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TEMPERATURE DEPENDENCE OF
SILVER-SILVER CHLORIDE EXCHANGE

By
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Department of Chemistry

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T. W. Olcott

October 12, 1956

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U. S. ATOMIC ENERGY COMMISSION

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ABSTRACT

The temperature dependence of the silver-silver chloride exchange has been studied at 2°, 26°, 38°, 53°, 64°, 74°, 84° and 96°C. using radioactive silver-110. The silver chloride is present as a thin coating on a platinum gauze electrode. The preparation of the electrode, the exchange procedure, the results of the experiments and the errors inherent in the method used are discussed in detail.

TEMPERATURE DEPENDENCE OF SILVER-SILVER CHLORIDE EXCHANGE

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A. Langer (1) originally studied the exchange of radioactive silver ion with solid silver chloride. Sunderman and Meinke (2) developed a separation method for radioactive silver involving this exchange reaction and made a preliminary study (3) of the temperature dependence of the exchange at 25°C. and 95°C. This paper deals with the observed temperature dependence and related phenomena of this first order reaction through the range of 2°C. to 96°C.

A known amount of silver-110 in 2 M nitric acid solution was contacted in a tube with a platinum gauze on which 10 mg. of silver chloride had previously been plated. The solution was stirred magnetically. The gauze was removed at various intervals and counted; then recontacted as the exchange rate seemed to warrant. The percent exchange after each contact was determined by comparing with the activity found on the gauze after thirty minutes contact. Since the slowest exchange observed showed a half time of exchange of 2 minutes, this 30 minute interval did represent 100% exchange.

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APPARATUS

Electrolytic and exchange vessels were 6" pyrex test tubes cut to 3 1/2" to accomodate the electrodes and to situate them in proximity to the stirrer. These tubes were flattened on the bottom to facilitate the stirring and had a capacity of about 18 ml. Magnetic stirrers consisted of 5 mm. pieces of iron nail sealed in a 6-7 mm. section of soft glass tubing.

Platinum gauzes 10 mm. diameter, 30 mm height, 52 mesh per inch and weighing approximately 2.8 gram were used as a support for the silver chloride. The other electrode consisted of a small platinum wire.

The heating element for the exchange solution consisted of a two-foot Briskeat Flexible Heating Tape which was wrapped around the exchange tube. The current in the tape (and thus the temperature) was controlled by a Variac and was measured with a calibrated laboratory thermometer. For the measurement at 2°C., the tube was placed in an ice bath contained in a stainless steel beaker so that magnetic stirring could be maintained through the container.

A battery eliminator, Heathkit, Model BE-4, Heath Company, Benton Harbor, Michigan, was used for the source of DC current in electroplating.

A scintillation well counter, Nuclear Instrument and Chemical Corporation, Model DS-3 with 2-in. additional lead shielding was used for counting in conjunction with a Model 162

scale of 128 scaler from the same company, modified to count with preset time and preset count and to reset automatically.

PREPARATION OF THE ELECTRODES

One ml. of 5 N sodium hydroxide, 7.6 mg. of silver carrier (12 drops of laboratory stock solution) and 8 ml. of 3 N sodium cyanide were placed in a cell with the magnetic stirrer, the electrodes introduced, and the voltage set at approximately 4 volts on the battery eliminator. Since the voltage on this instrument is not well calibrated and may vary, the procedure followed was to increase the voltage until the plating reaction commenced and then increase the voltage 1/4 volt more. Electrodeposition was allowed to continue for at least 5 minutes. When the voltage was too high or the stirring ceased for some reason, numerous side reactions took place, tinting the solution amber and generally resulting in a loosely adhering electrode surface which flaked off readily.

To transform this silver electrode into silver chloride, the electrode was washed in water and placed in a similar cell containing a 0.05 N hydrochloric acid solution (10 ml. of water and one drop of concentrated hydrochloric acid), and one drop of 10% hydroxylamine hydrochloride. The current polarity was reversed and the voltage set at 1.5 volts. Again this was best determined by observing the minimum voltage necessary to blacken the anode. The blackening appeared initially and then gradually turned to a gray or red-gray tint. This coating probably indicated the formation of some type

of silver oxide. The current was stopped when the black coloration completely disappeared. If continued for too long a time or at too high a voltage, flaking and stringing of the coating was observed. Five minutes was found to be a maximum time for this conversion to the chloride. The electrode was then removed, washed with 1:1 nitric acid and used immediately or stored in 1:1 nitric acid. Neither Sunderman (3) nor this experimenter have observed aging effects over a period of 4 or 5 days when the electrodes were stored in this manner.

EXCHANGE PROCEDURE

The active solution containing about 10,000 counts per minute (well counter) of the silver-110 as the nitrate was placed in a tube containing 10 ml. of 2 M nitric acid, stirred, and allowed to reach thermal equilibrium. The heated silver chloride electrode (preheated or cooled to the desired temperature in another tube of distilled water) was rapidly and completely dipped under the surface of the solution, held there for the desired time while the stirring continued, and then rapidly removed. It was then rinsed with a drop or two of distilled water (which was returned to the active solution), put in a lusteroid tube and counted in the well counter to a probable error of about 0.4% (250 scalers on the 128 scale). For low activities 125 scalers were considered sufficient. The electrode was then again contacted, removed, counted and so on until the desired amount of data was obtained.

Initially, attempts were made to determine the amount of activity present after each contact by meticulous assaying of the tracer solution remaining by carefully pipetting known aliquots into counting tubes. However, this was found undesirable because tiny suspended, unexchangeable particles developed in the stock solution; because solubility errors were in no way compensated; and because the assays proved time-consuming.

Instead it was finally decided to run each gauze for a total of 30 minutes of contact time no matter how many smaller intervals had been used. The amount of activity on the gauze at the end of 30 minutes was considered to be the value for 100% exchange. Thus the values for (100% - % exchange) can be obtained by merely subtracting the activity measured on the gauze after each contact period from the 100% value.

There is a great tendency for losses through handling to become large after four contacts so that one electrode generally was not recontacted more than three times in addition to the terminal counting. If more data points were required at a given temperature another run was made. For a given run, all activity measurements were made in the same lusteroid (rimmed) tube which was assayed for activity before and after each run.

After thirty minutes contact silver nitrate was added to the remaining depleted tracer solution and silver chloride precipitated with hydrochloric acid. The tube was rinsed several times and the rinsings added to the solution.

This precipitate contains the small amount of "residual activity", the activity present in solution after 100% of the silver theoretically should have been exchanged (excluding solubility considerations). The activity of this precipitate was determined in the well counter and normalized to equivalent silver activity on the gauze. The factor used in this normalization is given in Table II and was determined by comparing the activity of precipitated silver chloride with the activity of the same amount of silver plated on an electrode. It was found to be reproducible to within $\pm 1\%$ if the initial placement of the gauze when silverplating was constantly $1/8"$ below the surface of the electrolyte.

Silver chloride activity was removed instantaneously from the gauze with sodium cyanide so that special cleaning procedures were not required.

RESULTS

First order isotherms of $\log (\% \text{ activity remaining})$ vs. time of contact were drawn and half-times determined for a number of different temperatures. The results of these experimental runs are given in Table I and plotted in Figs. 1-3. Figs. 1 and 2 show the points listed in the Table. Certain of the points especially for values below 10% scatter considerably. Another cause for the scatter of points is too many contacts on one electrode. Fig. 3 gives the best lines drawn through the data points for all temperatures studied.

Since the relationship $D_T = D_0 e^{-Q/RT}$ holds for this reaction and since time is indirectly proportional to D , a graph of log time at a given exchange ratio vs. $1/T$ should give a straight line (1). These values are given in Table III and Fig. 4 shows this plot for 50% and 90% exchange.

Good stirring is essential to eliminate diffusion control of the exchange. The effects of insufficient stirring on an exchange isotherm are shown in Fig. 5. The effects of excessive contacts of the electrode and of the inhibiting action of drying the electrode with acetone between contacts are shown in Fig. 6.

In one case (at 53°C.) the exchange has also been calculated as a percentage of the activity found on the gauze plus the "residual activity" found in the solution after thirty minutes. The difference in the exchange curves resulting from these two types of treatment of the data is shown in Fig. 7. The difference ranges from 0.5% to 2% per point depending on the temperature and the handling errors.

ERRORS

Counting errors are reported as probable errors and for 250 scalars on the 128 scale amount to $\pm 0.37\%$. The small errors inherent in the background count were disregarded. The effect of counting errors on an isotherm is shown in Fig. 8.

Errors in contact time are estimated at ± 2.5 seconds. These result from errors in coordination of clock and contact in addition to errors from unavoidable times of partial contact during the careful insertion and withdrawal of the electrode.

The error in temperature was estimated at $\pm 1.5^{\circ}\text{C}$. with one reservation. This reservation enters in because, after the first contact, the gauze must be heated back to the appropriate temperature by the solution, resulting in a lowering of the temperature of the solution. Since the specific heat of platinum is fairly small, this should be rapid and slight but the coating might have a substantial insulating effect. Experimentation with a thermometer stem indicated this drop to be $1\text{-}2^{\circ}\text{C}$. with temperature regaining normalcy after one minute.

The resultant error from the solubility of silver chloride can only be guessed. My estimate is that the error is 0.2 - 1.5% from 0° - 50°C . and 1.5 - 3% above 50°C . There is a twenty-fold increase in solubility from 15° to 100° ; 0.015 mg. of silver chloride dissolves in 10 ml. of water at 20°C ., which is 0.15% of the electrode. Therefore, between 2 and 3% of the silver chloride dissolves at 100°C . A 10 mg. electrode surface was used since smaller electrodes would introduce larger solubility errors and larger electrodes were found to flake and chip readily.

Sunderman (3) found a fairly consistent error of 0.3-0.5% resulting from normal handling of the electrodes. Naturally, any chipping from the gauze would greatly increase this figure. When chipping became apparent during a run by the fluctuation of the plotted data, new runs on new electrodes were made.

It might be said here that wide fluctuations result from these errors when the values get below 10% so that the isotherms were almost exclusively determined by the points in the first cycle of the semi-log graphs. Values above 95% exchange have little or no significance other than as an indication of a nearly complete exchange. All isotherms given in Figs. 1 - 3 are a composite of one or more runs.

SUGGESTIONS FOR POSSIBLE IMPROVEMENT

Naturally, methods for improvement are based on the errors discussed above. Therefore, the important questions are: How can one improve temperature control? Minimize solubility? Minimize handling errors? Minimize counting errors? Minimize errors in time of contact?

The latter two are the easiest to answer. The counting errors are relatively minor in respect to the others and could be improved by longer counting times, although they are already rather small. It is my belief that drying effects would more than over-ride any improvement here so that no more improvement could be attained. Counting in a solution which would not affect the exchange and in which silver chloride is not soluble could alter this, but it would only be worthwhile when the more important errors have been minimized. To minimize errors in time only, some mechanism for rapid dipping with a trip mechanism for clock control could be used. Even then, it is doubtful that any noticeable improvement would be offered over a steady-handed manual method.

The other three errors can readily be reduced. The most obvious method of improvement would be the use of a thermostatted bath. The Variac-Heating Tape method is crude, to say the least, since fluctuations in voltage and evaporation cause the temperature to fluctuate. Also, the time required for the bath to reach equilibrium is as long as 2 hours, greatly increasing the time involved per run. A larger exchange chamber could also be used so that temperature loss resulting from heating the electrode would not be as great. In this case, solubility losses would also increase, so that it would be necessary to see if improved temperature control would more than compensate for this.

Preheating of the electrode before each contact would also improve the temperature control. This could best be done in some solvent in which silver chloride is not soluble thus eliminating solubility errors. Heating must be done in liquids since direct heating diminishes the surface area and thus retards the exchange rate.

Solubility errors also are great and can only be eliminated by the use of larger electrodes since smaller exchange vessels are not feasible. Difficulty was encountered with large electrodes but further experimentation on the preparation of these electrodes could result in a suitable method. Of course the dependence of the exchange on the size of the electrode coating would first have to be determined.

Lastly, to minimize handling errors, one or at the most two contacts, other than the 30 minute terminal contact, could be set as the maximum for each run. This would be laborious but yet accurate if solubility errors were minimized.

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TABLE I. Temperature Dependence of Silver-Silver Chloride Exchange

<u>Temperature</u>	<u>Run</u>	<u>Time of Contact</u>	<u>Net c/min.</u>	<u>% exchange</u>	<u>100-%Exchange</u>
2° C.	I	1 minute	3019	30.9	69.1
		2	4995	51.1	48.9
		3	6207	63.5	36.5
		4	7270	74.4	25.6
		6	8155	83.4	16.6
		54	9773	100	
		Residual Soln.	107		
	II	2	5002	51.9	48.1
		4	7406	76.9	23.1
		6	8602	89.3	10.7
		52	9634	100	
		Residual Soln.	88		
26° C.	III	1	5837	47.3	52.7
		2	8804	71.1	28.9
		4	11326	91.9	8.1
		6	12086	97.6	2.4
		12	12227	98.8	1.2
		30	12330	100	
		Residual Soln.	85		
		Stirrer	0		
	IV	6	11472	98.7	1.3
		8	11474	98.7	1.3
		30	11638	100	
		Residual Soln.	136		
	V	10	11892	99.8	.2
		13	11902	99.9	.1
		30	11915	100	
		Residual Soln.	71		
38° C.	II	1	6319	55.7	44.3
		2	9117	80.4	19.6
		4	10935	96.4	3.7
		6	11280	99.5	.5
		30	11342	100	
		Residual Soln.	46		
	III	3	10236	90.4	9.6
		5	11104	98.1	1.9
		7	11306	99.8	.2
		30	11324	100	
53° C.	I	0.5	5836	42.3	57.7
		1	9266	67.2	32.8
		2	12071	87.5	12.5
		3	13103	95.0	5.0
		5	13793	100	
		30	13793	100	
		Residual Soln.	142		
	II	0.75	6183	57.3	42.7
		1.5	8870	82.2	17.8
		2.5	10246	94.9	5.1
		30	10791	100	
		Residual Soln.	113		

TABLE I. (Continued)

<u>Temperature</u>	<u>Run</u>	<u>Time of Contact</u>	<u>Net c/min.</u>	<u>% exchange</u>	<u>100-%Exchange</u>
64° C.	I	0.5	5504	51.5	48.5
		1.5	9266	86.7	13.3
		2.5	10299	96.4	3.6
		3.5	10613	99.3	.7
		30	10687	100	
		Residual Soln.	94		
	II	0.75	6908	69.0	31.0
		2	9397	93.9	6.1
		3	9985	99.8	.2
		30	10008	100	
		Residual Soln.	56		
	III	0.5	5004	50.3	49.7
		1.25	8219	82.6	17.4
		2.25	9419	94.7	5.3
		3.25	9735	97.9	2.1
		27	9945	100	
		Residual Soln.	56		
74° C.	I	0.5	5138	51.4	48.6
		1.25	8427	84.3	15.7
		2	9573	95.7	4.3
		30	9994	100	
		3	9737	97.4	2.6
		Residual Soln.	41		
	II	0.75	6741	69.8	30.2
		1.5	8657	89.6	10.4
		2.25	9258	95.9	4.1
		3	9468	98.0	2.0
		30	9658	100	
		Residual Soln.	85		
	III	0.75	7047	74.6	25.4
		1.5	8798	93.1	6.9
		2.25	9338	98.8	1.2
		30	9451	100	
		Residual Soln.	180		
85° C.	II	0.67	6937	71.9	28.1
		1.33	8724	90.5	9.5
		2	9203	95.4	4.6
		30	9643	100	
		Residual Soln.	157		
	III	0.5	5685	64.1	35.9
		1	7676	86.5	13.5
		1.75	8542	96.3	3.7
		2.5	8659	97.6	2.4
		30	8873	100	
		Residual Soln.	202		
	II	0.75	7036	75.4	24.6
		1.25	8522	91.3	8.7
		2	9013	96.6	3.4
		30	9333	100	
		Residual Soln.	171		
96° C.	I	0.5	5685	64.1	35.9
		1	7676	86.5	13.5
		1.75	8542	96.3	3.7
		2.5	8659	97.6	2.4
		30	8873	100	
		Residual Soln.	202		
	II	0.75	7036	75.4	24.6
		1.25	8522	91.3	8.7
		2	9013	96.6	3.4
		30	9333	100	
		Residual Soln.	171		

TABLE II. Geometry Factor for Counting:

Activity of reprecipitated AgCl
Activity of AgCl on Pt electrode

<u>Run</u>	<u>Value</u>
1.	1.212
2.	1.203
3.	1.207
4.	1.211
5.	1.220
Average	1.210

TABLE III. Times for Partial Exchange

<u>Temperature °C.</u>	<u>Time for 50% Exchange (Sec.)</u>	<u>Time for 90% Exchange (Sec.)</u>
2° ± 1.5°	115	380
26	66	220
38	51	166
53	36	120
64	31	100
74	28	92
85	23	85
96	22	71

Fig. 1 Temperature dependence of silver-silver chloride exchange.

Fig. 2 Temperature dependence of silver-silver chloride exchange.

Fig. 3 Temperature dependence of silver-silver chloride exchange.

Fig. 4 Log T vs $1/T$ plot.

Fig. 5 Effects of stirring on the exchange.

Fig. 6 Handling effects on the exchange.

Fig. 7 Two methods of measuring "100% activity".

Fig. 8. Measurement errors in the exchange.

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