THE PRECIPITATION OF SILVER CHLORIDE FROM AQUEOUS SOLUTIONS

PART 6.—KINETICS OF DISSOLUTION OF SEED CRYSTALS

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The dissolution of silver chloride seed crystals into subsaturated solutions of silver chloride has been studied by a conductimetric method at 15, 25 and 35° and at various [Ag+]/[Cl−] ratios. Evidence is advanced that the process is one of diffusion and for the most part it follows a first-order equation.

Since the publication of Nernst's theory of heterogeneous reactions,[1] a number of experimental investigations of dissolution processes have been made. Noyes and Whitney [2] had already discovered that the dissolution of rods of benzoic acid and lead chloride followed an equation involving the first order of the subsaturation and later workers [3] found similar equations to hold for the dissolution of a number of metals in acids.

The Nernst theory of diffusion undoubtedly contains a number of assumptions which are not entirely correct. Thus it assumes that there is a linear concentration gradient confined to a thin layer of solution adhering to the surface and that the thickness of the diffusion layer so formed is independent of the viscosity of the solution and of the temperature. The assumption that the diffusion layer is stationary with respect to the surface has been criticized by a number of workers who advanced experimental evidence that fluid motion persists down to very short distances from the solid surface, if not to the surface itself. Despite these criticisms there is equally strong evidence in certain cases in favour of a stationary layer of liquid adjacent to a solid surface.[4]

In continuation of the previous work,[5] the rates of dissolution of silver chloride into subsaturated solutions have been measured at 15, 25 and 35° under various conditions of stirring and at equivalent and non-equivalent concentrations of silver and chloride ions.

EXPERIMENTAL

The conductivity apparatus and the preparation of materials have been described previously.[6] Seed suspensions contained 0·5 to 1·2 mg/ml of crystals of side 2-7 μ. Mobility and solubility data at 15 and 35° were those reported earlier.[5] Most of the dissolution experiments were carried out using a conductivity cell stirred by an efficient rotary four-bladed glass stirrer. In order to alter the dynamics of the fluid flow in the stirred system, some 30 experiments were also made using a glass disc stirrer sealed to the end of a glass rod driven up and down by a vibratory motor (Shandon Scientific Co.). The maximum amplitude of the oscillations was only about 0·03 in. so that the disc could be set at a fixed position in the cell for each experiment. This eliminated slight positional errors in the measured resistance observed with the moving blade stirrer.

Subsaturated solutions of silver chloride were prepared by mixing silver nitrate and potassium chloride solutions. Their concentrations were such that when 4-6 mg of seed crystals were added, the subsequent rates of dissolution were not too fast for accurate measurement.

Some dissolution experiments were also made with silver chromate. Potassium chromate was substituted for potassium chloride and after measuring the final pH of the cell solutions, corrections were applied for the presence of $HCrO_4^-$ ions as described previously.[7]

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RESULTS

Experiments at 25° employing rotary stirring (subscript r) and turbulent stirring (subscript t) are summarized in table 1 in which % subsaturation is expressed as 10^2 (sol. product—initial conc. product)/sol. product.   Typical smooth curves obtained on plotting (resistance)$^{-1}$ against time after the addition of seed crystals are shown in fig. 1. The rates of solution at any instant were obtained from the slopes of these curves and in fig. 2, these are plotted against $(c_0 - c)$ where c_0 is the solubility value.
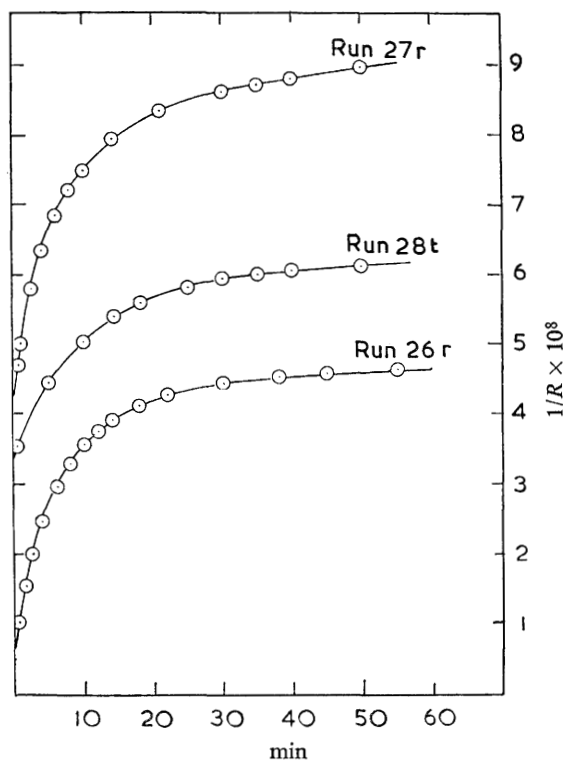
FIG. 1.—Time plots of $1/R$.

The equation

$$dc/dt = ks(c_0 - c) \qquad (1)$$

is seen to be obeyed very satisfactorily and values of ks are included in table 1.

TABLE 1.—DISSOLUTION AT 25°; $[Ag^+]/[Cl^-] = 1$

expt. no	initial concentrations (mole/l.)			seed susp.	% sub-saturation	ks
	$[Ag^+] \times 10^5$	$[Cl^-] \times 10^5$	$[Ag^+][Cl^-] \times 10^{10}$			
6_r	1·115	1·115	1·244	A	30	0·168
8_r	1·116	1·115	1·244	A	30	0·162
9_r^*	1·115	1·115	1·244	A	30	0·112
26_r	1·116	1·116	1·245	B	30	0·126
27_r	1·116	1·116	1·245	C	30	0·140
46_r	1·116	1·115	1·244	D	30	0·120
28_t	1·115	1·115	1·244	H	30	0·09
29_t	1·114	1·114	1·241	H	30	0·08
35_t	1·1125	1·1125	1·238	H	31	0·09

* stirring rate reduced from normal 600 rev/min to 320 rev/min.

Since the total amount of silver chloride dissolved during a run was only about 4 % of the weight of seed crystals present, changes in surface area, s, could be neglected.

A number of experiments were made in which the initial ionic ratio $[Ag^+]/[Cl^-]$ was not unity. Some of these are summarized in table 2 and in fig. 3, the rates of solution are plotted against Δ, the amount of silver chloride to be dissolved before equilibrium is
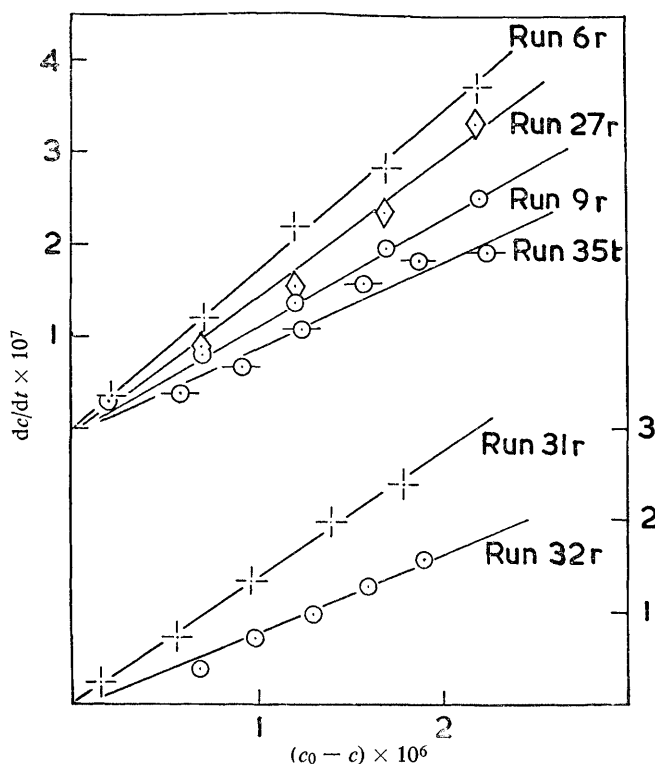

FIG. 2.—Rate of dissolution of silver chloride plotted against (c_0-c); $[Ag^+] = [Cl^-]$.

reached; when $[Ag^+] = [Cl^-]$, $\Delta = (c_0-c)$. The equation $dc/dt = k's\Delta$ is followed in a number of cases but there is a tendency for the rate to fall off during dissolution.

TABLE 2.—DISSOLUTION AT 25°C; $[Ag^+]/[Cl^-] \neq 1$

expt. no	initial concentrations (mole/l.)			ionic ratio	seed susp.	% sub-saturation
	$[Ag^+]\times 10^5$	$[Cl^-]\times 10^5$	$[Ag^+][Cl^-]\times 10^{10}$			
12_r	1·577	0·789	1·244	2·0	A	30
13_r	0·789	1·577	1·244	0·5	A	30
10_t	1·696	0·850	1·458	2·0	E	19
33_t	1·577	0·789	1·244	2·0	H	30
31_t	1·930	0·652	1·258	3·0	H	29
30_t	0·652	1·930	1·258	0·3	H	29
32_t	0·652	1·930	1·258	0·3	H	29
34_t	2·231	0·558	1·248	4·0	H	30
20_t	0·592	2·366	1·400	0·25	F	22
21_t	0·592	2·366	1·400	0·25	F	22

The results of experiments at 15 and 35° are given in table 3. As is seen in fig. 2, eqn. (1) is again obeyed.

Three runs were made of the dissolution of silver chromate seed crystals into sub-saturated solutions of silver chromate. Parallel pH runs exactly analogous to those in the

crystallization work [7] were carried out, and it was found that for dissolution as well as for crystallization, the pH was constant to within ± 0.01 during the run. From the pH of the cell solution at the end of each dissolution experiment, $\alpha = [HCrO_4^-]/[CrO_4^{2-}]$ was obtained
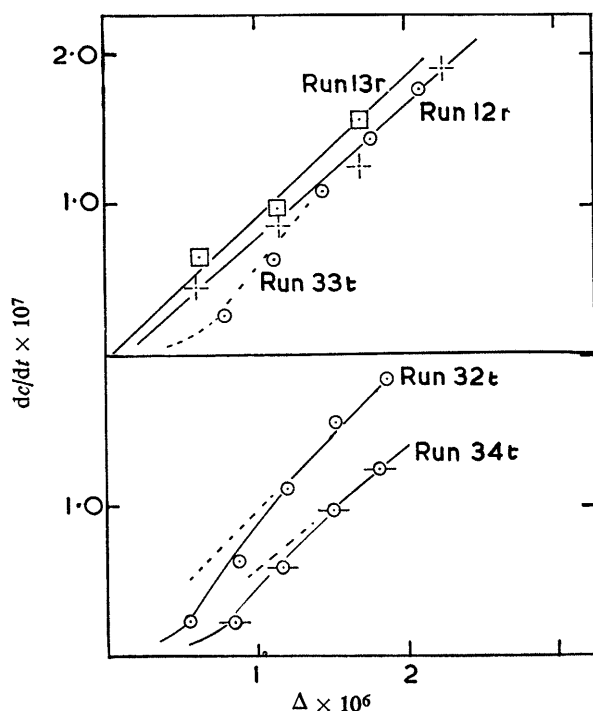

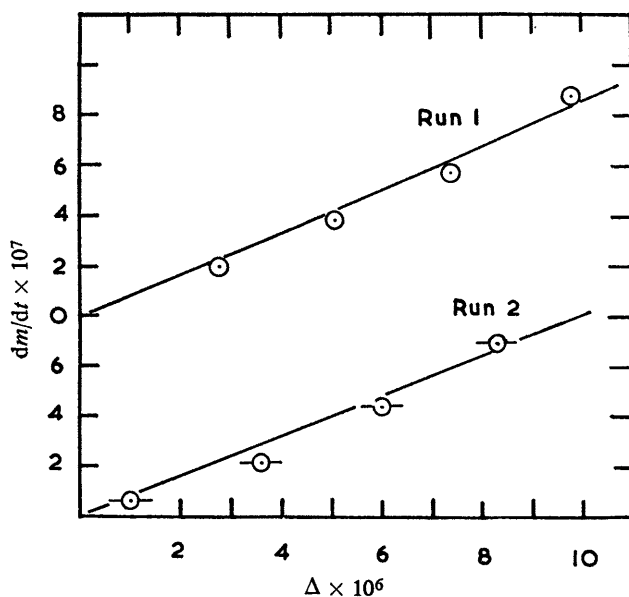FIG. 3.—Rate of dissolution of silver chloride plotted against Δ; $[Ag^+] \doteqdot [Cl^-]$.

FIG. 4.—Rate of dissolution of silver chromate plotted against Δ.

and the changes in ionic concentrations $\delta[Ag^+]$ and $\delta[CrO_4^{2-}]$ during dissolution were calculated from the observed specific conductivity as described previously.[7] The data are given in table 4 and plots of dm/dt against Δ are shown in fig. 4. It is seen that for silver chromate the dissolution also follows first-order kinetics.

TABLE 3.—DISSOLUTION AT 15 AND 35°

expt. no.	temp.	initial concentrations (mole/l.)			seed susp.	% sub-saturation
		$[Ag^+] \times 10^5$	$[Cl^-] \times 10^5$	$[Ag^+][Cl^-] \times 10^{10}$		
32_r	15	0·618	0·618	0·382	C	0·080
33_r	15	0·618	0·618	0·382	C	0·088
29_r	35	1·800	1·800	3·240	C	0·141
31_r	35	1·813	1·814	3·289	C	0·138

TABLE 4.—DISSOLUTION OF SILVER CHROMATE AT 25°

expt. no.	pH	initial concentrations (mole/l.)			% sub-saturation
		$[Ag^+] \times 10^4$	$[CrO_4^{2-}] \times 10^4$	$[Ag^+]^2[CrO_4^{2-}] \times 10^{12}$	
1	7·6	1·60	0·74	1·89	31
2	7·2	1·66	0·69	1·91	30
3	6·9	1·71	0·61	1·78	35

DISCUSSION

Although crystallization of silver chloride and silver chromate under similar conditions has been found to follow second- and third-order equations respectively,[6, 7] the dissolution of both salts is a first-order reaction. This is in conformity with the results of most other workers which point to dissolution being a diffusion controlled process. The rate is proportional to the total surface area of seed crystals present. Assuming the seed crystals to be uniform cubes, the rate constant, 0·140, of expt. 27, becomes 0·120 when corrected for the difference in surface area of seed crystals used in expt. 26 and 27. This compares favourably with the value 0·126 found for expt. 26.

Previous study of the solution of silver chloride seed crystals into water[5] gave 3/2-order kinetics at 25° and it was suggested that this may have been due to the concentration gradient surrounding the particles being a significant fraction of the mean distance between particles. In the present work, when the initial subsaturation was increased to about 70 % the process tended to follow a kinetic equation of a higher order then unity and it would seem that this effect may be dependent upon the size of the concentration gradient at the crystal surface, notwithstanding the Nernst assumption that the diffusion layer is of constant thickness.

It is interesting to note that the kinetics are not affected by the nature of the stirring : the vibration method indeed produces considerable turbulency. Equations relating the rotary stirring rate of diffusion controlled dissolution reactions with the rate constant k are usually of the form $k \propto (rev/min)^a$, values[8] of a ranging from 0·56 to 1·0. When stirring rate was reduced from the normal 600 rev/min (expt. 6 and 8) to 320 rev/min (expt. 9), the reduction in k corresponds to $a = 0·6_1$.

A more important test of Nernst's theory is afforded by the influence of temperature upon the rate of dissolution. The activation energy E_A may be derived graphically from the equation

$$\ln k = \ln A - (E_A/RT)$$

and the slope of the good straight line obtained on plotting log ks against $1/T$ gives an E_A of 5 kcal. This is very close to the activation energy for diffusion, 4·5 kcal and again points to diffusion being the controlling mechanism.

When either ion is in excess, it is seen from fig. 3 that the rate of dissolution falls off more rapidly than would be expected from a first-order equation ; the effect is

more noticeable when Ag^+ ion is in excess. When $[Ag^+] = [Cl^-]$, however, the process follows eqn. (1) for at least 96 % of the available reaction. Adsorption of the ion in excess will begin immediately on adding the seed crystals to the sub-saturated solution. Since it is unlikely that adsorption equilibrium will be maintained during the reaction, the process of dissolution will be opposed by that of adsorption and the surface will not be allowed to attain the potential necessary for the optimum release of Ag^+ and Cl^- ions in equal numbers. The result is a lowering of the rate of dissolution. Differences in the relative rates of adsorption of Ag^+ and Cl^- ions at the surface may account for the much larger lowering of dissolution rate when Ag^+ ions are in excess. Unfortunately the rates of adsorption are not known at present but it is hoped that some data may be available soon. It is interesting that the effect has not been detected previously in dissolution studies since these were usually followed for only 50-60 % of the available reaction in solutions containing stoichiometric proportions of the lattice ions.

[1] Nernst, *Z. physik. Chem.*, 1904, **47**, 52.
[2] Noyes and Whitney, *Z. physik. Chem.*, 1897, **23**, 689.
[3] e.g. King and Braverman, *J. Amer. Chem. Soc.*, 1932, **54**, 1744.
    King and Schack, *J. Amer. Chem. Soc.*, 1935, **57**, 1212.
[4] King and Brodie, *J. Amer. Chem. Soc.*, 1937, **59**, 1375.
    Antweiler, *Z. Elektrochem.*, 1938, **44**, 719.
[5] Davies and Nancollas, *Trans. Faraday Soc.*, 1955, **51**, 818.
[6] Davies and Jones, *Faraday Soc. Discussions*, 1949, **5**, 105.
[7] Howard and Nancollas, *Trans. Faraday Soc.*, 1957, **53**, 1449.
[8] Bircumshaw and Riddiford, *Quart. Rev.*, 1952, **6**, 157.