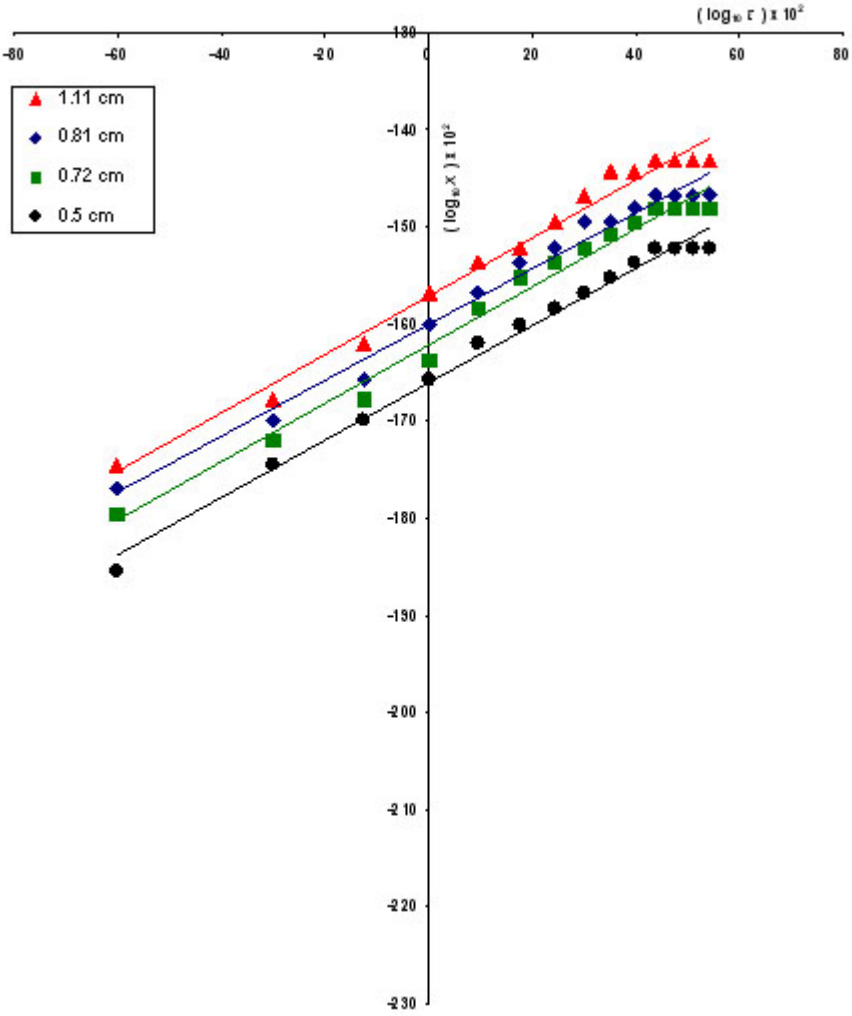

Fig. 3(a): Solid-solid reactions between (CuI+$HgCl_2$), with different bore sized capillary used at, 100°C

peters out long before the reactants have been exhausted. In this phase, complications set in and the simple straight line behaviour vanishes to produce a complicated behaviour of the *x* vs. *t* curves. We are not concerned with this complicated phase of the reaction. Only the nearly straight line part should normally interest us.

Identification of the parameters

First let us briefly discuss what has been called the order of a capillary reaction. It has been denoted by n. At the very outset, it may be pointed out that the traditional definition of the order *n* of a chemical reaction is based on the concentration of the participating chemical species. For a solid-solid reaction in bulk or in a capillary, it does not seem possible to define concentration of a participating chemical species. So, we try to define the order as the number of the molecules participating to give the product or products[11].

We find from the present study as also from

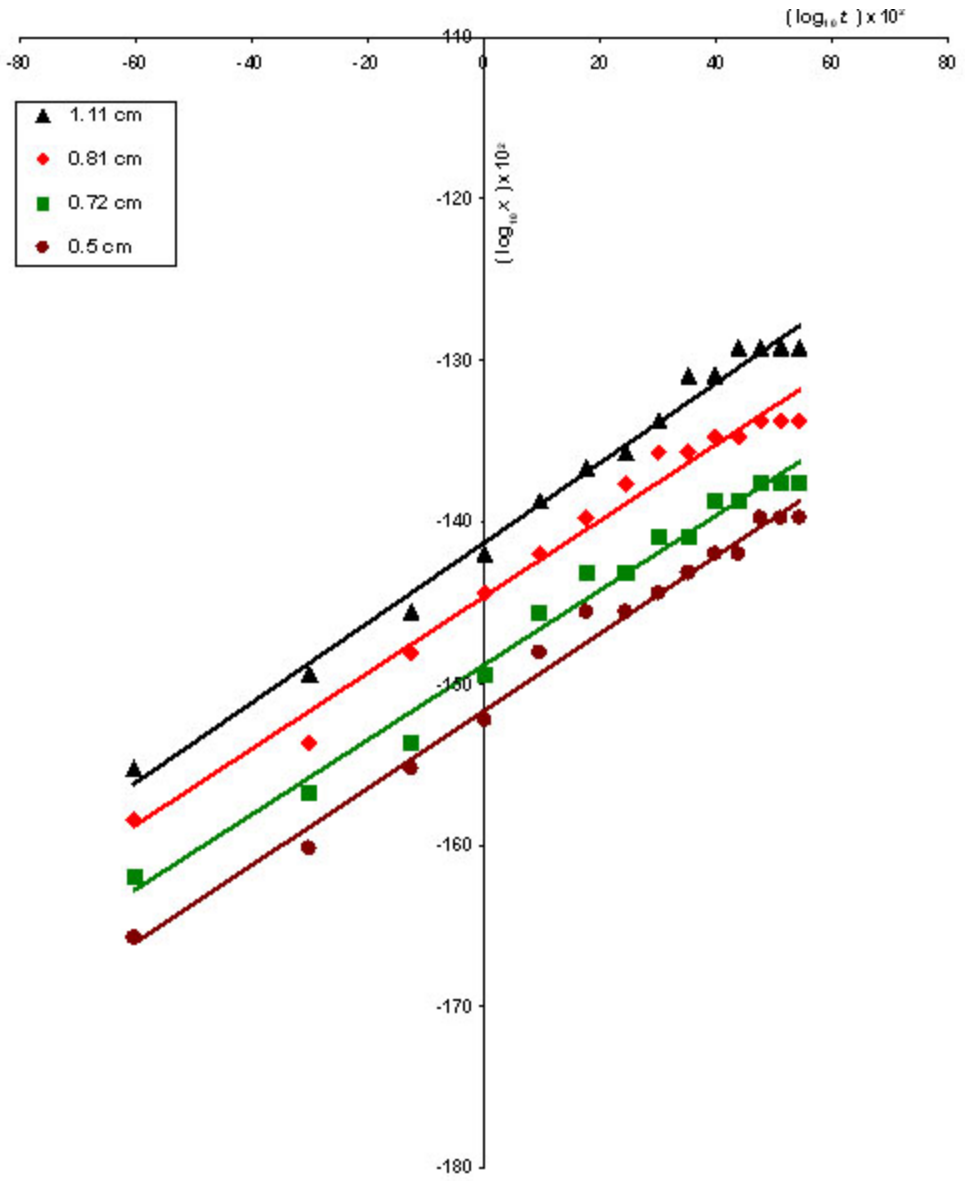

Fig. 1(b): Solid-solid reactions between ($KI+HgCl_2$), with different bore sized capillary, used at 80°C

many other studies which we have carried out earlier that, for pure reactants, the value of *n* lies roughly as given by the following inequality:

$$2 < n < 6 \qquad ...(6)$$

i.e. in most cases more than two molecules participate in the reaction and it is generally less than five or six. If this picture of *n*, being a measure of the number of interacting particles, is accepted, one finds that most often three or four or even more molecules react to form the product. In a small number of cases, only two molecules form the product. One finds that *n* for solid-solid reactions are generally more than that in solution reactions. Let us briefly discuss its plausibility.

We are inclined to believe that the reaction occurs at the molecular level and not when the reactants are solid crystallites. The molecules are provided by thermal vapourization. The released molecules combine to form the product molecule. The reaction starts at the interface resulting in the formation of the product. It is seen (in the

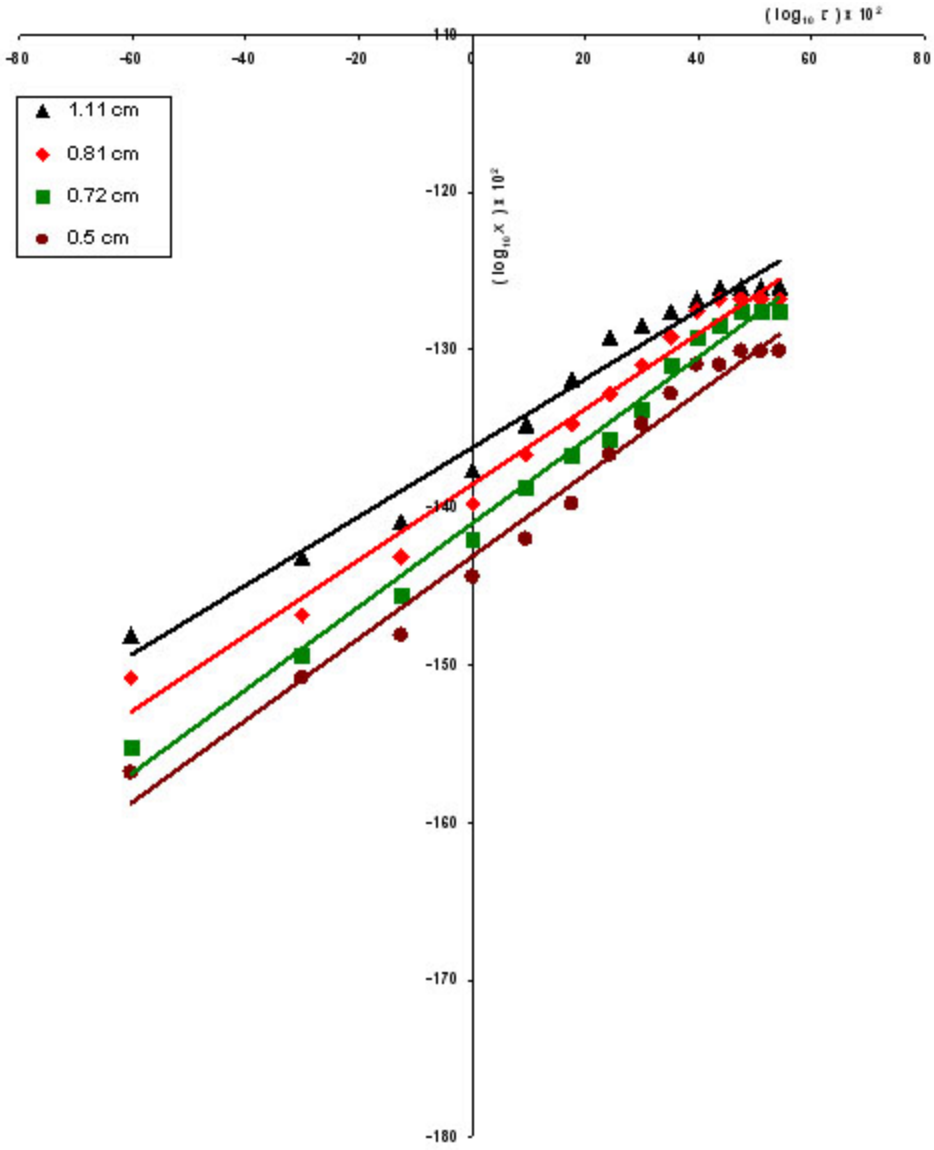

Fig. 2(b): Solid-solid reactions between ($KI+HgCl_2$), with different bore sized capillary used at 90°C

microscope) that only one of the molecular species, in a solid - solid reaction, preferably diffuses to the other side to cause reaction. When this starts, at the reaction site there is a small number of the molecules of the diffusing species surrounded by a much larger number of the molecules of the other species. So well over two molecules would be expected to take part in the capillary reaction. This offers qualitative support to the rather high values of *n*. In the presence of an impurity, the value of *n* has generally been found to increase (say, 3.5 < *n* < 7.5) (to be reported in due course). The impurity attracts more of the available molecules to come together, say , through its electric dipole moment interaction. This causes *n* to somewhat increase from the value for the pure reactants.

A direct experimental test of the above picture of the reaction, in detail, is difficult as a very small amount of the product is formed in a capillary experiment. However, it would be interesting to test the above picture experimentally by some means.

Qualitatively, identification of as rate constant seems justified from this study or rather even from common sense. A look at the Tables 4(a),

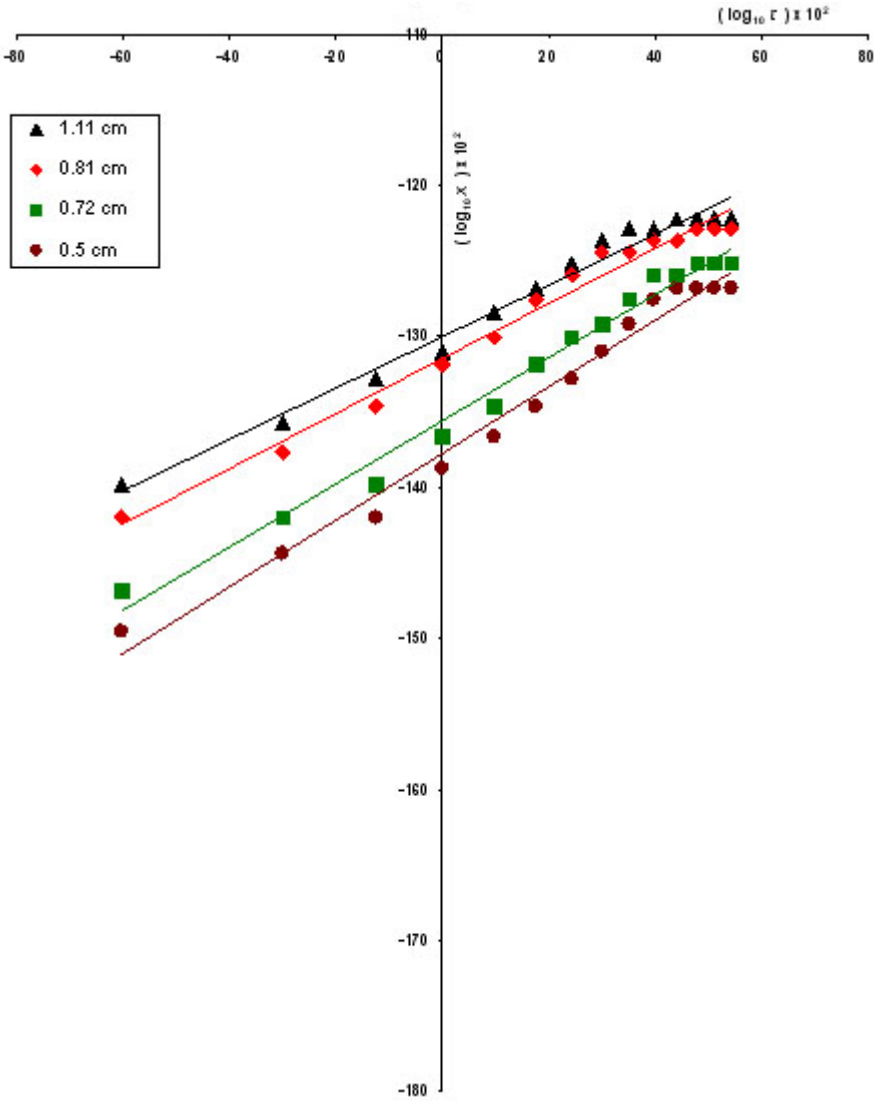

Fig. 3(b): Solid-solid reactions between KI+$HgCl_2$, with different bore sized capillary, at 100°C

Table 1(a): Solid-solid reactions between CuI+$HgCl_2$, with different bore sized capillary used at 80°C.

Time (Mint)	Time (Hours)	($\log_{10}t$) x10^2	Thickness × in cm for 0.5cm bore	($\log_{10}x$) x10^2	Thickness × in cm for 0.72cm bore	($\log_{10}x$)x10^2	Thickness × in cm for 0.81cm bore	($\log_{10}x$) x10^2	Thickness × in cm for 1.11cm bore	($\log_{10}x$) x10^2
15	0.25	-60.21	0.009	-204.58	0.010	-200.00	0.011	-195.86	0.013	-188.61
30	0.5	-30.10	0.011	-195.86	0.012	-192.08	0.013	-188.61	0.015	-182.39
45	0.75	-12.49	0.013	-188.61	0.014	-185.39	0.015	-182.39	0.017	-176.96
60	1	0.00	0.015	-182.39	0.016	-179.59	0.017	-176.96	0.019	-172.12
75	1.25	9.69	0.016	-179.59	0.018	-174.47	0.019	-172.12	0.021	-167.78
90	1.5	17.61	0.017	-176.96	0.020	-169.90	0.021	-167.78	0.023	-163.83
105	1.75	24.30	0.019	-172.12	0.022	-165.76	0.023	-163.83	0.025	-160.21
120	2	30.10	0.020	-169.90	0.024	-161.98	0.025	-160.21	0.027	-156.86
135	2.25	35.22	0.021	-167.78	0.024	-161.98	0.025	-160.21	0.029	-153.76
150	2.5	39.79	0.022	-165.76	0.025	-160.21	0.026	-158.50	0.030	-152.29
165	2.75	43.93	0.022	-165.76	0.025	-160.21	0.027	-156.86	0.030	-152.29
180	3	47.71	0.023	-163.83	0.026	-158.50	0.027	-156.86	0.031	-150.86
195	3.25	51.19	0.023	-163.83	0.026	-158.50	0.027	-156.86	0.031	-150.86
210	3.5	54.41	0.023	-163.83	0.026	-158.50	0.027	-156.86	0.031	-150.86

Table 1(b): Solid-solid reactions between KI+$HgCl_2$, with different bore sized capillary used at 80°C

Time (Mint)	Time (Hours)	($\log_{10}t$) x10^2	Thickness × in cm for 0.5cm bore	($\log_{10}x$) x10^2	Thickness × in cm for 0.72cm bore	($\log_{10}x$)x10^2	Thickness × in cm for 0.81cm bore	($\log_{10}x$) x10^2	Thickness × in cm for 1.11cm bore	($\log_{10}x$) x10^2
15	0.25	-60.21	0.022	-165.76	0.024	-161.98	0.026	-158.50	0.028	-155.28
30	0.5	-30.10	0.025	-160.21	0.027	-156.86	0.029	-153.76	0.032	-149.49
45	0.75	-12.49	0.028	-155.28	0.029	-153.76	0.033	-148.15	0.035	-145.59
60	1	0.00	0.03	-152.29	0.032	-149.49	0.036	-144.37	0.038	-142.02
75	1.25	9.69	0.033	-148.15	0.035	-145.59	0.038	-142.02	0.041	-138.72
90	1.5	17.61	0.035	-145.59	0.037	-143.18	0.04	-139.79	0.043	-136.65
105	1.75	24.30	0.035	-145.59	0.037	-143.18	0.042	-137.68	0.044	-135.65
120	2	30.10	0.036	-144.37	0.039	-140.89	0.044	-135.65	0.046	-133.72
135	2.25	35.22	0.037	-143.18	0.039	-140.89	0.044	-135.65	0.049	-130.98
150	2.5	39.79	0.038	-142.02	0.041	-138.72	0.045	-134.68	0.049	-130.98
165	2.75	43.93	0.038	-142.02	0.041	-138.72	0.045	-134.68	0.051	-129.24
180	3	47.71	0.04	-139.79	0.042	-137.68	0.046	-133.72	0.051	-129.24
195	3.25	51.19	0.04	-139.79	0.042	-137.68	0.046	-133.72	0.051	-129.24
210	3.5	54.41	0.04	-139.79	0.042	-137.68	0.046	-133.72	0.051	-129.24

Table 2(a): Solid-solid reactions between CuI+$HgCl_2$, with different bore sized capillary used at 90°C

Time (Mint)	Time (Hours)	($\log_{10}t$) x10^2	Thickness × in cm for 0.5cm bore	($\log_{10}x$) x10^2	Thickness × in cm for 0.72cm bore	($\log_{10}x$)x10^2	Thickness × in cm for 0.81cm bore	($\log_{10}x$) x10^2	Thickness × in cm for 1.11cm bore	($\log_{10}x$) x10^2
15	0.25	-60.21	0.012	-192.08	0.014	-185.39	0.015	-182.39	0.016	-179.59
30	0.5	-30.10	0.015	-182.39	0.017	-176.96	0.018	-174.47	0.019	-172.12
45	0.75	-12.49	0.017	-176.96	0.019	-172.12	0.020	-169.90	0.021	-167.78
60	1	0.00	0.019	-172.12	0.021	-167.78	0.023	-163.83	0.024	-161.98
75	1.25	9.69	0.021	-167.78	0.022	-165.76	0.024	-161.98	0.026	-158.50
90	1.5	17.61	0.022	-165.76	0.023	-163.83	0.026	-158.50	0.028	-155.28
105	1.75	24.30	0.024	-161.98	0.025	-160.21	0.027	-156.86	0.029	-153.76
120	2	30.10	0.025	-160.21	0.027	-156.86	0.028	-155.28	0.029	-153.76
135	2.25	35.22	0.026	-158.50	0.028	-155.28	0.029	-153.76	0.031	-150.86
150	2.5	39.79	0.027	-156.86	0.028	-155.28	0.029	-153.76	0.031	-150.86
165	2.75	43.93	0.028	-155.28	0.029	-153.76	0.030	-152.29	0.031	-150.86
180	3	47.71	0.028	-155.28	0.029	-153.76	0.030	-152.29	0.031	-150.86
195	3.25	51.19	0.028	-155.28	0.029	-153.76	0.030	-152.29	0.031	-150.86
210	3.5	54.41	0.028	-155.28	0.029	-153.76	0.030	-152.29	0.031	-150.86

Table 2(b): Solid-solid reactions between KI+$HgCl_2$, with different bore sized capillary used at 90°C

Time (Mint)	Time (Hours)	($\log_{10}t$) x10^2	Thickness × in cm for 0.5cm bore	($\log_{10}x$) x10^2	Thickness × in cm for 0.72cm bore	($\log_{10}x$)x10^2	Thickness × in cm for 0.81cm bore	($\log_{10}x$) x10^2	Thickness × in cm for 1.11cm bore	($\log_{10}x$) x10^2
15	0.25	-60.21	0.027	-156.86	0.028	-155.28	0.031	-150.86	0.033	-148.15
30	0.5	-30.10	0.031	-150.86	0.032	-149.49	0.034	-146.85	0.037	-143.18
45	0.75	-12.49	0.033	-148.15	0.035	-145.59	0.037	-143.18	0.039	-140.89
60	1	0.00	0.036	-144.37	0.038	-142.02	0.04	-139.79	0.042	-137.68
75	1.25	9.69	0.038	-142.02	0.041	-138.72	0.043	-136.65	0.045	-134.68
90	1.5	17.61	0.04	-139.79	0.043	-136.65	0.045	-134.68	0.048	-131.88
105	1.75	24.30	0.043	-136.65	0.044	-135.65	0.047	-132.79	0.051	-129.24
120	2	30.10	0.045	-134.68	0.046	-133.72	0.049	-130.98	0.052	-128.40
135	2.25	35.22	0.047	-132.79	0.049	-130.98	0.051	-129.24	0.053	-127.57
150	2.5	39.79	0.049	-130.98	0.051	-129.24	0.053	-127.57	0.054	-126.76
165	2.75	43.93	0.049	-130.98	0.052	-128.40	0.054	-126.76	0.055	-125.96
180	3	47.71	0.05	-130.10	0.053	-127.57	0.054	-126.76	0.055	-125.96
195	3.25	51.19	0.05	-130.10	0.053	-127.57	0.054	-126.76	0.055	-125.96
210	3.5	54.41	0.05	-130.10	0.053	-127.57	0.054	-126.76	0.055	-125.96

Table 3(a): Solid-solid reactions between CuI+$HgCl_2$, with different bore sized capillary used at 100°C

Time (Mint)	Time (Hours)	($\log_{10}t$) x10^2	Thickness × in cm for 0.5cm bore	($\log_{10}x$) x10^2	Thickness × in cm for 0.72cm bore	($\log_{10}x$)x10^2	Thickness × in cm for 0.81cm bore	($\log_{10}x$) x10^2	Thickness × in cm for 1.11cm bore	($\log_{10}x$) x10^2
15	0.25	-60.21	0.013	-188.61	0.015	-182.39	0.017	-176.96	0.018	-174.47
30	0.5	-30.10	0.018	-174.47	0.019	-172.12	0.020	-169.90	0.021	-167.78
45	0.75	-12.49	0.020	-169.90	0.021	-167.78	0.022	-165.76	0.024	-161.98
60	1	0.00	0.022	-165.76	0.023	-163.83	0.025	-160.21	0.027	-156.86
75	1.25	9.69	0.024	-161.98	0.026	-158.50	0.027	-156.86	0.029	-153.76
90	1.5	17.61	0.025	-160.21	0.028	-155.28	0.029	-153.76	0.030	-152.29
105	1.75	24.30	0.026	-158.50	0.029	-153.76	0.030	-152.29	0.032	-149.49
120	2	30.10	0.027	-156.86	0.030	-152.29	0.032	-149.49	0.034	-146.85
135	2.25	35.22	0.028	-155.28	0.031	-150.86	0.032	-149.49	0.036	-144.37
150	2.5	39.79	0.029	-153.76	0.032	-149.49	0.033	-148.15	0.036	-144.37
165	2.75	43.93	0.030	-152.29	0.033	-148.15	0.034	-146.85	0.037	-143.18
180	3	47.71	0.030	-152.29	0.033	-148.15	0.034	-146.85	0.037	-143.18
195	3.25	51.19	0.030	-152.29	0.033	-148.15	0.034	-146.85	0.037	-143.18
210	3.5	54.41	0.030	-152.29	0.033	-148.15	0.034	-146.85	0.037	-143.18

Table 3(b): Solid-solid reactions between KI+$HgCl_2$, with different bore sized capillary used at 100°C

Time (Mint)	Time (Hours)	($\log_{10}t$) x10^2	Thickness × in cm for 0.5cm bore	($\log_{10}x$) x10^2	Thickness × in cm for 0.72cm bore	($\log_{10}x$)x10^2	Thickness × in cm for 0.81cm bore	($\log_{10}x$) x10^2	Thickness × in cm for 1.11cm bore	($\log_{10}x$) x10^2
15	0.25	-60.21	0.032	-149.49	0.034	-146.85	0.038	-142.02	0.04	-139.79
30	0.5	-30.10	0.036	-144.37	0.038	-142.02	0.042	-137.68	0.044	-135.65
45	0.75	-12.49	0.038	-142.02	0.04	-139.79	0.045	-134.68	0.047	-132.79
60	1	0.00	0.041	-138.72	0.043	-136.65	0.048	-131.88	0.049	-130.98
75	1.25	9.69	0.043	-136.65	0.045	-134.68	0.05	-130.10	0.052	-128.40
90	1.5	17.61	0.045	-134.68	0.048	-131.88	0.053	-127.57	0.054	-126.76
105	1.75	24.30	0.047	-132.79	0.05	-130.10	0.055	-125.96	0.056	-125.18
120	2	30.10	0.049	-130.98	0.051	-129.24	0.057	-124.41	0.058	-123.66
135	2.25	35.22	0.051	-129.24	0.053	-127.57	0.057	-124.41	0.059	-122.91
150	2.5	39.79	0.053	-127.57	0.055	-125.96	0.058	-123.66	0.059	-122.91
165	2.75	43.93	0.054	-126.76	0.055	-125.96	0.058	-123.66	0.06	-122.18
180	3	47.71	0.054	-126.76	0.056	-125.18	0.059	-122.91	0.06	-122.18
195	3.25	51.19	0.054	-126.76	0.056	-125.18	0.059	-122.91	0.06	-122.18
210	3.5	54.41	0.054	-126.76	0.056	-125.18	0.059	-122.91	0.06	-122.18

Table 4(a): Finding k and *n* by least square fit with x^n=kt of solid-solid reactions CuI+$HgCl_2$, for different bores and different temperatures

Bore size	80°C		90°C		100°C		Avg. *n*
	k	*n*	k	*n*	k	*n*	
0.5cm	1.05E-06	2.755	1.90E-06	3.472	3.67E-06	2.646	3.28
0.72cm	1.29E-06	3.003	3.16E-06	3.472	4.25E-06	3.279	
0.81cm	1.58E-06	3.236	4.25E-06	3.367	5.59E-06	3.731	
1.11cm	2.27E-06	3.718	4.89E-06	3.610	7.20E-06	3.472	

Table 4(b): Finding k and *n* by least square fit with x^n=kt of solid-solid reactions KI+$HgCl_2$, for different bores and different temperatures

Bore size	80°C		90°C		100°C		Avg. *n*
	k	*n*	k	*n*	k	*n*	
0.5cm	1.06E-08	4.444	2.76E-08	4.980	4.80E-08	5.780	5.23
0.72cm	1.49E-08	5.025	3.67E-08	4.629	6.19E-08	6.135	
0.81cm	2.76E-08	4.274	4.80E-08	5.348	13.9E-08	6.061	
1.11cm	6.19E-08	4.608	17.1E-08	5.952	25.4E-08	6.803	

Table 5(a): Finding the activation energy of solid-solid reaction CuI+$HgCl_2$, with different bore

S. No.	Bore size	Activation energy (kj/mol)	Mean Value (kj/mol)	Average *n*
1	0.5cm	29.80±0.64	28.53±0.55 kj/mol	3.28
2	0.72cm	27.81±0.36		
3	0.81cm	29.46±0.47		
4	1.11cm	27.03±0.75		

Table 5(b): Finding the activation energy of solid-solid reaction KI+$HgCl_2$, with different bore

S. No.	Bore size	Activation energy (kj/mol)	Mean Value (kj/mol)	Average *n*
1	0.5cm	35.42±0.14	35.15±0.94 kj/mol	5.23
2	0.72cm	33.53±0.18		
3	0.81cm	38.64±1.75		
4	1.11cm	33.02±1.07		

4(b) shows that increases with increasing bore size as also with temperature, for both the reactions. Both these things are on expected lines. The observed temperature dependence follows from equation (4) and can even be qualitatively understood. Dependence on the bore size seems to be due to the increase in the number of the interacting molecules, with increasing bore size.

From the Tables we find that the excitation energy E_o depends little on the bore size. This is very reasonable. So, the parameters obtained from capillary studies make a lot of sense. They give us valuable information about the solid-solid reaction process in a capillary. However, corroborative studies are desirable. The present one is the only one we are aware of. Some more studies of this kind are desirable. The idea of such an attempt is to show that the numbers obtained are consistent with their definition and this seems to be the case.

CONCLUSION

The parameters obtained from capillary studies make a good deal of sense; the order of the reaction may be regarded as a measure of the number of the molecules participating to produce the product in the reaction. The rate constant has plausible dependence on the bore size and the temperature. The almost non-dependence of the activation energy on the bore size; makes a lot of sense. Therefore, such studies tell important things. These parameters provide a plausible understanding of the solid-solid reactions. However, the parameters obtained from capillary studies need not be same as for solid-solid reactions in bulk, and even more so from those that may be obtained from solution-chemistry for the same reaction.

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REFERENCES

1. Beg, M.A. and Ansari S.M., *J. Solid State Chem*., **20**: 103 (1977).
2. Beg, M.A. and Saud R., *Indian J. Chem.,* **25**A: 373 (1986).
3. Beg, M.A. and Jain A.*, Polyhedron,* **11**(21): 2775 (1992).
4. Rahman, R., Ph.D. *Thesis*, Aligarh Muslim University, Aligarh, 126 (1984).
5. Beg, M.A. and Ahmad A., *Bull. Chem. Soc., Japan,* **55**: 3607 (1982).
6. Beg, M.A. and Ahmad A., *Bull. Chem. Soc., Japan,* **55**: 297 (1982).
7. Beg, M.A., Ahmad A. and Askari H., *J. Solid State Chem.,* **67**: 3717 (1987).
8. Beg, M.A. and Ansari S.M., *J. Solid State Chem.,* **18**: 57 (1976).
9. Husain S., *Physics Bulletin*, Aligarh Muslim University, **37** (2009).
10 . Soni, P. L., *Text book of Inorganic Chemistry*, Sultan publication, Chap. **8**: 2.224.
11. Maron, S. H. and Prutton C. F., *Principles of Physical Chemistry*, 4th Edition, Amerind Publishing Co. Pvt. Ltd. , New Delhi, 548-onwards (1972).