TABLE II

EQUILIBRIUM FILM PRESSURE, π_e, SPREADING COEFFICIENT, $S_{L/S}$. FREE ENERGY OF EMERSION, $f_{E(SL)}$, AND WORK OF ADHESION $w_{A(SL)}$, BETWEEN LIQUIDS AND VARIOUS GRAPHITES (IN ERG CM.$^{-2}$)

Graphite (ash content), %	π_e	$S_{L/S}$	$f_{E(SL)}$	$w_{A(SL)}$
	A. Water			
10	56	−10	62	134
0.46	19	−47	25	97
Less than 0.004	19	−47	25	97
	B. Normal Heptane			
10	60	60	80	100
0.46	69	69	89	109
Less than 0.004	63	63	83	103

coefficient, free energy of emersion, and work of adhesion for the two pure graphites but would not change the negative sign of the spreading coefficient. In order that the spreading coefficient should change sign for the two pure graphites, it would be necessary for the contact angle to be less than 42°.

The relations observed with water, are somewhat unexpected; *i. e.*, a contact angle not zero, the adsorption of more than a monomolecular film, presumably not caused by capillary condensation, and the low value of the decrease of free surface energy. While all of these facts are compatible with the known thermodynamic relationships, it is difficult to conceive from a molecular point of view, how a thick film can be formed which is not duplex, *i. e.*, the contact angle equal to zero. It is hoped that when our calorimetric study of the water–graphite system is completed, additional facts may aid in clarifying the picture of the water-graphite system. For this reason, a detailed discussion is deferred until the facts become available.

Summary

1. The adsorption isotherms of water and *n*-heptane have been determined on two samples of graphite containing 0.46% ash by weight and less than 0.004% ash by weight. The latter sample had also been treated so that the surface should be free of any oxygen–carbon "complex."

2. The films of water became thicker than a monolayer at relative pressures above 0.9, attaining an average of thickness of three layers at the maximum pressures measured, 0.98.

3. A detailed study of the curve for low values of p/p_0 show that the adsorption curves are convex rather than concave to the pressure axis. The curves, however, flatten out when only a small fraction of a tightly packed monomolecular film has been adsorbed, whereas, for hydrophilic solids this occurs when enough gas to form a monomolecular layer has been adsorbed.

4. The spreading coefficient free energy of emersion and work of adhesion of water are found to be −47, 25 and 97 ergs cm.$^{-2}$, respectively, while for *n*-heptane the corresponding values are 69, 89 and 109 ergs cm.$^{-2}$.

5. The X-ray diffraction patterns of clean graphite were found to be identical with those for the solid saturated with water and *n*-heptane. The cell constants found are a_0 = 2.455 Å. and c_0 = 6.70 Å.

CHICAGO, ILLINOIS RECEIVED DECEMBER 17, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

The Stability of Chelate Compounds. III. Exchange Reactions of Copper Chelate Compounds

BY R. B. DUFFIELD[1] AND M. CALVIN

In previous papers of this series[1a,2] experiments were reported in which the relative stabilities of a series of copper chelate compounds were determined on the basis of measurements of chemical equilibrium. The present paper contains a report of experiments designed to determine the relative stabilities of the same series of copper chelates from kinetic measurements of the rate of their reactions. The reaction selected was the exchange reaction between the chelate and copper ion, the copper ion being marked by containing a radioactive copper isotope

$$\mathrm{Cu^{II}Ke_2} + \mathrm{Cu^{++*}} \longrightarrow \mathrm{Cu^{II*}Ke_2} + \mathrm{Cu^{++}}$$

indicated by the superscribed asterisk. Ke represents one equivalent of chelating substance usually filling two coördination positions of the metal.

A number of scattered experiments of this type are already in the literature[3,4,5,6] usually in connection with other problems, and no exchange between metal ions and a chelated metal has been studied in sufficient detail to determine its kinetics.

Experimental

Chelate Compounds.—The chelate compounds were made by the general methods of Pfeiffer.[7] Several not

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[1] Abstracted from the thesis submitted by R. B. Duffield to the University of California, Berkeley, in 1943, in partial fulfillment of the requirements for the Ph.D. degree.

[1a] Calvin and Wilson, THIS JOURNAL, **67**, 2003 (1945).

[2] Calvin and Bailes, **68**, May (1946).

[3] Long, THIS JOURNAL, **61**, 570 (1939); **63**, 1353 (1941).

[4] Flagg, *ibid.*, **63**, 557 (1941).

[5] Ruben, Kamen and Frankel, *J. Phys. Chem.*, **46**, 710 (1942).

[6] Ruben, Kamen, Allen and Nahinsky, THIS JOURNAL, **64**, 2297 (1942).

[7] Pfeiffer, Breith, Lubbs and Tsumaki, *Ann.*, **503**, 84 (1933).

described by him were made and analyzed in the usual fashion.

Pyridine.—J. T. Baker reagent grade pyridine was dried over potassium hydroxide and distilled through a Widmer column (b. p. 115.2–115.4°).

Organic Solvents.—Reagent grade used without further treatment.

Radioactive Copper.—The 12.8-hour activity of copper (Cu^{64})[8] can be produced by an n,γ reaction on Cu^{63}.[9] In this case it was made by exposing solid $CuAc_2 \cdot Py$ to slow neutrons on the 60-inch cyclotron at Berkeley. The neutrons were produced by the action of 13.7 Mev. deuterons on beryllium. This produced the 12.8-hour copper uncontaminated by other activities. A fraction of each bombarded portion of $CuAc_2 \cdot Py$ was followed on an electroscope or Geiger counter to check its decay. Through a time equal to four half-lives no measurable departure from the 12.8-hour half-life was ever found.

Procedure.—All the exchange experiments were run in pyridine solution. The method of measuring the rate of exchange was to mix a solution containing the chelate compound with a solution of copper acetate which had been made radioactive by neutron bombardment as described in the preceding section. After a certain length of time the chelate compound and the copper acetate were separated and the amount of activity in each was determined. This separation process in practice was a matter of some difficulty, particularly for those compounds which it was later found exchanged most rapidly and were most soluble.

An extraction method was worked out which served satisfactorily in most cases. A pyridine solution 0.0152 *M* in the chelate compound and another 0.0152 *M* in the radioactive copper acetate monopyridinate were made up and placed in a thermostat for one hour to come to temperature equilibrium. A 50-ml. glass-stoppered reaction flask was similarly brought to temperature. Twenty ml. of the solution of the chelate compound and 20 ml. of the solution of active copper acetate were then introduced into the reaction vessel and left in the thermostat the desired length of time. At the end of this time the solution was poured from the flask into a 100-ml. separatory funnel containing 20 ml. of chloroform and 20 ml. of water immediately added. This gave two layers, one of chloroform and part of the pyridine and the other of water and the rest of the pyridine. These two layers were separated and the chloroform layer extracted once more with 20 ml. of water and the water layer extracted once more with 20 ml. of chloroform. The two water solutions were then combined: they contained a small amount of the chelate compound and more than 98% of the copper acetate as indicated by a measurement of the radioactivity in blank experiments. The two chloroform solutions were also combined: they contained most of the organic compound, the exact amount to be measured in the next step.

Both the chloroform and water solutions were then made acid with acetic acid and about 1 g. of ammonium acetate added. Hydrogen sulfide was then run in to precipitate the copper as copper sulfide. (Hydrogen sulfide decomposes the chelate compounds immediately. The ammonium acetate was added to secure better coagulation of the colloidal copper sulfide.) Each solution was then boiled, centrifuged and filtered through a Büchner funnel so modified as to keep all the solid in the center of the filter. The copper sulfide was collected on a hard filter paper (Whatman no. 50) which had been previously weighed. The precipitate was washed thoroughly with water, then with acetone, dried in an oven and weighed again. The weight of the copper sulfide recovered from the chloroform solution gave the amount of the chelate compound found in the chloroform layer. The total amount recovered from both solutions checked any loss which might have occurred during the procedure. It was found by repeated trials that this method of analysis was precise to 5%. The samples of copper sulfide on the filter papers were then mounted on cards, covered with cellophane and their activity measured either on a Geiger counter or an electroscope.

A 20-ml. sample of the original pyridine solution of active copper acetate was also taken and a copper sulfide precipitate removed in the same way. This was also mounted on a card. Its activity represented the total amount introduced in the exchange experiment. It will be referred to as the "standard."

The radioactivities were measured on an electroscope or a Geiger counter depending on their strength. The electroscope used was of the Lauritsen quartz fiber type with a 3.5 mg. per square cm. aluminum window. The samples were measured by placing them immediately under the ionization chamber in a holder which kept them in a reproducible position. The background was measured before and after each series of measurements and was always between 0.001 and 0.005 scale division per second. The Geiger counters used were of the copper wall type with mica windows varying from 3 to 4 mg. per square cm. in thickness. The tubes were enclosed in a lead house and had backgrounds of 50 to 70 counts per minute. The background was measured before and after each series of measurements. A scale of eight circuit and a mechanical recorder were used.

Each sample and standard were counted four or five times over a period equal to one half-life; a plot was then made of the log of the counting rate versus the time. The activity of each sample at some convenient common time was then read off from this plot for the purpose of calculation.

No corrections were made for self-absorption of radiation. Cu^{64} decays by emission of β^- and β^+ particles and by K electron capture.[10] The energy of the β^- rays is 0.58 mev. and that of the β^+ is 0.66 mev.[11] Radiation of this hardness is transmitted almost completely by samples of the thickness measured.

The samples compared varied in thickness from 3.2 to 5.3 mg. per square cm. From an absorption curve published by Strain[12] it can be seen that this variation in thickness would produce an extreme variation in percentage of radiation transmitted of 3%. No correction was made for this.

This was the procedure followed for all experiments run at a concentration of 0.0152 *M*. In those experiments for which the concentrations were lower, separate solutions were made up and a new standard of radioactive copper acetate prepared corresponding to the amount of copper added in the experiment. The remainder of the procedure was the same.

Results

Regardless of the actual kinetics of the exchange reaction, the rate of appearance of the radioactivity in the compound which was originally inactive will be first order with respect to the radioactivity. This is generally recognized but its proof has appeared only once in the literature[13] and then only in outline and the final result obtained was in error. It has seemed worth while to go through the entire argument here.

Let the exchange reaction be represented by the following equation where the superscripts (*) refer to radioactive substances.

$$BX^* + AX = AX^* + BX$$

Let the concentrations be represented by

$$(AX)^* = x \quad (AX)^* + (AX) = a \quad x = x_\infty \text{ at } t = \infty$$
$$(BX)^* = y \quad (BX)^* + (BX) = b \quad y = y_\infty \text{ at } t = \infty$$

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[8] Van Voorhis, *Phys. Rev.*, **50**, 895 (1936).

[9] Heyn, *Physica*, **4**, 1224 (1937).

[10] Alvarez, *Phys. Rev.*, **54**, 486 (1938).

[11] Tyler, *ibid.*, **56**, 125 (1939).

[12] Strain, *ibid.*, **54**, 1023 (1938).

[13] McKay, *Nature*, **142**, 997 (1938).

TABLE I

EXCHANGE AT 25° FOR DERIVATIVES OF COPPER SALICYLALDEHYDE

Addendum	Copper sulfide fraction precipitated from Chelate Wt.	Activity[a]	CuAc$_2$ Wt.	Activity	Activity of standard	Δt	Ratio r	Exch., %	$t_{1/2}$
None	18	0.068	38	0.139	0.214	15 sec.	0.51	102	< 15 sec.
-Anil	22	.086	33	.145	.244	15 sec.	.465	93	< 15 sec.
-Methylimine	26	.123	32	.230	.345	15 sec.	.40	80	< 15 sec.
-1,8-Diiminonaphthalene	28	2401	27	3424	6200	2 min.	.39	78	1 min.
-Ethylenediimine	29	272	29	1600	1900	1 hr.	.145	29	2.1 hr.
-Ethylenediimine	29	1280	29	3700	5240	2 hr.	.245	49	2.1 hr.
-*o*-Phenylenediimine	25	10	31	1540	1600	4 hr.	.006	0	>4 hr.
-*p*-Phenylenediimine	24	0.005	33	1.020	1.040	3 hr.	.005	1	>3 hr.
-Ethylenediimine[b]	29	79	29	7389	7500	30 sec.	.0107	2	....
-Acetylacetone ethylenediimine[c]	..[d]	0.012	..	0.880	0.901	0.5 hr.	.013	2	....
-Acetylacetone ethylenediimine[c]	..	270	..	7200	7850	4 hr.	.038	8	37 hr.
-*o*-Phenylenediimine at 50°	26	0.189	32	1.29	1.56	4 hr.	.135	27	9 hr.
-Ethylenediimine at 0°	..[d]	.119	..	1.32	1.50	12 hr.	.08	16	90 hr.

[a] Fractional numbers are electroscope scale divisions per second, others are Geiger counts per minute. [b] Solution allowed to stand for fifteen minutes after addition of chloroform before separation of layers. [c] Concentration of solutions 0.0076 *M* (limited to this by solubility of chelate compound). This compound has acetylacetone as the carbonyl component in place of salicylaldehyde. [d] Extraction of chelate into chloroform layer previously measured and found to be complete. Samples not weighed.

The rate of appearance of x is some function of a and b.

$$\mathrm{d}x/\mathrm{d}t = k\alpha(a)\beta(b)$$

Let the rate of the reaction be R, where R is a function of the total concentrations, etc., and will be a constant in any given run.

$$\frac{\mathrm{d}x}{\mathrm{d}t} = R\frac{y}{b} - R\frac{x}{a} = \frac{R}{ab}(ay - bx)$$

Since $y = x_\infty + y_\infty - x = x_\infty + x_\infty\frac{b}{a} - x$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{R}{ab}\left[a(x_\infty + x_\infty\frac{b}{a} - x) - bx\right]$$

$$= \frac{R}{ab}[(a + b)(x_\infty - x)]$$

$$\frac{\mathrm{d}x}{x_\infty - x} = \frac{R}{ab}(a + b)\mathrm{d}t$$

$$-\ln(x_\infty - x) = \frac{R}{ab}(a + b)t + \text{const}$$

since at $t = 0, x = 0$; const $= -\ln x_\infty$

$$-\ln\left(1 - \frac{x}{x_\infty}\right) = \frac{R}{ab}(a + b)t$$

This is the usual form of the first-order rate law. It provides a convenient check for the experimental data: in Fig. 1 is plotted the logarithm of the quantity one hundred minus the per cent. exchange $(100 - \frac{x}{x_\infty}100)$ which had taken place after various times, t, against t, for one experiment with copper salicylaldehyde ethylenediimine.

In Table I are given the rates of exchange which were found for seven compounds. In the second and fourth columns are given the weights of copper sulfide obtained from the chelate compound and from the copper acetate. If complete recovery had been attained, the weight of each of these fractions would have been the same, namely, 29 mg., since the concentrations of chelate compound and copper acetate were the same in the solution, 0.0152 *M* (except in the case of the copper acetylacetone ethylenediimine where the concentration was 0.0076 *M*). The third, fifth, and sixth columns give the activity found in each of these fractions and in the standard. The seventh column gives Δt, the length of time over which the exchange was allowed to proceed. The percentage exchange which has taken place is measured by the specific activity of the recovered compound, *i. e.*, the exchange has gone to completion when the specific activity of the chelate compound has become equal to that of the copper acetate. In this case, since the total number of moles of chelate compound is equal to the number of moles of copper acetate, at complete exchange one half of the original activity will be found in the chelate compound. The observed activity in this fraction, however, must be corrected to what would have been found if all the copper from this chelate compound had been recovered, *i. e.*, the observed activity must be multiplied by 29 divided by the actual number of milligrams of copper sulfide recovered from the chelate compound. The ratio of this corrected activity to the activity of the standard is labelled r and is recorded in the eighth column of Table I. A value of 0.5 for r

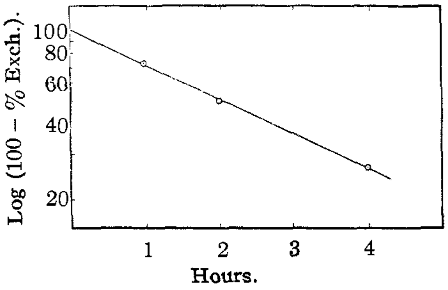


Fig. 1.—Copper salicylaldehyde ethylenediimine exchange.

corresponds to complete exchange. In column nine is given the percentage exchange found and in the last column the time for the exchange to go half way to completion.

The experiment for copper salicylaldehyde-ethylenediimine with Δt = 30 sec. was run to ascertain that, in a case where the exchange was proceeding at a known rate in pyridine solution, the addition of the chloroform did not produce any rapid interchange.

Results at Other Temperatures.—Also in Table I are the results of two experiments at temperatures other than 25°, one for copper salicylaldehyde-*o*-phenylenediimine at 50°, and one for copper salicylaldehydeëthylenediimine at 0°. From the latter result an apparent heat of activation of 23 kcal. can be obtained.

TABLE II

TIME OF HALF-EXCHANGE WITH COPPER SALICYLALDEHYDE-ETHYLENEDIIMINE AT VARIOUS CONCENTRATIONS PYRIDINE SOLUTION; TEMP., 25°

	Activity of CuS[a] fraction pptd. from						
Concn.	Chelate	$CuAc_2$	Standard	Δt, hr.	r	% Exch.	$t_{1/2}$, hr.
0.0152	272	1600	1903	1	0.145	29	2.1
.0076	483	..	4210	2	.114	23	5.25
.0076	281	2150	2500	2	.111	22	5.8
.0030	352	..	3560	4	.099	20	12
.0030	397	3062	3521	4	.113	22	11
.0015	246	..	1810	12	.134	27	26

[a] Weight of CuS found from each fraction not measured since earlier experiments had proved this separation to be quantitative (see Table I).

Results at Other Concentrations.—In Table II is shown the dependence of the rate of exchange for copper salicylaldehydeëthylenediimine on the concentration. In each case the concentration of the chelate compound was equal to that of the copper acetate. These concentrations are in the ratios 10:5:2:1. In Fig. 2 have been plotted the observed half-lives of exchange against the reciprocal of the concentration. The reason for this will become apparent from the kinetics.

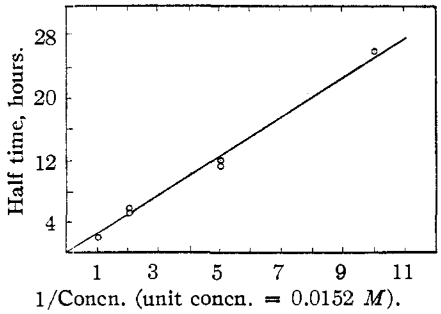


Fig. 2.—Copper salicylaldehyde ethylenediimine exchange.

Discussion

Kinetics.—Let the following equation represent the exchange process

$$Cu^*Ac_2 + CuKe_2 = Cu^*Ke_2 + CuAc_2$$

where $CuKe_2$ represents the chelate compound whatever it may be. As before, let the concentrations be denoted by

$$(Cu^*Ac_2) = y \qquad (Cu^*Ac_2) + (CuAc_2) = b$$
$$(Cu^*Ke_2) = x \qquad (Cu^*Ke_2) + (CuKe_2) = a$$

since the radioactivity is originally all in the copper acetate

$$x = 0 \quad \text{when } t = 0$$
$$x = x_\infty \quad \text{when } t = \infty$$

Since these are the conditions previously set for the general case, we have

$$-\ln\left(1 - \frac{x}{x_\infty}\right) = \frac{R}{ab}(a + b)t$$

For all the cases to be considered $a = b$ and therefore $x_\infty = y_\infty$

If we define a term r which is the ratio of the activity in $CuKe_2$ to the total activity, it is obvious that

$$r = \frac{x}{x_\infty + y_\infty} = \frac{x}{2x_\infty}$$

Making these two substitutions in the above rate law we find

$$-\ln(1 - 2r) = \frac{R}{a^2}(2a)t$$

Now at half complete exchange ($t = t_{1/2}$)

$$r = 0.25 \text{ and } -\ln(1 - 0.5) = \ln 2 = \frac{R}{a^2}(2a)t_{1/2}$$

$$t_{1/2} = \frac{a^2}{2a}\frac{\ln 2}{R}$$

The rate R may be any function of a and b (as well as of other substances present). We will consider only two cases.

Let us assume first that R depends only on the first power of a, *i. e.*, $R = k_1\,(a)$. Then

$$t_{1/2} = \frac{a^2}{2a}\frac{\ln 2}{k_1 a} = \frac{\ln 2}{2k_1}$$

The time of half reaction is independent of the concentration of a. This is characteristic of first order reactions. The same result would have been obtained if we had assumed that the reaction depended only on b.

If R depends on both a and b to the first power, *i. e.*

$$R = k_2ab = k_2a^2 \qquad t_{1/2} = \frac{a^2}{2a}\frac{\ln 2}{k_2a^2} = \frac{\ln 2}{2k_2a}$$

For this case the time of half reaction is proportional to the reciprocal of the concentration. This was found to be true for the copper salicylaldehydeethylenediimine exchange as is shown by Fig. 2. This is the only compound for which the law was tested but the reaction seems quite definitely to be bimolecular here.

Although this knowledge does not allow an unequivocal identification of the reacting species, it does place some rather narrow limits upon them. A simple analysis will show that no dimer (or higher polymer) can be involved in the rate determining step since this would require the half-life

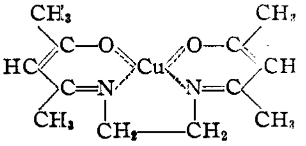
($t_{1/2}$) of the exchange to be inversely proportional to the square (or higher power) of the concentration. Similarly an ionization and recombination mechanism can be eliminated since this would require the half-life of the exchange to be independent of the total concentration.

A possible mechanism for the interchange which is at least not in disagreement with any of the known facts is a simple displacement of the copper atom from the chelate compound by a collision with a copper ion (or copper acetate molecule) which copper ion then takes the place of the original one. This process would be expected to follow a second order rate law.

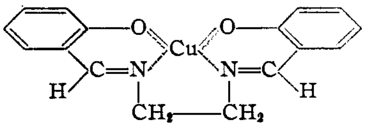
Relative Rates.—A comparison of the relative rates of exchange of these compounds with their reduction potentials at the dropping mercury electrode[2] shows that the order is exactly the same; *i. e.*, the higher the reduction potential, the slower the exchange.

The remarks and conclusions concerning the effect of the organic structure upon the stability of the chelates as determined from equilibrium studies can be applied here. The most pronounced effect is that of tying the two chelating groups together.

The interference with the benzenoid resonance of the chelate ring involving the metal is also apparent in these rate measurements, but here it can be observed even in the "closed" compounds a distinction which was not observed in the previous studies. This may be seen in the following pair of compounds measured under the same conditions of concentration and temperature.

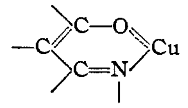


$t_{1/2}$ = 37 hr.

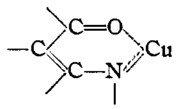


$t_{1/2}$ = 2.1 hr.

This decrease in stability in the salicylaldehyde compound is undoubtedly due in large part to the interference with the chelate benzenoid resonance by the requirement that in structure B the benzene ring of the salicylaldehyde be quinoidal.

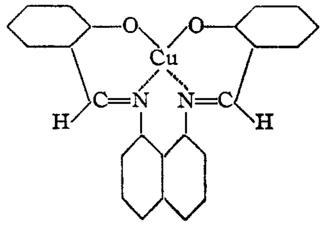


A



B

Another interesting compound is that derived from salicylaldehyde and 1,8-diaminonaphthalene.



Although this compound belongs to the "closed" type, it exchanges at a rate only slightly slower than that of the open type compounds. The same observation was made concerning its half-wave potential, which was found to lie between that characteristic of the "open" and that characteristic of the "closed" type compounds. This would appear to be due to a steric effect. If the compound be drawn out to scale, using approved interatomic distances and angles, one finds that it is quite impossible to have the compound completely coplanar about the copper atom. If then the chelate benzenoid resonance requires a coplanar structure this would be interfered with and hence the stability of the compound reduced. This effect would be much exaggerated if the salicylaldehyde were replaced by *o*-hydroxyacetophenone, an experiment which should be tried.

Summary

1. The rates of exchange of a series of copper chelate compounds with copper acetate in pyridine solution have been measured.

2. The kinetics of this exchange for a selected compound have been studied, and it has been found to be bimolecular in the chelate and the copper acetate.

3. Certain observations have been made on the effect of structure on the exchange rate, and a complete correlation between the exchange rate and the stability as previously measured has been found.

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