

# THE TIME OF SETTING OF GELS FORMED BY THE MUTUAL INTERACTION OF OPPOSITELY CHARGED SOLS AT DIFFERENT TEMPERATURES

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Received August 2, 1949

RECENTLY Prasad and Mehta<sup>1, 2</sup> have shown for the first time that gelation takes place when certain well-defined volumes of some oppositely charged sols of suitable concentrations, dialysed or undialysed, are mixed together in suitable proportions. They have also measured the time of setting ( $t$ ) of such gels which follows the relation  $t = Ra^{-m}$ , where 'a' is the volume of one of the oppositely charged sols added to 5 c.c. of the other, and R and  $m$  are constants.

The present authors have established that gels are obtained by mixing (i) the positively charged aluminium hydroxide sol with negatively charged sols of antimony sulphide, silicic acid and manganese dioxide, and (ii) the negatively charged nickel hydroxide sol, dialysed to different extent, with the positively charged sol of silicic acid and undialysed and dialysed sol of ferric hydroxide. They have measured the time of setting of these gels and have examined the effect of temperature on the time of setting which for inorganic gels generally decreases as the temperature is increased.<sup>3</sup>

## EXPERIMENTAL

(a) *Preparation of gels*: (1) *Aluminium hydroxide sol (+ ve)*.—It was prepared by Crum's method and was dialysed for 1, 2, 3 and 4 days. Three different samples of the sol (A, B and C) were prepared and the undialysed and dialysed samples were labelled as A, A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub> and A<sub>4</sub>, B, B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub> and B<sub>4</sub> and C, C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub>. One litre of each of the three samples was found to contain aluminium hydroxide corresponding to 2.30 g., 2.33 g., and 2.31 g. of Al<sub>2</sub>O<sub>3</sub>, respectively. The aluminium hydroxide content of the undialysed and the dialysed samples were found to be practically constant.

(2) *Antimony sulphide sol (- ve)*.—It was prepared by adding slowly a saturated solution of H<sub>2</sub>S to a dilute solution (3 g. in 300 c.c.) of potassium antimony tartrate. The excess of H<sub>2</sub>S was driven out by slow boiling and the last traces were removed by bubbling hydrogen gas. The sol was labelled as D. Its colloidal content was found to correspond to 0.72 g. of Sb<sub>2</sub>S<sub>3</sub> per litre.

(3) *Manganese dioxide sol* (— ve).—It was prepared by the reduction of potassium permanganate with sodium arsenite and its colloidal content was found to correspond to 0.52 g. of MnO<sub>2</sub> per litre. It was labelled as E.

(4) *Silicic acid sol* (+ ve).—It was prepared by adding gradually a solution of sodium silicate to a solution of HCl with vigorous stirring. The resultant mixture was dialysed until it was nearly free from chloride ions. The dialysate was replaced with fresh distilled water as frequently as considered necessary. The colloidal content of the sol was found to correspond to 29.74 g. of SiO<sub>2</sub> per litre of the sol. It was labelled as F.

(5) *Silicic acid sol* (— ve).—The negatively charged sol was obtained by adding suitable amount of sodium hydroxide solution to the positively charged sol prepared in the manner described above. Its colloidal content was found to correspond to 27.27 g. of SiO<sub>2</sub> per litre. It was labelled as G.

(6) *Nickel hydroxide sol* (— ve).—It was prepared by the method of Prasad and Mehta.<sup>4</sup> The samples of the undialysed sol and those of the sol dialysed for 1, 2, 3 and 4 days were labelled as H, H<sub>1</sub>, H<sub>2</sub>, H<sub>3</sub> and H<sub>4</sub>. The colloidal content of the sol corresponded to 3.33 g. of nickel in one litre, and was found to be practically constant in all the five samples.

All sols were stored in Jena glass bottles.

(b) *Cataphoretic speed*.—The cataphoretic speeds ( $V$  = in cm. per second per volt) of the sols were measured by Mukerjee's apparatus under conditions given below:

E.M.F. applied = 100 volts; distance between the side tubes = 4.2 cm.; potential applied at the boundary = 6.06 volts; current passed for 1,260 seconds in sols A, B, C, D, E and G and for 840 secs. in F and H.

TABLE I

Sol.	$V \times 10^4$	Sol.	$V \times 10^4$	Sol.	$V \times 10^4$	Sol.	$V \times 10^4$
A	3.664	B <sub>1</sub>	5.269	C <sub>2</sub>	5.299	G	1.208
A <sub>1</sub>	5.039	B <sub>2</sub>	5.955	C <sub>3</sub>	6.985	H	7.264
A <sub>2</sub>	6.528	B <sub>3</sub>	6.916	C <sub>4</sub>	8.017	H <sub>1</sub>	8.762
A <sub>3</sub>	8.017	B <sub>4</sub>	7.902	D	9.990	H <sub>2</sub>	10.300
A <sub>4</sub>	9.990	B <sub>5</sub>	3.321	E	2.107	H <sub>3</sub>	5.611
B	3.550	C <sub>1</sub>	5.153	F	1.218	H <sub>4</sub>	4.982

The upper liquid was dilute solutions of HCl (Merck's extra pure) in the case of aluminium hydroxide sol and KCl (Merck's extra pure) for other sols. The conductivities of the solutions were nearly the same as those of the sols but their densities were slightly lower. The colourless sols were coloured by the addition of 0.01 c.c. of 1 per cent. solution of neutral red to 40 c.c. of the sol. The results obtained are given in Table I.

(c) *Characters of the gels obtained by mutual gelation.*—The gels obtained by mixing the oppositely charged sols vary in transparency, firmness and colour. The characteristics of these gels have been observed in Table II.

TABLE II

+ve sol.	—ve sol.	Colour	Transparency	Firmness
1. Aluminium hydroxide	Antimony sulphide	Orange-yellow	Transparent	Not very firm
2. „	Silicic acid	Colourless	Semi-transparent	Quite firm
3. „	Manganese dioxide	Dark brown	Semi-transparent	Not very firm
4. Silicic acid	Nickel hydroxide	Green	Quite transparent	Very firm

(d) *Measurement of the time of setting.*—The times of setting were measured at various temperatures, by Hurd and Letteron's method<sup>7</sup> modified by Miss Nathan.<sup>5</sup>

A number of test-tubes were filled with 5.0 c.c. of one sol, marked I. In another set of test-tubes, different known volumes (measured by a micro-pipette reading upto 0.01 c.c.) of the oppositely charged sol, marked II, were taken and diluted to 5.0 c.c. by the addition of distilled water. The test-tubes were well corked and were placed in the thermostat for half an hour. The contents of the two test-tubes were mixed a number of times and well shaken. The mixture was then poured into a small weighing bottle and a stop-watch was started. A glass rod 3" long and 1 mm. in diameter was introduced in position. When the glass rod could remain in its position without the aid of the mechanical support, the stop-watch was stopped and the time noted. To increase the accuracy of measurements, a number of readings were taken, each time disturbing the gel-forming mixture as few times as possible. The minimum time obtained in this manner was taken as the time of setting of the gel.

The results obtained are given in Tables III–XIV in which (*t*) with a suffix denotes the time of setting of the gel at the temperature in centi-grade indicated by the suffix.

TABLE III  
 $I(A) (+ ve), II(D) (- ve)$

D. in c.c.	$t_{35}$	$t_{40}$	$t_{45}$
1.8	1'-13"	1'-7"	0'-58"
1.9	0'-54"	0'-53"	0'-50"
2.0	0'-42"	0'-40"	0'-38"
2.1	0'-32"	0'-29"	0'-28"
2.2	0'-24"	0'-23"	0'-23"
2.3	0'-20"	0'-17"	0'-16"

TABLE IV  
 $I(A_1, A_2) (+ ve), II(D) (- ve)$

D in c.c.	$t_{35}$	$t_{40}$	$t_{45}$	D in c.c.	$t_{35}$	$t_{40}$	$t_{45}$
2.0	2'-3"	1'-44"	1'-26"	2.5	3'-30"	3'-3"	2'-30"
2.1	1'-29"	1'-16"	1'-1"	2.6	2'-55"	2'-35"	2'-5"
2.2	1'-12"	1'-4"	0'-56"	2.7	2'-32"	2'-12"	1'-53"
2.3	0'-55"	0'-46"	0'-40"	2.8	2'-15"	1'-52"	1'-32"
2.4	0'-40"	0'-34"	0'-32"	2.9	1'-58"	1'-39"	1'-21"
2.5	0'-33"	0'-28"	0'-25"	3.0	1'-45"	1'-27"	1'-13"

TABLE V  
 $I(A_3A_4) (+ ve), II(D) (- ve)$

D. in c.c.	$t_{35}$	$t_{40}$	$t_{45}$	D in c.c.	$t_{35}$	$t_{40}$	$t_{45}$
3.0	2'-35"	2'-18"	2'-4"	4.1	2'-45"	2'-27"	2'-15"
3.1	2'-7"	1'-52"	1'-40"	4.2	2'-7"	1'-48"	1'-42"
3.2	1'-49"	1'-33"	1'-21"	4.3	1'-31"	1'-24"	1'-21"
3.3	1'-22"	1'-11"	1'-4"	4.4	1'-13"	1'-5"	1'-0"
3.4	1'-4"	0'-59"	0'-53"	4.5	0'-56"	0'-49"	0'-44"
3.5	0'-52"	0'-44"	0'-44"	4.6	0'-41"	0'-39"	0'-36"

TABLE VI

 $I(B) (+ ve), II(G) (- ve)$ 

G in c.c.	$t_{35}$	$t_{40}$	$t_{45}$
2.0	3'-19"	2'-56"	2'-46"
2.1	2'-50"	2'-38"	2'-28"
2.2	2'-29"	2'-16"	2'-4"
2.3	2'-2"	1'-50"	1'-29"
2.4	1'-42"	1'-29"	1'-19"
2.5	1'-20"	1'-15"	1'-3"

TABLE VII

 $I(B_1B_2) (+ ve), II(G) (- ve)$ 

G in c.c.	$t_{35}$	$t_{40}$	$t_{45}$	G in c.c.	$t_{35}$	$t_{40}$	$t_{45}$
2.3	2'-25"	2'-12"	2'-5"	2.5	2'-54"	2'-43"	2'-0"
2.4	1'-54"	1'-50"	1'-45"	2.6	2'-16"	1'-48"	1'-38"
2.5	1'-43"	1'-36"	1'-33"	2.7	1'-43"	1'-34"	1'-13"
2.6	1'-30"	1'-26"	1'-20"	2.8	1'-16"	0'-49"	1'-1"
2.7	1'-16"	1'-11"	1'-5"	2.9	0'-59"	0'-41"	0'-40"
2.8	1'-5"	1'-2"	1'-1"	3.0	0'-49"	..	0'-38"

TABLE VIII

 $I(B_3B_4) (+ ve), II(G) (- ve)$ 

G in c.c.	$t_{35}$	$t_{40}$	$t_{45}$	G in c.c.	$t_{35}$	$t_{40}$	$t_{45}$
2.8	2'-5"	1'-59"	1'-53"	3.0	2'-20"	2'-13"	2'-5"
2.9	1'-35"	1'-30"	1'-27"	3.1	2'-8"	2'-2"	1'-53
3.0	1'-78"	1'-13"	1'-9"	3.2	1'-56"	1'-49"	1'-40"
3.1	1'-3"	1'-0"	0'-56"	3.3	1'-43"	1'-38"	1'-34"
3.2	0'-47"	0'-46"	0'-43"	3.4	1'-34"	1'-29"	1'-24"
3.3	0'-38"	0'-35"	0'-34"	3.5	1'-25"	1'-21"	1'-20"

TABLE IX  
 $I(C) (+ ve), II(E) (- ve)$

E in c.c.	$t_{35}$	$t_{40}$	$t_{45}$
2.5	3'-26"	3-12"	2'-59"
2.6	3'-4"	2'-52"	2'-42"
2.7	2'-48"	2-38"	2'-27"
2.8	2'-32"	2'-20"	2'-12"
2.9	2'-12"	2'-2"	1'-54"
3.0	1'-42"	1'-41"	1'-23"

TABLE X  
 $I(C_1C_2) (+ ve), II(E) (- ve)$

E in c.c.	$t_{35}$	$t_{40}$	$t_{45}$	E in c.c.	$t_{35}$	$t_{40}$	$t_{45}$
2.8	3'-51"	3'-35"	3'-20"	2.7	3'-8"	2'-54"	2'-38"
2.9	3'-33"	3'-18"	3'-2"	2.8	2'-45"	2'-36"	2'-12"
3.0	3'-16"	3'-2"	2'-44"	2.9	2'-18"	2'-11"	2'-5"
3.1	2'-56"	2'-46"	2'-34"	3.0	2'-2"	1'-55"	1'-50"
3.2	2'-45"	2'-37"	2'-18"	3.1	1'-41"	1'-37"	1'-13"
3.3	2'-30"	2'-20"	2'-20"	3.2	1'-16"	1'-9"	0'-47"

TABLE XI  
 $I(C_3C_4) (+ ve), II(E) (- ve)$

E in c.c.	$t_{35}$	$t_{40}$	$t_{45}$	E in c.c.	$t_{35}$	$t_{40}$	$t_{45}$
2.5	3'-25"	3'-7"	2'-46"	2.8	4'-5"	3'-44"	3'-27"
2.6	3'-2"	2'-47"	2'-28"	2.9	3'-47"	3'-29"	3'-11"
2.7	2'-42"	2'-29"	2'-12"	3.0	3'-18"	3'-5"	2'-46"
2.8	2'-20"	2'-10"	1'-53"	3.1	2'-58"	2'-46"	2'-30"
2.9	1'-58"	1'-49"	1'-32"	3.2	2'-37"	2'-28"	2'-17"
3.0	1'-20"	1'-14"	1'-2"	3.3	2'-25"	2'-22"	2'-18"

TABLE XII

 $I(H) (-ve), II(F) (+ve)$ 

F in c.c.	$t_{35}$	$t_{40}$	$t_{45}$
3.3	6'-14"	6'-3"	5'-50"
3.4	4'-49"	4'-37"	4'-24"
3.5	3'-55"	3'-44"	3'-29"
3.6	2'-12"	1'-59"	1'-45"
3.7	0'-59"	0'-55"	0'-49"
3.8	0'-34"	0'-30"	0'-23"

TABLE XIII

 $I(H_1H_2) (-ve), II(F) (+ve)$ 

F in c.c.	$t_{35}$	$t_{40}$	$t_{45}$	F in c.c.	$t_{35}$	$t_{40}$	$t_{45}$
3.4	6'-10"	5'-54"	5'-40"	3.5	6'-2"	5'-50"	5'-35"
3.5	4'-44"	4'-31"	4'-16"	3.6	5'-21"	5'-3"	4'-50"
3.6	4'-12"	3'-58"	3'-44"	3.7	4'-37"	4'-21"	4'-5"
3.7	3'-27"	3'-12"	2'-58"	3.8	3'-42"	3'-25"	3'-12"
3.8	2'-36"	2'-20"	2'-14"	3.9	2'-49"	2'-33"	2'-29"
3.9	1'-50"	1'-41"	1'-36"	4.0	2'-12"	2'-3"	1'-53"

TABLE XIV

 $I(H_3H_4) (-ve), II(F) (+ve)$ 

F in c.c.	$t_{35}$	$t_{40}$	$t_{45}$	F in c.c.	$t_{35}$	$t_{40}$	$t_{45}$
3.6	6'-17"	5'-51"	5'-38"	3.7	5'-48"	5'-25"	5'-14"
3.7	5'-16"	4'-53"	4'-36"	3.8	5'-8"	4'-42"	4'-29"
3.8	4'-24"	4'-1"	3'-46"	3.9	4'-20"	3'-38"	3'-43"
3.9	3'-36"	3'-14"	2'-59"	4.0	3'-48"	3'-24"	3'-20"
4.0	2'-31"	2'-4"	1'-52"	4.1	2'-52"	2'-30"	2'-16"
4.1	1'-58"	1'-28"	1'-20"	4.2	2'-3"	1'-50"	1'-28"

DISCUSSION OF RESULTS

(a) *Effect of volumes of sols.*—It will be seen from the above tables that the time of setting of gels obtained by the mutual interaction of oppositely charged sols decreases as increasing amounts of sol II are added to the same amount of the sol I. The decrease is rapid for the first few additions but slows down when larger amounts are added. The values of the logarithm of the different volumes ( $a$ ) in c.c. of sol II added to sol I were plotted against the logarithms of the times of setting at 35°, 40° and 45°, and in all cases the plotted points were found to lie either on single straight lines or two intersecting straight lines. The tangents of the inclinations of the lines are negative, showing thereby that the relation  $t = Ra^{-m}$  is obeyed in all cases. The values of  $m$  and  $\log R$ , or of  $m_1$  and  $m_2$ , and  $\log R_1$  and  $\log R_2$ , in cases where the plotted points lie on two intersecting straight lines, were read from the graphs and the applicability of the above relation was confirmed.

(b) *Effect of temperature.*—It will be observed that, in all cases, the time of setting of the same gel-forming mixture decreases as the temperature is increased.

Hurd and Letteron<sup>6</sup> have found that the time of setting ( $t$ ) of silicic acid gels at several absolute temperatures ( $T$ ) follows the relation  $\frac{d \ln t}{dT} = \frac{Q}{RT^2}$ , where  $Q$  is the heat of activation of the formation of these gels. They have calculated the values of  $Q$  by multiplying the slopes of the straight lines obtained by plotting  $\log t$  against  $\frac{1}{T}$  by  $2.3 R$ . Prasad and Desai<sup>7</sup> have found that the aforesaid relation also applies to the gels studies by them, and have calculated the heat of activation of the formation of these gels.

The values of  $\log t$  for the same gel-forming mixtures were plotted against  $\frac{1}{T}$  and with few exceptions the curves obtained were found to be a set of parallel straight lines. The values of  $Q$  were calculated from the slopes of these straight lines and their mean values are given in Table XV.

It was found that several values of  $Q$  do not differ from the mean by more than three per cent. in most cases. The obedience of the relation  $\frac{d \ln t}{dT} = \frac{Q}{RT^2}$  by gels formed either by metathetical reaction or by the addition of electrolytes to sols, or by mutual gelation, shows that the three methods of the formation of gels are similar.



TABLE XV

Sols	Q	Sols	Q	Sols	Q	Sols	Q
A, D ..	1787	B, G .	2929	C, E ..	2825	H, F ..	1607
A <sub>1</sub> , D ..	6642	B <sub>1</sub> , G ..	3447	C <sub>1</sub> , E ..	3073	H <sub>1</sub> , F ..	1478
A <sub>2</sub> , D ..	7270	B <sub>2</sub> , G ..	6598	C <sub>2</sub> , E ..	3727	H <sub>2</sub> , F ..	1925
A <sub>3</sub> , D ..	5246	B <sub>3</sub> , G ..	1636	C <sub>3</sub> , E ..	5020	H <sub>3</sub> , F ..	2337
A <sub>4</sub> , D ..	3849	B <sub>4</sub> , G ..	2327	C <sub>4</sub> , E ..	3413	H <sub>4</sub> , F ..	2539

(c) *Effect of dialysis.*—The volumes of the sols of antimony sulphide, silicic acid and manganese dioxide required to form gels with the same volume of aluminium hydroxide sol dialysed to different extent, which set in the same time at the same temperature were determined and are given in Table XVI. Table XVII brings out the same effect in the case of gels obtained by mixing the same volume of nickel hydroxide sol, dialysed to different extent with the silicic acid sol.

TABLE XVI

Days of dialysis of sol A or B or C (+ ve)	Time of setting = 1 minute						Time of setting = 2 minutes		
	c.c. of D (-ve) required for setting with A at			c.c. of G (-ve) required for setting with B at			c.c. of E (-ve) required for setting with C at		
	35°	40°	45°	35°	40°	45°	35°	40°	45°
0 day ..	1.86	1.84	1.78	2.63	2.61	2.51	3.25	2.91	2.85
1 day ..	2.26	2.18	2.11	2.87	2.83	2.81	3.52	3.45	3.37
2 days ..	3.42	3.20	3.17	2.89	2.84	2.75	3.02	2.98	2.91
3 days ..	3.43	3.38	3.34	2.15	3.09	3.06	2.90	2.83	2.77
4 days ..	4.46	4.43	4.39	3.82	3.76	3.71	3.51	3.45	3.36

It will be observed from Table XVI that the greater the period of dialysis of the aluminium hydroxide sol, the larger is the volume of the oppositely charged sol of antimony sulphide and silicic acid required to cause gelation. Table I shows that the cataphoretic speed of the aluminium hydroxide sol increases as it is dialysed for longer period. If the cataphoretic velocity is assumed to be proportional to the density of the electric charge on the colloid

particles of the sol, the data given in the above table support the view that the mutual coagulation of oppositely charged sols, used in these two cases, which precedes gelation, is brought about mostly by the neutralisation of opposite electric charges. The mutual gelation of aluminium hydroxide and manganese dioxide sols show no regularity in this respect.

The results given in Table XVII show that greater the period of dialysis of the nickel hydroxide sol, larger is the volume of the silicic acid

TABLE XVII

Days of dialysis of sol H (-ve)	Time of setting = 2 minutes		
	c.c. of F (+ ve) required for setting with H at		
	35°	40°	45°
0 day ..	3.61	3.60	3.57
1 day ..	3.88	3.85	3.83
2 days ..	4.05	4.01	3.98
3 days ..	4.10	4.02	3.98
4 days ..	4.25	4.18	4.15

sol required to cause gelation in the same time (2 minutes). The cataphoretic speed of the nickel hydroxide sol increases for the first two days of dialysis and then regularly decreases during the subsequent two days (*cf.* Table I). Hence it appears probable that in this case, besides the neutralisation of charges, factors such as the mutual adsorption of colloidal particles, or the interaction between stabilising ions or the excess of free electrolytes in the two sols, also play some part in bringing about the mutual coagulation of sols.

SUMMARY

Gels have been obtained by mixing (i) the positively charged aluminium hydroxide sol (dialysed and undialysed) with negatively charged sols of antimony sulphide, silicic acid and manganese dioxide and (ii) the negatively charged nickel hydroxide sol dialysed to different extent with the positively charged sol of silicic acid.

2. The time of setting (*t*) of these gels decreases as increasing volumes (*a*) of a sol are added to the same amount of the oppositely charged

sol. The experimental results show that the relation  $t = Ra^{-m}$  is obeyed in most cases.

3. The effect of temperature on the time of setting of these gels shows that Hurd and Letteron's relation  $\frac{d \ln t}{dT} = \frac{Q}{RT^2}$  is obeyed in most cases. This indicates that the method of formation of these gels is similar to those of the other gels.

4. The study of the cataphoretic speed and the effect of dialysis on the time of setting of the gels support the view that the mutual coagulation of oppositely charged sols of aluminium hydroxide and (i) antimony sulphide and (ii) silicic acid is brought about mostly by the neutralisation of the opposite electric charges. The other gels studied in this paper do not support this view, probably because other factors also play some part in bringing about mutual coagulation.

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