

CONDITION OF SPARINGLY SOLUBLE SUBSTANCES IN GELS.

Part I. Silver Chromate in Gelatine.

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WILLIAMS and Mackenzie,¹ Bolam and co-workers² and Desai and Nabar³ have shown from conductivity and e.m.f. measurements that prior to the appearance of red colour the yellow mixture of silver nitrate and potassium chromate in gelatine contains silver chromate in supersaturated solution and that the red colour is due to the actual formation of the solid phase, and not to the coagulation of a solid phase which is already present in the form of colloidal particles. Dhar and collaborators⁴ have, on the other hand, shown from conductivity and diffusion experiments that the yellow mixture contains particles which are negatively charged through adsorption of chromate ions, while the red substance is a less stable sol containing particles which are positively charged through adsorption of silver ions. Naik, Desai and Desai⁵ have observed that whatever changes in the conductivity are to occur take place immediately the solutions of silver nitrate in gelatine and potassium chromate in gelatine are mixed and that there is no gradual decrease of conductivity with changes in the colour of the mixtures—observation against the views of Bolam and co-workers. The cataphoretic experiments did not show presence of any charged particles either in the yellow or red mixtures—observation against the view of Dhar and co-workers. They have suggested that immediately the solutions are mixed some insoluble substance is produced, the particles of which are in a very highly dispersed condition—probably in molecular condition—and that changes in the colour of the mixtures are due to growth of these very fine particles into larger ones.

The present work was undertaken to find out causes of differences in the results of various investigators about the condition of silver chromate in gelatine.

Experimental.

The gelatine used in these experiments contained 1.177% ash and 18% moisture and its p_H (determined colorimetrically) was 5.45. Samples of gelatine having different p_H were prepared by adding suitable amounts of acetic acid and sodium acetate. The conductivity experiments were carried out exactly in the same manner as done by Naik, Desai and Desai.⁵ N/100 solutions of $AgNO_3$ and K_2CrO_4 and 3% solution of gelatine were used throughout. The reacting mixtures ($AgNO_3$ in gelatine and K_2CrO_4 in gelatine) were allowed to attain the required temperature by placing them in an electrically heated thermostat and then mixed by passing from tube to tube several times in a uniform manner; the mixture was then transferred to the conductivity cell, which was immediately kept in the thermostat for conductivity measurements. The total volume of the mixture in each experiment was 16 c.c. The time when colour change took place was carefully noted. The percentage of silver chromate in ionic condition was calculated exactly in the same manner as before.⁵

On allowing the gelatine solution to stand for different periods it was observed that its inhibitive power (power to prevent appearance of red coloured precipitate of silver chromate from yellow mixture) is not affected to any appreciable extent even when the mixture of gelatine and reactants is kept standing for 72 hours.

Results and Discussion.

A. Changes in the inhibitive power of gelatine and condition of silver chromate at different temperatures.—In Fig. 1 are plotted the values of conductivity (observed) of silver chromate alone at different times for 4.5 c.c. of reactants at different temperatures. The curves for other concentrations of the reactants are exactly similar. It was observed that in each case the conductivity did not change further on allowing the mixture to stand even for 24 hours or more. A summary of the results of all these experiments is given in the following table.

TABLE I.

Concentration of gelatine = 3%, p_H of gelatine = 5.45.

Total volume = 16 c.c. [2X c.c. of electrolyte + 4.4 c.c. of 3% gelatine + (16 - 2X - 4.4) c.c. conductivity water].

c.c. of electrolyte (X)	Temperature °C.	% of Ag_2CrO_4 in ionic condition before red colour appears	% of Ag_2CrO_4 in ionic condition after appearance of red colour and when conductivity does not change further on standing	Time for appearance of red colour in minutes	Time when conductivity begins to decrease in minutes
3.5	20	91	59	200	215
	30	87	69	300	330
	35	86	75	430	470
	40	84	84	600	>720
4.0	20	88	49	29	30
	30	87	57	45	47
	40	85	65	90	94
	50	84	80	305	340
	55	83	83	460	>650
4.5	20	87	39	5	5.5
	30	85	44	8	8.5
	40	84	51	15	16
	50	82	61	28	30
	60	80	75	120	160
	65	78	78	200	>600
5.0	20	77	30	2	2.5
	30	76	35	3	3.5
	40	75	41	4	4.5
	50	74	47	5	6
	60	73	53	6	7
	65	72	55	7	9

The following conclusions can be drawn from the results:—

- (1) The inhibitive power (time for appearance of red colour) increases with a rise of temperature.
- (2) The difference between the times of appearance of red colour and the decrease of conductivity increases with a rise of temperature, the colour change and conductivity decrease occurring more or less simultaneously at relatively low temperatures.
- (3) The temperature at which the conductivity does not decrease in spite of colour change even when the mixture is allowed to stand

for 24 hours or more is higher for mixtures containing larger amounts of reactants than those containing smaller amounts.

- (4) For each concentration of the reactant the % of Ag_2CrO_4 in ionic condition before the appearance of red colour decreases with a rise of temperature, while that after the appearance of the red colour and when conductivity does not decrease any further on standing increases at the same time.
- (5) For each temperature the smaller the amount of reactants, the larger the % of Ag_2CrO_4 in ionic condition before and after the appearance of red colour.
- (6) If the difference between the amounts of silver chromate in ionic condition before and after the appearance of red colour is taken roughly as a measure of degree of supersaturation, it is seen that the degree of supersaturation decreases with an increase of temperature.
- (7) In each case at relatively low temperatures the conductivity first remains constant, then decreases for some time and remains constant afterwards (Fig. 1).

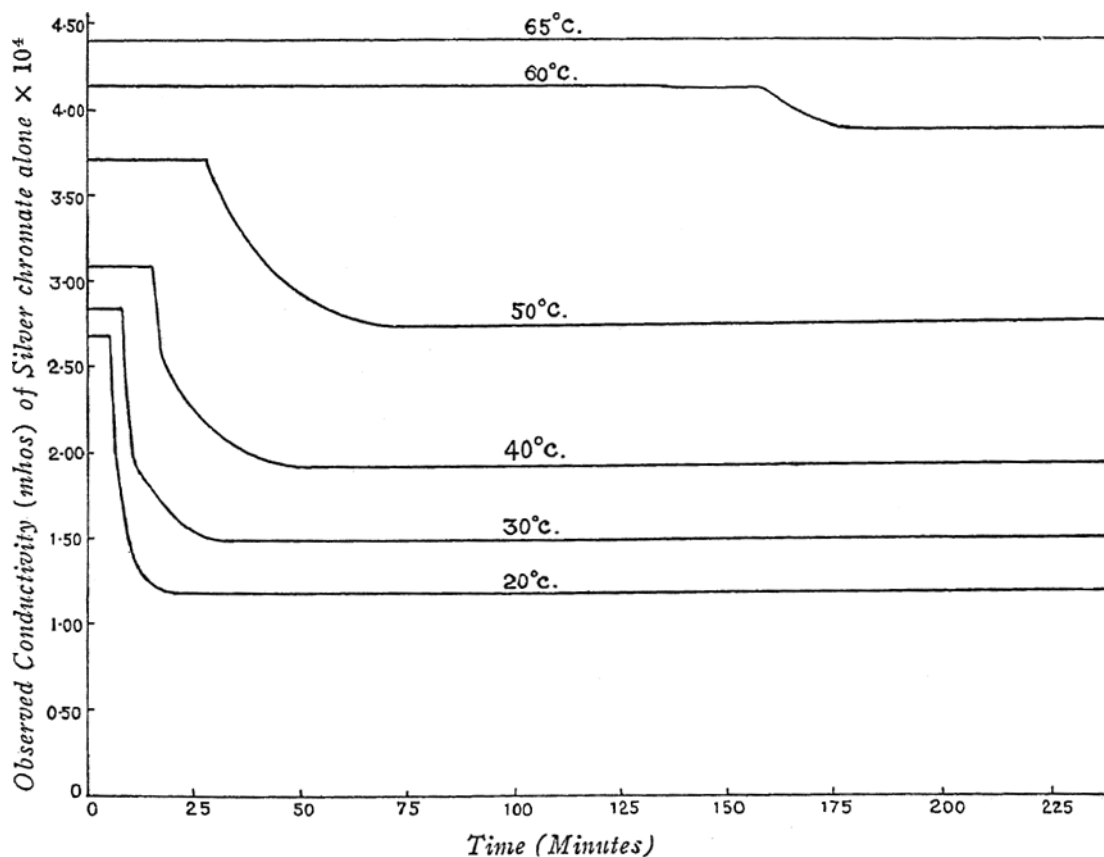


FIG. 1.

It is now proposed to discuss the above changes. (1) One might consider that the increase in the inhibitive power with a rise of temperature might be due to a change in the p_H of gelatine. The measurements of p between temperatures 20°C . and 70°C ., however, showed that p_H changes, if any, are very insignificant and therefore cannot be considered to have any appreciable influence on the large inhibitive power of gelatine at relatively high temperatures. An increase in the solubility of Ag_2CrO_4 with a rise of temperature cannot also alone explain these changes because although the solubility of Ag_2CrO_4 in water at 60°C . is about $2\frac{1}{2}$ times that at 20°C ., the inhibitive power has become more than $2\frac{1}{2}$ times within this temperature range as will be seen from Table I. It is likely that the degree of dispersity of gelatine might have increased with a rise of temperature, resulting in an increase of inhibitive power.

(2) At relatively low temperatures the colour change and decrease in conductivity take place more or less simultaneously probably because most of the silver chromate in those cases exists in ionic condition at first and a part of it is thrown out later as red Ag_2CrO_4 due to release of supersaturation (*cf.* Bolam and co-workers² and Desai and Nabar³). In each case at a certain temperature the conductivity does not decrease in spite of appearance of red coloured precipitate because a small portion of the silver chromate probably exists in a very highly dispersed condition—may be even molecularly dispersed—in the yellow mixture and the appearance of red colour is probably due to formation of molecular aggregates, conductivity not decreasing due to absence of supersaturation (*cf.* Naik, Desai and Desai⁵). It may be mentioned that even at relatively low temperatures a slight amount of silver chromate might be existing in highly dispersed condition and these very fine particles probably help release of supersaturation; the colour change and conductivity decrease occur more or less simultaneously because supersaturation being also relatively great, even very fine particles could help its release. During the intermediate stages the small portion of silver chromate which might be existing in highly dispersed condition in the yellow mixture probably gives rise to molecular aggregates (appearance of red colour), which later act as crystallisation centres for release of supersaturation (decrease of conductivity).

(3) The temperature at which conductivity does not decrease in spite of colour change is higher for mixtures containing large amounts of reactants than those containing smaller amounts probably because the amount of gelatine having remained the same, a higher degree of dispersity of gelatine is necessary in the former case than in the latter in order to increase the inhibitive power. As stated in (1) above, the degree of dispersity of gelatine

probably increases with temperature; a higher temperature is therefore necessary for mixtures having larger amounts of reactants than those containing smaller amounts, other conditions having remained the same.

(4) The % of Ag_2CrO_4 in ionic condition in the beginning and before the appearance of red colour decreases with a rise of temperature probably because the degree of dispersity of gelatine having increased [see (1) above], a relatively large amount of Ag_2CrO_4 might have either been adsorbed by, or chemically interacted with, gelatine at relatively high temperatures.

The % of Ag_2CrO_4 in ionic condition after appearance of red colour increases with a rise of temperature probably because of an increase in the (a) solubility of Ag_2CrO_4 [see (1) above] and (b) inhibitive power of gelatine. As stated in (1) above the increase in inhibitive power is probably due to greater degree of dispersity of gelatine at higher than at lower temperatures; this effect seems to be similar to that of hydrolysis studied by Desai and Nabar,³ where it was noticed that the final values of the activity of the silver ion increase with an increase in hydrolysis.

(5) This is probably due to the fact that a greater amount of Ag_2CrO_4 has either been adsorbed by, or chemically interacted with, gelatine in mixtures containing larger amounts of reactants than those containing smaller amounts.

(6) The degree of supersaturation with an increase of temperature has decreased but the inhibitive power of gelatine increased at the same time. Obviously, as stated by Naik, Desai and Desai,⁵ the inhibition experiments cannot always be utilised to give an idea about the degree of supersaturation although they can be in some cases and under certain circumstances. The decrease in the degree of supersaturation with a rise of temperature might probably be due to an increase in the solubility of Ag_2CrO_4 . The increased adsorption by, or chemical interaction with, gelatine of Ag_2CrO_4 at high temperatures might also to a certain extent decrease supersaturation.

(7) The conductivity-time curves are similar to the activity of Ag ion-time curves obtained by Desai and Nabar³ except for the fact that the point at which the conductivity commences to decrease does not in every case correspond with the first appearance of red colour.

B. Influence of changes in p_{H} of gelatine on the condition of silver chromate.—The nature of the curves obtained on plotting the values of conductivity (observed) of silver chromate alone at different times is similar to that of the conductivity-time curves given in Fig. 1. A summary of the results of these experiments is given in the following table.

TABLE II.

Concentration of gelatine = 3%.

Temperature of experiments = 30° C.

Total volume = 16 c.c. [2X c.c. of electrolyte + 4.4 c.c. of 3% gelatine + (16 - 2X - 4.4) c.c. conductivity water].

c.c. of electrolyte (X)	p _H of gelatine	% of Ag ₂ CrO ₄ in ionic condition before red colour appears	% of Ag ₂ CrO ₄ in ionic condition after red colour appears and when conductivity does not change further on standing	Time of appearance of red colour in minutes	Time when conductivity begins to decrease in minutes
3.5	5.45	87	69	300	330
	5.75	81	58	180	190
	6.00	77	64	240	267
	6.25	73	73	300	>600
4.0	5.25	87	60	120	124
	5.45	87	57	45	47
	5.75	68	45	24	25
	6.00	66	50	32	40
	6.25	63	55	43	60
	6.50	60	60	65	>240
4.5	5.00	84	51	50	54
	5.25	85	47	22	23
	5.45	85	44	8	8.5
	5.75	58	32	4.5	5
	6.00	56	37	5	8
	6.25	53	42	6	15
	6.50	50	50	10	>180

The following conclusions can be drawn from these results :—

(1) For all the concentrations of reactants the inhibitive power of gelatine is minimum for p_H 5.75, it being greater for higher or lower values of p_H.

(2) The difference between the times of appearance of red colour and the decrease of conductivity increases with p_H for samples of gelatine having p_H greater than 5.75; for gelatine samples of p_H smaller than 5.75 this difference increases with decrease of p_H only in those cases where the concentration of the reactants is not too large and the inhibitive power is proportionately great.

(3) For samples of gelatine having p_H greater than 5.75 the greater the concentration of the reactants the higher is generally the p_H at which the colour change appears but the conductivity does not decrease at all.

(4) For each concentration of the reactants the % of Ag_2CrO_4 in ionic condition before the appearance of red colour generally decreases regularly with an increase of p_H ; the % of Ag_2CrO_4 in ionic condition after the appearance of red colour and when conductivity does not decrease any further on standing is lowest for p_H value 5.75 for 3.5 and 4.5 c.c. of reactants, and for p_H value 5.45 for 4.0 c.c. of reactants, it being greater for higher or lower values of p_H .

(5) For each value of p_H the smaller the amount of the reactants, the larger the % of Ag_2CrO_4 in ionic condition before and after the appearance of red colour.

(6) If the difference between the amounts of silver chromate in ionic condition before and after the appearance of red colour is taken roughly as a measure of degree of supersaturation, it is seen that the supersaturation is highest for p_H value 5.75. for 3.5 and 4.5 c.c. of reactants, and for p_H value 5.45 for 4.0 c.c. of reactants, it being smaller for higher or lower values of p_H .

The causes of these changes may now be discussed.

(1) The results support the observation of Desai and Naik⁶ that the inhibitive power of gelatine with reference to p_H 5.75 is minimum, it being higher for samples of gelatine having greater or smaller p_H . The causes of minimum inhibitive power for p_H 5.75 are not clear. It may be that the degree of dispersity of gelatine at this p_H might be lowest.

(2) The colour change and decrease in conductivity occur more or less simultaneously in all cases for p_H 5.75. It will appear from conclusion (6) that the degree of supersaturation is also highest in samples of gelatine having p_H near about 5.75. It is likely that a small amount of Ag_2CrO_4 which might be present in molecularly dispersed condition from the beginning helps in releasing supersaturation. For higher or lower values of p_H the degree of supersaturation decreases; at sufficiently low or high values of p_H characteristic of each concentration of the reactants, there will not be any supersaturation and therefore the colour changes which will occur in these cases will be due to formation of molecular aggregates from Ag_2CrO_4 which probably exists in molecularly dispersed condition from the beginning. It is clear from these results that for each concentration of the reactants the colour change and decrease in conductivity will occur more or less simultaneously for p_H 5.75; *i.e.*, the p_H is gradually lowered below or raised

above 5.75, the difference between the times of colour change and decrease of conductivity will continuously increase, and ultimately at certain values of p_H higher and lower than 5.75—characteristic of each concentration of the reactants, the conductivity will not decrease at all in spite of colour change.

(3) This is probably due to the fact that for relatively high concentrations of the reactants, the amount of gelatine having remained the same, the p_H will have to be increased relatively to a large extent in order to increase the inhibitive power. From the trend of the present results it appears that for samples of gelatine having p_H smaller than 5.75, the higher the concentration of the reactants the lower will generally be the p_H at which the colour change will occur but the conductivity will not decrease at all.

(4) The % of Ag_2CrO_4 in ionic condition before the appearance of red colour decreases with increase of p_H probably because a relatively large amount of Ag_2CrO_4 might have either been adsorbed by, or chemically interacted with, gelatine at relatively high values of p_H .

The % of Ag_2CrO_4 in ionic condition after the appearance of red colour is lower for p_H 5.75 probably because the inhibitive power being minimum, a relatively large amount of Ag_2CrO_4 is thrown out in condition other than ionic.

(5) The causes of this might be similar to those given under (5) in Section (A).

(6) The fact that gelatine samples of p_H near about 5.75 show higher supersaturation than those with higher or lower p_H in spite of minimum inhibitive power support the view stated before, namely, that the experiments on inhibitive power should not be utilised to get idea about degree of supersaturation.

On page 876 of their paper, Bolam and Donaldson² have calculated the degree of supersaturation according to the theory of von Weimarn and found that the degree of supersaturation increases slightly as the p_H decreases from 5.7 to 5.0, and then falls off more rapidly as the p_H is further decreased. They conclude that the degree of supersaturation and therefore the inhibitive action of gelatine, probably has an optimum value at p_H 5.0. The present results do not support the conclusion of Bolam and Donaldson.

C. Determination of temperatures at which colour change occurs but conductivity does not decrease at all in mixtures of silver chromate in gelatine of different p_H .—The results of these experiments are given in the following table.

TABLE III.

Concentration of gelatine = 3%.

Total volume = 16 c.c. [2X c.c. of electrolyte + 4.4 c.c. of 3% gelatine + (16 - 2X - 4.4) c.c. conductivity water].

c.c. of electrolyte (X)	p _H of gelatine	Temperature at which red colour appears but conductivity does not change
3.5	5.45	40° C.
	5.75	50
	6.00	40
	6.25	30
4.0	5.25	50
	5.45	55
	5.75	60
	6.00	50
	6.25	40
4.5	5.00	55
	5.25	60
	5.45	65*
	5.75	65
	6.00	55
	6.25	45

* The temperature, at which colour change occurs but conductivity does not decrease might be about 62° to 63° C. in this case.

It will appear from the table that for each concentration of the reactants the temperature at which no change in conductivity will occur in spite of a change in colour is highest for gelatine of p_H 5.75, it being lower for higher or lower values of p_H. It has been stated in Section B that the inhibitive power of gelatine is minimum for p_H 5.75. In Section A it is suggested that the degree of dispersity of gelatine might be increasing with a rise of temperature. It thus appears possible that the degree of dispersity of gelatine might be smallest for p_H 5.75—hence minimum inhibitive power—because the temperature at which colour change occurs but conductivity does not decrease is highest for that value of p_H. There is, however, no direct evidence to support this statement.

In each case for temperatures lower than those given in Table III, the conductivity will decrease either simultaneously with a change of colour or sometime after it.

D. Influence of changes in concentration of gelatine on the conductivity of silver chromate.—The results of these experiments are given in Table IV.

TABLE IV.

Temperature of experiments = 30° C.

p_H of gelatine = 5.45.

Total volume = 16 c.c. [2X c.c. of electrolyte + 2Z c.c. of 3% gelatine + (16 - 2X - 2Z) c.c. of conductivity water].

c.c. of electrolyte (X)	c.c. of 3% gelatine (Z)	% of Ag_2CrO_4 in ionic condition before red colour appears	% of Ag_2CrO_4 in ionic condition after red colour appears and when conductivity does not change further on standing	Time for appearance of red colour in minutes	Time when conductivity begins to decrease in minutes
3.5	1.0	95	43	5	6
	1.5	92	51	52	54
	2.0	89	60	225	250
	2.2	87	69	300	330

It will appear that the time for the appearance of red colour increases with an increase in the amount of gelatine and that although the colour change and decrease in conductivity occur more or less simultaneously when the amounts of gelatine are relatively small, the conductivity decrease occurs later and later than colour change as the amount of gelatine increases. These changes become intelligible if we examine the values given in columns 3 and 4 of the table; the degree of supersaturation, as judged roughly from the difference in the values of % of silver chromate in ionic condition before and after the appearance of red colour, has decreased with an increase in the amount of p_H .

From the trend of the values given in columns 3 and 4 it will be clear that for a certain amount of gelatine (more than that contained in 4.4 c.c. of 3% gelatine solution), the % of silver chromate before and after the appearance of red colour will be the same, *i.e.*, the conductivity will not decrease in spite of appearance of red colour. This amount of gelatine will be different for different concentrations of the reactants.

The percentage of silver chromate in ionic condition before the appearance of red colour decreases with an increase in the amount of gelatine. This

is due to the fact that as the amount of gelatine increases the amount of silver chromate removed by it either as a result of adsorption or chemical interaction also increases.

The continuous increase in the percentage of silver chromate in ionic condition after the appearance of red colour with an increase in the amount of gelatine is due to the fact that a relatively large amount of silver chromate is thrown out when the amount of gelatine is relatively small.

Summary.

Changes in the conductivity and colour of silver chromate in gelatine solution have been studied. It is observed that by suitable adjustment of the (i) temperature of the experiments, (ii) p_H of gelatine, (iii) concentration of the reactants ($AgNO_3$ and K_2CrO_4) and (iv) amount of gelatine, the conductivity may (a) not decrease at all till the colour remains yellow, (b) decrease sometime after the colour change or (c) not change at all in spite of the colour change.

In the end we would like to mention that our preliminary experiments on the precipitation of lead iodide in agar have shown that the (a) temperature at which the experiments are carried out, (b) p_H of agar, (c) amount of agar and (d) concentration of the reactants [$Pb(NO_3)_2$ and KI] have a very marked influence upon the times when the colour change and decrease in conductivity take place⁷ as in the case of precipitation of silver chromate in gelatine.

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- ⁶ Desai and Naik, *J. Univ. Bombay*, 1933, 2 (2), 90.
- ⁷ See in this connection Bolam, *Trans. Faraday Soc.*, 1928, 24, 463; *ibid.*, 1930, 26, 133; and Chatterjee and Dhar, *J. Indian Chem. Soc.*, 1930, 7, 177.