[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Equilibrium of the Light and Heavy Isotopes of Hydrogen with Crystalline Cuprous Chloride

BY A. F. KAPUSTINSKY

After the work of Ribalquine[1] which was only of a preliminary character, Parravano and Malquori[2] using a static method determined the equilibrium constants for the reaction

$$H_2 + 2CuCl \rightleftarrows 2HCl + Cu(s) \qquad (1)$$

for the range of temperatures from 300 to 500°. However, it seems that equilibrium was not attained in their experiments. The constants obtained by them do not display the expected variations with temperature. Criticism and revision of this determination were carried out by Watanabe[3] who investigated the above system also by means of a static method. Unfortunately the apparatus used by Watanabe which he utilized previously to study the reduction of silver sulfide by hydrogen could not lead to correct results this time. Watanabe was withdrawing his gaseous mixture for analysis from a cold part of the apparatus and therefore his equilibrium constants for the reduction of cuprous chloride are too high; the source of his error lies in thermal diffusion.[4]

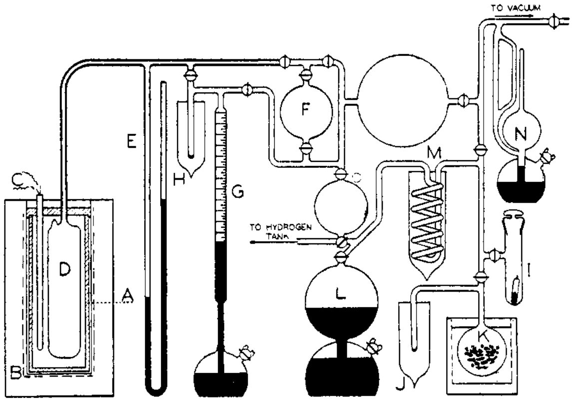

Fig. 1.—Apparatus.

In this work I was interested in measuring the precise values of the equilibrium constants and also in studying the equilibrium between cuprous chloride and the heavy isotope of hydrogen.

Apparatus

For this purpose an apparatus was constructed excluding the possibility of an error due to thermal diffusion which was present in the above mentioned static methods (see Fig. 1). A heavy-walled copper cylinder (A) with a lid which is placed on top, was put into a resistance furnace (B) the temperature of which was controlled by a rheostat within 2°. The purpose of the cylinder was to ensure the establishment of thermal equilibrium within the furnace. The temperatures were determined by means of a chromel–alumel thermocouple (C) and a Leeds and Northrup potentiometer with an accuracy of 1°. The Pyrex reaction vessel of 200-cc. capacity (D) was placed inside the cylinder and charged with cuprous chloride and hydrogen. The course of the reaction (1) is accompanied by a change in the number of the gaseous molecules. Therefore the establishment of the equilibrium at a constant temperature can be observed by obtaining constant readings on a mercury manometer (E). The readings were made by means of a cathetometer with an accuracy of 0.05 mm. Due to thermal diffusion the composition of the gas in the narrow tubes of the cold part of the apparatus and the composition in the reaction vessel proper are not identical. Therefore, before withdrawing a portion of the gas for the analysis, the cold part of the apparatus was rapidly evacuated. This was accomplished by means of an evacuated bulb of 70-cc. capacity (F). Only after this was a portion of the gas withdrawn over mercury into an evacuated sampling buret (G). The volume of the gaseous sample was recorded. Then the tube (H) was cooled by means of liquid air, and after hydrogen chloride was solidified the remainder was measured as hydrogen.

To obtain hydrogen[5] an open ampoule containing water was introduced into the vessel (I). The water was frozen with the help of liquid air, the apparatus was evacuated, and the water was distilled under vacuum into the vessel (J) surrounded by liquid air. Before this distillation, zinc dust in flask (K) was previously heated in a vacuum at 500° to expel all gases. Water vapor was allowed to come into contact with the zinc (heated again to 450°), at which temperature the reaction producing hydrogen is complete. The hydrogen while being transferred to the storage bulbs (L) where it was kept over mercury had to pass through a liquid air trap (M) to solidify any traces of water vapor present in the gas. In our first experiments we also used electrolytic hydrogen from a steel tank.

The vacuum was measured by means of a McLeod gage (N). The evacuation was effected by the use of an oil pump and a Langmuir pump.

Before admitting hydrogen, the reaction vessel (D) containing cuprous chloride was evacuated down to 10 mm. and kept for two days at 300° in order to remove completely all of the gases from the powdered cuprous chloride.

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[1] Ribalquine, *Bull. acad. imp. sci.* (Petersburg), 281 (1890).

[2] Parravano and Malquori, *Gazz. chim. ital.*, **56**, 3 (1926).

[3] Watanabe, *Bull. Inst. Phys. Chem. Research* (*Tokyo*), **9**, 94 (1930).

[4] *Cf.* Emmett and Shultz, THIS JOURNAL, **55**, 1376 (1933); Kapustinsky, Britzke and Schaschkina, *Z. anorg. Chem.*, **219**, 287 (1934); Eastman and Ruben, THIS JOURNAL, **57**, 97 (1935).

[5] *Cf.* Claussen and Hildebrand, *ibid.*, **56**, 1820 (1934).

Preparation of the Materials

Deuterium was prepared from 100% deuterium oxide of sp. gr. 1.1079 at 25° by the method described above.

Cuprous chloride was prepared from Kahlbaum cupric chloride, C. P. hydrochloric acid and electrolytic copper according to the method of Groger.[6] The dry powdered cuprous chloride obtained was purified in a stream of hydrogen at 300° until the evident appearance of red metallic copper.

Experiments with Ordinary Hydrogen

The results of these experiments are shown in Tables I, II and III. The first line in each table gives the pressure in mm. in the apparatus. The second line gives the volume per cent. of hydrogen chloride in the equilibrium gaseous reaction mixture. The third line gives the equilibrium constants. The average values of the constants are shown for each temperature. As the possibility of reducing cuprous chloride from a practical point of view depends on the relation of hydrogen chloride content to the temperature and pressure, the following data are listed in Table IV.

TABLE I

EQUILIBRIUM CONSTANTS FOR THE REDUCTION OF CuCl BY HYDROGEN

At 390°

p, mm.	588.6	491.5	444.8	372.3	313.6
Vol. % HCl	42.9	47.4	48.6	52.1	58.3
$K_p^1 = P^2_{HCl}/P_{H_2}$	0.249	0.266	0.269	0.277	0.333

Average $P^2_{HCl}/P_{H_2} = 0.279 \pm 0.050 = K_p^1$.

TABLE II

At 366°

p, mm.	625.0	559.5	405.5	332.1	295.9
Vol. % HCl	37.35	36.9	43.0	44.6	48.9
$K_p^1 = P^2_{HCl}/P_{H_2}$	0.182	0.1605	0.173	0.157	0.182

Average $P^2_{HCl}/P_{H_2} = 0.171 \pm 0.013 = K_p^1$.

TABLE III

At 320°

p, mm.	536.0	506.1	300.0
Vol. % HCl	23.4	26.55	33.35
$K_p^1 = P^2_{HCl}/P_{H_2}$	0.0505	0.0631	0.0658

Average $P^2_{HCl}/P_{H_2} = 0.059 \pm 0.009 = K_p^1$.

TABLE IV

VOLUME PER CENT. HCl AT SEVERAL PRESSURES AND TEMPERATURES, IN EQUILIBRIUM WITH Cu–CuCl

T, °C.	Pressure, mm.			
	200	400	600	760
320	38	29	23	19
366	55	43	36	32
390	64	51	43	39

The results obtained can be expressed well by a simple equation

$$\log_{10} K_p^1 = -(3820/T) + 5.211 \qquad (2)$$

This is illustrated in Table V which compares the experimental values of K_p^1 (second column) with K_p^1 calculated from Equation (2) (third column), and also shows the deviation between the two values (fourth column). Comparison of our results with those of Watanabe and of Parravano and Malquori is given in Fig. 2. Critical remarks concerning the work of the above authors appear in the introduction to this article.

TABLE V

THE DEPENDENCE OF THE CONSTANTS OF THE EQUILIBRIUM BETWEEN CuCl AND H_2 UPON THE TEMPERATURE

T, °A.	K_p^1 exptl.	K_p^1 calcd. eq. (2)	Δ
593	0.0597	0.0591	−0.0004
640	.171	.174	+ .003
663	.279	.282	+ .003

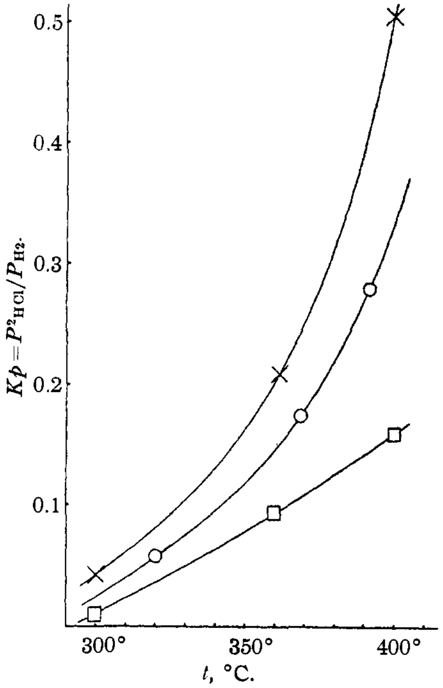

Fig. 2.—Dependence of equilibrium H_2 + CuCl upon temperature: ○, our results; □, Parravano and Malquori; ×, Watanabe.

Thermodynamic Part

We know the molal heat capacities[7] of the components of reaction (1)

Cu(s) $C_p = 5.08 + 0.00251T$
HCl $C_p = 6.50 + 0.0010T$
CuCl(s) $C_p = 13.7$
H_2 $C_p = 6.50 + 0.0009T$

Calculating ΔH by the use of Van't Hoff's equa-

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[6] Groger, *Z. anorg. Chem.*, **28**, 160 (1901).

[7] *Cf.* Watanabe, ref. 3, p. 98.

tion from our experimental results we obtain at 640°

$$\Delta H = 17{,}450 \text{ cal.} \qquad (3)$$

Utilizing all of the foregoing we can easily obtain the heat of the reaction at the absolute zero

$$\Delta H_0 = 17{,}450 + 10.74 \times 640 - 0.00306 \times 640^2 = 23{,}075 \text{ cal.} \qquad (4)$$

as well as the relation between ΔH and the temperature

$$\Delta H = 23{,}075 - 10.74T + 0.00306T^2 \qquad (5)$$

from which we have for reaction (1)

$$\Delta H_{298} = 20{,}143 \text{ cal.} \qquad (6)$$

According to the "International Critical Tables" the heat of formation of hydrogen chloride from chlorine and hydrogen is equal to 44,000 cal. Using this and our value of ΔH (6) we obtain for the reaction

$$\text{Cu(s)} + {}^1/_2\text{Cl}_2 = \text{CuCl(s)} \quad \Delta H_{298} = 32{,}072 \text{ cal.} \qquad (7)$$

Our value closely corresponds to the figure obtained by Thomsen (32,870 cal.) and by Watanabe (32,605 cal.) but deviates considerably from that determined by Berthelot (35,400 cal.).[8]

According to our data the relation of the free energy to the temperature may be expressed by the following equation

$$\Delta F^\circ = 23{,}075 + 24.73T \log T - 0.00306T^2 - 107.1T \qquad (8)$$

from which we calculate

$$\Delta F^\circ_{298} = 9104 \text{ cal.} \qquad (9)$$

According to Lewis and Randall[9] the free energy of formation of hydrogen chloride (2 moles)

$$\Delta F^\circ_{298} = -45{,}384 \text{ cal.}$$

From this it is a simple matter to calculate ΔF for reaction (7)

$$\Delta F^\circ_{298} = -27{,}244 \text{ cal.} \qquad (10)$$

which is in good agreement with the value of −27,800 cal. obtained by Thompson by the electrochemical method.[10]

The dissociation pressure of cuprous chloride computed from our data is

$$\log P_{\text{Cl}_2} = -40.7 \text{ atm.} \qquad (11)$$

This is also in satisfactory agreement with the value calculated by Brönsted[11] from his electrochemical measurements.

$$\log P_{\text{Cl}_2} = -41.6 \text{ atm.}$$

Both of the above values are given for $T = 298°$K.

The change of entropy of the reagents can be found from the values of ΔH and ΔF. It is

$$\Delta S_{298} = \frac{\Delta H_{298} - \Delta F_{298}}{T} = \frac{-32{,}072 + 27{,}244}{298} = -16.202 \text{ cal./deg.} \qquad (12)$$

The entropies of solid copper and of gaseous chlorine are 8.18 and 26.30, respectively[9] (p. 464). Therefore we can calculate that the entropy of cuprous chloride is

$$S_{\text{CuCl}} = \Delta S + S_{\text{Cu}} + S_{1/2\text{Cl}_2} = 18.28 \text{ cal./deg.}$$

Experiments with Deuterium

Up to this time no one has studied the equilibrium between the heavy isotope of hydrogen and the compounds of the metals. I undertook to measure the equilibrium constants for the reaction between deuterium and the same preparation of cuprous chloride as was used in the experiments with ordinary hydrogen. The apparatus used was also the same.

First, the cuprous chloride was kept hot at the temperature of 360–380° during the course of several hours in a high vacuum measured by means of a McLeod gage. After that the apparatus was rinsed with deuterium. Only after a second evacuation was the deuterium admitted into the reaction vessel and the measurements begun. Table VI gives the data on the reduction of cuprous chloride by deuterium. The first column gives the absolute temperatures. The second column presents the relation between the deuterium and the deuterium chloride, $K''_{\text{p}} = P^2_{\text{DCl}}/P_{\text{D}_2}$, in accordance with the equilibrium

$$\text{D}_2 + \text{CuCl(s)} = 2\text{DCl} + \text{Cu(s)} \qquad (13)$$

The third and the fourth columns show the values of log K''_{p} as computed from our experimental data and calculated from the empirical equation (14) derived from our data, respectively. The fifth column gives the deviations between the two values for log K''_{p}.

TABLE VI

EQUILIBRIUM IN THE REDUCTION OF CuCl BY DEUTERIUM

T, °A.	K''_{p}, exptl.	Log K''_{p}, exptl.	Log K''_{p} calcd. eq. (14)	Δ
657	0.502	−0.30	−0.30	0
665	.525	− .28	− .24	+0.04
673	.708	− .15	− .18	− .03
676	.742	− .13	− .16	− .03
684	.759	− .12	− .11	+ .01
688	.795	− .10	− .09	+ .01
691	.891	− .05	− .07	− .02

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[8] *Cf.* Landolt and Börnstein, *Phys. Chem. Tab.*, **2**, 1531 (1923).

[9] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 503.

[10] Thompson, THIS JOURNAL, **28**, 731 (1906).

[11] Brönsted, *Z. physik. Chem.*, **80**, 206 (1912).

Equation (14) is as follows

$$\log K_p'' = \log \frac{P_{DCl}^2}{P_{D_2}} = -\frac{3200}{T} + 4.57 \qquad (14)$$

and was found from the graph of the relation between log K_p'' and $1/T$ (see diagram 3) plotted from our data.

Summing up equations (1) and (13) we find

$$H_2 + 2DCl = D_2 + 2HCl \qquad (15)$$

It is evident that

$$K = \frac{P_{HCl}^2 P_{D_2}}{P_{H_2} P_{DCl}^2} = \frac{K_p^1}{K_p''} \qquad (16)$$

For the two temperatures, 690 and 658°K, we find that K is equal to 0.6 and 0.5, respectively, while Urey and Rittenberg[12] basing their computations of the free energies of deuterium and its compounds on the statistics of Fermi and of Bose–Einstein, find that at the same temperatures K is equal to 0.9 and 0.8, respectively. Thus theory and experiment result in values of the same order of magnitude, although the theoretical figures are higher than those found experimentally.

The author wishes to express his gratitude to Professor G. N. Lewis for suggesting this field of research, and for his valuable advice and helpful criticism during the course of the investigation.

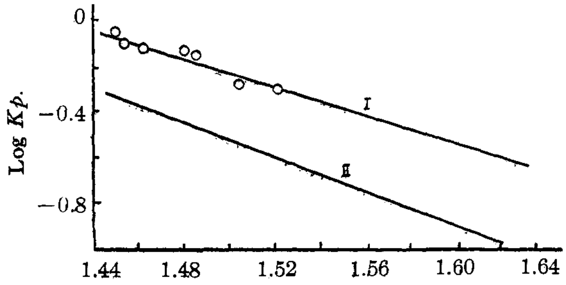

Fig. 3.—Dependence of equilibria $D_2 + CuCl$ and $H_2 + CuCl$ upon temperature: I, $H_2 + CuCl \rightleftarrows 2HCl + Cu$; II, $D_2 + CuCl = 2DCl + Cu$.

Summary

1. The equilibrium between the light and heavy isotopes of hydrogen and cuprous chloride was studied in the range of temperatures from 320 to 400°.

2. The entropy, free energy and the heat of formation of cuprous chloride were calculated from the experimental data. The constant of equilibrium for the reduction of hydrogen chloride by deuterium was also calculated.

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[12] Urey and Rittenberg, *J. Chem. Phys.*, **1**, 142 (1933).

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Further Studies on Dielectric Constant and Electrostriction of Amino Acids and Peptides

BY JESSE P. GREENSTEIN AND JEFFRIES WYMAN, JR.

In a recent communication[1] an account was given of studies on the electrostriction and dielectric constant of aqueous solutions of multivalent peptides. In the present paper further studies of this sort on other peptides and amino acids are reported.

I. Preparation of Materials.—*l*-Asparagine and *l*-glutamine were provided by Dr. E. J. Cohn of the Harvard Medical School. Their purification has been reported previously.[2] The 4,4′-diphenylbetaine was prepared and sent to us by Dr. Devoto of the University of Milan.

The peptides were prepared according to the methods of Emil Fischer[3] and were purified by repeated crystallization. Acetylhistidine was synthesized according to Bergmann and Zervas.[4] Creatine and β-indolepropionic acid were Hoffman–LaRoche products. The glycocyamine was prepared according to the usual procedure of treating sodium glycinate with an equivalent amount of S-methyl isothiourea sulfate in aqueous solution, finally crystallizing the product twice from hot water.

ε,ε-Diguanido-di(α-thio-*n*-caproic acid) was part of the original material reported by Greenstein[5] but purified by final crystallization from hot water rather than from an alcohol–water mixture. Under these conditions the m. p. of the diguanido acid was 205°; N calcd., 20.6; N found, 20.6.

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[1] Greenstein, Wyman and Cohn, THIS JOURNAL, **57**, 637 (1935).

[2] McMeekin, Cohn and Weare, *ibid.*, **57**, 626 (1935).

[3] Fischer, "Untersuchungen über Aminosäuren, Polypeptide, und Proteine," Vols. I and II, Verlag Julius Springer, Berlin, 1906.

[4] Bergmann and Zervas, *Biochem. Z.*, **203**, 280 (1928).

[5] Greenstein, *J. Biol. Chem.*, **109**, 529 (1935).