

## PYRIDINE COMPLEXES OF METALLIC PERCHLORATES.

### PART II.—DISSOCIATION PRESSURES AND PRESSURE-COMPOSITION ISOTHERMALS OF COPPER PYRIDINE PERCHLORATES.

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*Received 20th November, 1947.*

In a previous paper<sup>1</sup> the methods of preparation and the general properties of the pyridine complexes of copper (ic), silver, magnesium, calcium, strontium, barium, cadmium, zinc, mercury (ic), manganese, nickel and cobalt have been described. The investigation was undertaken with the object of determining what parallelism existed between the pyridine and ammonia complexes of metallic salts, since it was to be expected that, as in both cases the complex formation took place through the lone pair of electrons of the N atom, a close similarity would be found between the two classes of compounds. In the present paper, the dissociation pressures of the copper pyridine perchlorates have been measured at different temperatures, and the number of copper pyridine perchlorates, which are definitely formed under laboratory conditions, have been determined by an isothermal study of the copper perchlorate-pyridine system at 30° c. and 50° c.

The ammonia complexes of metallic salts or metallic amines have been investigated by a large number of workers. Measurements of dissociation pressures of amines of various salts were made on a limited scope by Bonnefoi,<sup>2</sup> Baud<sup>3</sup> and Girardet.<sup>4</sup> The dissociation pressures of compounds of ammonia with the halides of silver and the chlorides of magnesium, calcium, zinc and mercury were determined by Isambert<sup>5</sup> and he also measured the heats of dissociation calorimetrically. Measurements of the hexamines of molybdate, tungstate, chromate, selenate and sulphate of nickel were made by Ephraim and Müller.<sup>6</sup> Later Ephraim made detailed investigation of the lower amines and the higher, stable ammine complexes. Biltz and his co-workers made a more complete study of all the ammine complexes formed by each salt. The results were summarised and discussed by Biltz.<sup>7</sup> The relation of stability to heat of dissociation was discussed by Biltz, and Biltz and Grimm.<sup>8</sup> More recently,

<sup>1</sup> *J. Indian Chem. Soc.*, 1943, **20**, 32.

<sup>2</sup> *Ann. Chim. Phys.*, 1901, **23**, 317.

<sup>3</sup> *Compt. rend.*, 1901, **132**, 553.

<sup>4</sup> *Bull. Soc. Chim.*, 1910, **7**, 1028.

<sup>5</sup> *Compt. rend.*, 1868, **66**, 1259; 1876, **86**, 968.

<sup>6</sup> *Ber.*, 1921, **54**, 973.

<sup>7</sup> *Z. anorg. Chem.*, 1923, **130**, 93.

<sup>8</sup> *ibid.*, 1925, **145**, 63.

Hart and Partington<sup>9</sup> determined the dissociation pressures of the ammine and deuterammine systems of copper sulphate with varying temperatures and calculated the heats of dissociation from the slope of the linear graph of  $\log p$  against  $1/T$ .

### Experimental.

**Determination of Dissociation Pressures.**—The apparatus employed is shown diagrammatically in Fig. 1. It consisted of a close limb manometer M, the open end of which was sealed to a T-piece, and the bulb containing the substance was sealed to the vertical limb of the T-piece. To the other end of the T-piece, the U-tube S, about 80 cm. long, having two bulbs on the two arms, was sealed. At the bottom of the U-tube a small tube which was connected by means of pressure tubing to a reservoir of mercury which served as a levelling tube, was attached. The U-tube arrangement was inserted to avoid the use of a tap. The other end of the U-tube was connected to a rotary pump through the tap T and a wash-bottle containing  $H_2SO_4$  and a tube fitted with  $P_2O_5$  (not shown in Fig. 1) to absorb the pyridine. The whole apparatus except the tap T and the vacuum line was enclosed in a large electrically-operated air-thermostat provided with the heating lamp L, the heating coil H, the thermo-regulator R and the fan F for agitating the air inside vigorously. The motor of the fan

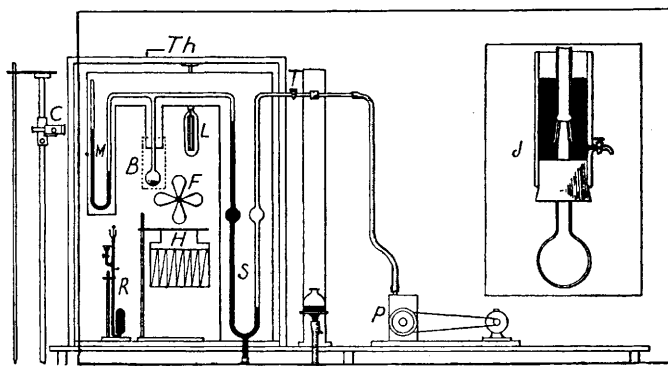


FIG. 1.

had to be kept outside the thermostat to prevent it from being unduly heated when measurements were made at high temperatures. Up to  $50^\circ C.$ , a mercury-toluene regulator was used, but for higher temperatures a xylene-mercury regulator was employed. The temperature could be kept constant to  $\pm 0.02^\circ$ . It was necessary to keep the whole of the equilibrium system inside the thermostat, otherwise pyridine condensed in the cooler parts and the pressure recorded was not the equilibrium pressure at the desired temperature. The difference in the heights of mercury in the two arms of the manometer was read off by means of the cathetometer C which was provided with a vertical scale and vernier.

In carrying out a measurement, about 1 g. of the highest pyridine complex together with 1 cc. of pure pyridine was introduced into the bulb B which was then sealed on to the vertical arm of the T-piece. The thermostat was set at the desired temperature, the mercury reservoir was lowered until a clear passage was established through the U-tube S, and the excess of pyridine pumped off through the tap T. When the excess of pyridine was almost completely removed, the passage through the U-tube was closed by raising the mercury reservoir. The equilibrium pressure at the particular temperature was measured. It coincided with the vapour pressure of pure pyridine at that temperature, showing that the apparatus had been properly set up and that the pressure readings were correct. The lowering of the mercury reservoir and the pumping were repeated as long as the pressure values corresponded with the vapour pressure of pure pyridine. Gradually the pyridine complex became entirely free from the excess of pyridine, and finally the dissociation pressure of the

<sup>9</sup> *J. Chem. Soc.*, 1943, 104.

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TABLE I.—TEMPERATURE-PRESSURE VALUES.

System:  $\text{Cu}(\text{ClO}_4)_2 \cdot 6/4 \text{C}_5\text{H}_5\text{N}$ .

$t^\circ \text{C.}$	35	49.5	55.2	57.3	64	69	74.6	79.4	82.0	85.4	92.3
$p$ (mm.)	16.8	33.0	40.0	43.2	55.6	66.1	82.0	96.4	106.0	120.1	149.0
$10^6/T^\circ \text{K.}$	3247	3101	3047	3027	2967	2924	2876	2838	2811	2790	2738
$\text{Log}_{10} p$	1.225	1.518	1.602	1.636	1.745	1.820	1.914	1.984	2.025	2.079	2.173

Mean value of the heat of dissociation (calculated from graph) = 8,450 cal.

System:  $\text{Cu}(\text{ClO}_4)_2 \cdot 4/0 \text{C}_5\text{H}_5\text{N}$ .

$t^\circ \text{C.}$	35.0	44.0	50.0	55.0	60.0	65.2	70.2	75.0	80.1	85.1	95.0
$p$ (mm.)	6.6	11.7	16.0	21.3	28.6	36.8	46.0	58.6	73.5	96.7	150.5
$10^6/T^\circ \text{K.}$	3247	3155	3096	3049	3003	2958	2914	2874	2832	2792	2717
$\text{Log}_{10} p$	0.819	1.070	1.204	1.328	1.456	1.566	1.663	1.768	1.866	1.985	2.178

Mean value of the heat of dissociation (calculated from graph) = 11,640 cal.

complex was obtained. When the equilibrium pressure at a particular temperature was obtained, the equilibrium was disturbed by connecting the system with the pump line and the pressure was allowed to attain its original value. This process was repeated two or three times at each temperature and the final

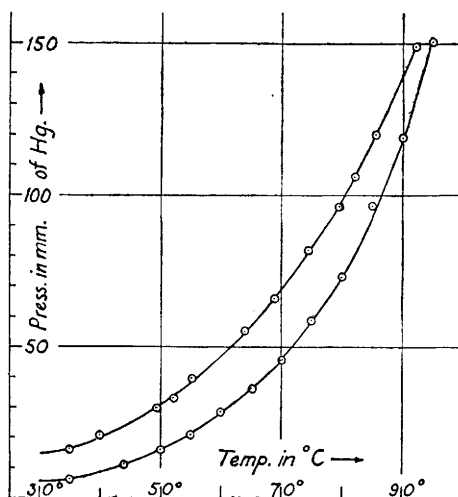


FIG. 2.

value was recorded. In this way the dissociation pressures were recorded with increasing temperatures. The dissociation pressures were then redetermined with falling temperatures, and the whole dissociation-pressure curves were determined, for both rising and falling temperatures. The experiments were repeated several times and reproducible results were obtained.

The results obtained are recorded in Table I and represented graphically in Fig. 2. The logarithms of pressures are also plotted against the reciprocals of the absolute temperature and the linear graphs obtained are shown in Fig. 3.

#### Determination of Isothermals.

—The apparatus employed for this purpose was essentially the same as shown in Fig. 1 except that the bulb containing the pyridine complex was provided with a tightly-fitting ground-glass joint which was surrounded by a glass jacket J filled with mercury. The arrangement is shown in the inset of Fig. 1. The mercury seal was necessary as no lubricant could be used for the ground joint, since the bulb had to be disconnected from time to time and weighed.

The experiment consisted essentially of the determination of the loss of weight of pyridine with its gradual removal at a fixed temperature. For this purpose, approximately 1 g. of the pyridine complex was introduced in the bulb with about 1 cc. of freshly distilled, pure pyridine. The bulb was weighed and fitted into the ground-glass joint. Mercury was then poured into the jacket and the thermostat set at a fixed temperature and when the contents of the bulb attains that temperature, some pyridine was removed by pumping. The tap T was then

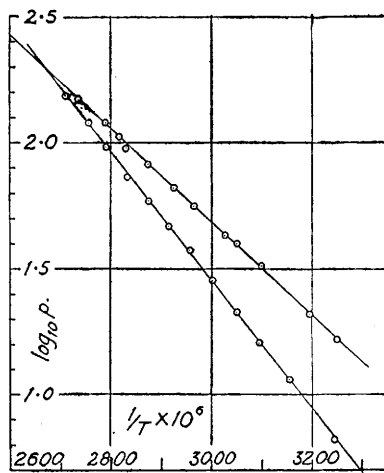


FIG. 3.

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closed and the bulb was left in the thermostat at the fixed temperature until the pressure reached its maximum value which was recorded. Air was then introduced into the apparatus, mercury was removed from the jacket J, the bulb detached, wiped clean and weighed. The process was repeated until no further change in the pressure could be noticed. A series of pressure values and the weights corresponding to each pressure were thus obtained. Isothermals were determined at 30° c. and 50° c. the room temperature being approximately 25° c. From the results the loss of the number of molecules of pyridine from the bulb and the number of molecules of pyridine that remained per molecule of the copper perchlorate were calculated. The results obtained are given in Fig. 4 where the pressures were plotted against the number of molecules of pyridine per molecule of copper perchlorate.

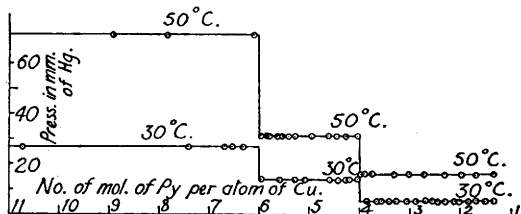


FIG. 4.

### Discussion.

It is evident from the dissociation-pressure curves (Fig. 2 and 3) that in the solid phase only two stable complexes are formed between pyridine and copper perchlorates within the range of temperatures investigated. It should be mentioned, however, that indications of two other complexes—one possessing higher dissociation pressures than  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{C}_5\text{H}_5\text{N}$ , and one intermediate between the two stable complexes,  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{C}_5\text{H}_5\text{N}$  and  $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{C}_5\text{H}_5\text{N}$ —were obtained, but as the dissociation-pressure curves of these complexes were not reproducible, they have been left out. It is probable that loose absorption compounds are formed with the stable complexes under certain conditions. The isothermal curves (Fig. 4) leave no doubt, however, that in the solid state only two complexes  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{Py}$  and  $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{Py}$  are formed.

The graphs (Fig. 3) obtained by plotting  $\log_{10} p$  against  $(1/T) \times 10^6$  are straight lines. The linear nature of the graphs is in agreement with previous results for heterogeneous systems as shown by Scheffer.<sup>10</sup> The dissociation pressure measurements can all be represented with sufficient accuracy by the equation,  $\log p = A/T + B$ , where  $A$  and  $B$  are constants. Thermodynamic consideration with approximations has been fully discussed by Schaffer (loc. cit.), who has shown that the equation may be written as  $\log_{10} p = Q/4.576T + B$ , where  $Q$  is the heat of dissociation absorbed per molecule of pyridine. The value of  $Q$  can thus be calculated, the value of  $B$  being obtained from the slope of the linear graph of  $\log_{10} p$  against  $1/T$ . The mean values of the heats of dissociation of the two complexes  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{Py}$  and  $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{Py}$  are thus found to be 8450 cal./g. and 11,640 cal./g. respectively, showing that the 4-pyridine complex is much more stable than the hexapyridine copper perchlorate. Hart and Partington (loc. cit.) found that the heat of dissociation of tetramine copper sulphate is 15,270 cal./g. and that of tetra-deuteramine copper sulphate 15,930 cal./g. It would therefore seem that the ammonia molecules are held more firmly by copper salts than pyridine molecules.

Dissociation pressures have been measured up to about 95°. The measurements could not be carried out at higher temperatures on account

<sup>10</sup> *Proc. Acad. Sci. Amst.* 1917, 19, 636.

of experimental difficulties, and partly also for the fact that the thermostat could not be kept quite constant at these temperatures. If, however, the pressure-temperature curves are extrapolated to higher temperatures (Fig. 3) they meet at  $100.8^{\circ}$  c. which may be regarded as the transition temperature of the hexapyridine complex into the tetrapyridine compound.

According to the laws of heterogeneous equilibrium, every substance which give off a gaseous dissociation product has, at a given temperature, a perfectly definite dissociation pressure that is independent of the amount of the dissociating substance. It will be observed from the isothermal curves (Fig. 4) that as pyridine is progressively removed from the bulb containing the complex richest in pyridine in presence of excess of free pyridine, the pressure remains constant, 27 mm. at  $30^{\circ}$  c. and 71.5 mm. at  $50^{\circ}$  c., until the whole of the free pyridine is lost. These are the pressures of pure pyridine at these temperatures respectively, but as soon as the ratio of pyridine to copper perchlorate reaches the value of about 6/1, there is sudden fall of pressure, 14 mm. at  $30^{\circ}$  c. and 31.5 mm. at  $50^{\circ}$  c. which are the dissociation pressures of hexapyridine copper perchlorate at these two temperatures respectively. After this the pressure again remains constant until the whole of the hexapyridine complex is decomposed. When the ratio of copper perchlorate to pyridine attains the value of about 1/4, there is again a second fall of pressure, 6 mm. at  $30^{\circ}$  c. and 16.5 mm. at  $50^{\circ}$  c., the dissociation pressures of tetrapyridine copper perchlorates at these temperature. No further break in the graphs was found even when the ratio of the copper perchlorate to pyridine fell to 1/1.35. These results leave no doubt that only two complexes, hexapyridine and dipyridine complexes, are formed under the conditions of the experiments.

In their investigation on the formations of complex compounds of ammonia and deuterammonia with some metallic salts, Hart and Partington (loc. cit.) have found that, in the solid phase, the highest ammonia complex formed with copper sulphate is the pentamine and the corresponding deuteramine. They also obtained tetra-, di- and mono-amines and the corresponding deuteramines. With copper perchlorate, however, pyridine forms only two complexes, hexapyridine and tetrapyridine compounds. It would seem therefore that, as pointed out by Biltz, and Biltz and Grimm (loc. cit.), complex formation is closely connected with the nature of the crystal lattice and the lattice energy of the salt forming the complex.

### Summary.

The dissociation pressures of the pyridine complexes of copper perchlorate have been measured at different temperatures and the isothermal curves showing pressures against number of molecules of pyridine per molecule of copper perchlorate have been determined at  $30^{\circ}$  c. and  $50^{\circ}$  c. From these results, it has been proved that in the solid phase only two stable complexes, namely  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{C}_5\text{H}_5\text{N}$  and  $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{C}_5\text{H}_5\text{N}$  are formed. The heats of dissociation of the two complexes have been calculated from the  $\log_{10} p$  against  $1/T \times 10^6$  graphs and these values correspond to 8,450 and 11,640 cal. per g. respectively, indicating that the 4-pyridine is much stabler than the 6-pyridine complex.

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