Summary.

Crystals of ammonium chloroplatinate ($(NH_4)_2PtCl_6$) probably have a structure which is analogous to that commonly assumed for fluorspar, if $PtCl_6$ groups replace the calcium atoms and if NH_4 groups are introduced in place of the fluorine atoms. This determination was made by and serves as an illustration of the general method (previously discussed) for the study of the structure of crystals which is based upon the theory of space groups.

The only assumption made that is not required in the ordinary determination of the wave length of X-rays from a reflection spectrum was that the 4 hydrogen atoms of the ammonium radical are exactly alike; with this exception, that in attempting to place the chlorine atoms with accuracy, it was assumed that atoms scatter X-rays in an amount which is roughly proportional to their atomic numbers and that in a lattice arrangement of atoms the intensities of reflection follow qualitatively the order of $1/(h^2 + k^2 + l^2)$.

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A DIFFERENTIAL THERMOMETER.

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One type of differential thermometer measures the difference of temperature existing at the same location at different times; a second type measures the difference in temperature existing simultaneously at different points in space. The thermometer here described is of the latter type.

A well-known differential thermoscope of this type consists of two glass bulbs containing air, otherwise closed but communicating with each other through a U-tube partly filled with oil, whose change of level indicates change of temperature by responding to change of gas pressure within the bulbs. When this instrument is developed into a differential thermometer, certain disadvantages become apparent, of which three will here be mentioned. (1) When the manometric liquid is caused to run into one of the bulbs by accidental tilting, perhaps during transportation, then it is difficult to return the liquid into precisely the same position as it occupied when the instrument was sealed. If stopcocks are introduced in the effort to avoid this inconvenience, the cure may become worse than the disease because of zero-creep. (2) In the presence of permanent gas, the manometric liquid becomes, in practice, not infrequently broken into threads, separated by short columns of the gas. This inconvenience, albeit only temporary, is nevertheless annoying. (3) Although oils furnish very sensitive manometric liquids, their use, or, indeed, the use of any liquid other than the insensitive mercury, allows the entrance of an error that has been too little appreciated. The incidence of this error in tensimetric work has been pointed out by the writer in another connection.[1] The error in question is caused by the fact that a gas at higher pressure has a larger weight solubility than the same gas at a lower pressure. The permanent gas, always slightly soluble in manometric liquids other than mercury, therefore passes by a process of solution and diffusion from the side of higher to that of lower pressure. For this reason, even stopcock-free instruments of the kind referred to suffer from slow creep of the zero point.

In order to avoid these and other disadvantages, all that is necessary is to abandon entirely the use of permanent gas. One selects as manometric fluid not oil but some liquid whose change of vapor pressure per degree in the range of temperature where the differential measurements are to be made is such as to cause differences of pressure in the two bulbs of the thermometer that will register themselves by adequate differences of level of the fluid itself. The diagram, Fig. 1, shows one simple form useful in ebullioscopy, made from glass tubing a few millimeters in bore and having, without its handle, a length of perhaps 12 cm. Permanent gas is removed prior to sealing by the process of boiling out familiar to many who have had occasion to measure vapor pressures. For reading the difference of level of the two liquid surfaces a millimeter scale may be etched on both limbs.

Fig. 1

From what has been said, it will be clear that, if the environment of both limbs of the instrument is the same in temperature, then the difference of level of the ends of the column of filling liquid will be merely that due to capillarity. If, however, the temperature of the lower bulb in Fig. 1, for example, be higher than that of the other limb, the consequent difference of pressure of vapor in the two limbs will cause in the liquid a correlative change of level whose value may be used, with the help of a suitable table, as a measure of the difference of temperature that caused it.

It is obvious that the sensitiveness in any particular range of temperature may be given widely different values according to the rate of change of vapor pressure of the liquid selected. The difference of temperature between upper and lower bulbs that will cause a change of level of, say, 1 mm. in the height of the column of the filling liquid may be computed from the known vapor pressures and densities of this liquid, and the results tabulated against the mean temperature of the instrument. Because of its suitability in other applications, and particularly because water is a filling liquid well adapted for use in these thermometers as employed in ordinary ebullioscopy, to be described in the article following, a table of precisely

[1] Menzies. This Journal, **42,** 1951 (1920).

the kind indicated is here furnished for a water-filled thermometer. The values for difference of pressure with temperature were obtained from the recent equation of Marvin,[2] which incorporates the best modern values, partly by direct differentiation and partly by the methods of interpolation. Against each tenth of a degree from 33° to 101.9° is tabulated the fraction of a degree centigrade that corresponds to an observed change of level of 1 mm. of water at this temperature. It may be noted that it is unnecessary at each observation to read the levels in both limbs, for the levels in the lower bulb that correspond to readings on the stem may be determined once for all, and the relationship graphed. The fact that such a graph should move parallel to itself as the total volume of contained water increases with temperature is immaterial when differential readings only are required, all close to the same temperature.

Table I.

Against each tenth of a degree from 33.0° to 101.9° is entered the change of temperature in ° C that would correspond to a vapor pressure change of water of 1 mm. head of water at the same temperature.

° C.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	Diff.
33	0.03449	3433	3417	3400	3384	3367	3351	3334	3317	3301	16
34	0.03286	3270	3254	3238	3222	3207	3192	3177	3161	3146	16
35	0.03130	3116	3101	3086	3071	3056	3041	3026	3011	2997	15
36	0.02984	2969	2955	2941	2927	2913	2899	2885	2872	2858	14
37	0.02844	2831	2818	2805	2791	2778	2765	2751	2738	2726	13
38	0.02713	2700	2687	2675	2663	2650	2637	2625	2613	2600	12
39	0.02588	2576	2564	2552	2540	2528	2517	2505	2494	2482	12
40	0.02471	2459	2447	2436	2425	2414	2403	2392	2381	2370	11
41	0.02359	2348	2338	2328	2317	2307	2296	2285	2275	2264	11
42	0.02254	2244	2233	2223	2213	2203	2193	2183	2173	2163	10
43	0.02154	2144	2134	2124	2114	2105	2096	2086	2077	2068	10
44	0.02059	2049	2040	2031	2022	2013	2004	1995	1986	1977	9
45	0.01969	1960	1951	1943	1934	1926	1917	1908	1900	1891	9
46	0.01883	1875	1866	1858	1850	1842	1834	1826	1818	1810	8
47	0.01802	1794	1786	1778	1770	1763	1755	1748	1740	1732	8
48	0.01725	1717	1710	1702	1694	1687	1680	1673	1665	1658	7
49	0.01651	1644	1637	1630	1623	1616	1609	1602	1595	1588	7
50	0.01581	1575	1568	1561	1554	1548	1542	1535	1529	1522	7
51	0.01516	1510	1503	1496	1490	1484	1478	1472	1466	1459	6
52	0.01453	1447	1441	1435	1429	1423	1417	1411	1405	1399	6
53	0.01393	1388	1382	1376	1370	1364	1358	1353	1348	1342	6
54	0.01336	1330	1325	1319	1314	1308	1303	1298	1292	1287	6
55	0.01281	1276	1271	1266	1261	1255	1250	1245	1240	1235	5
56	0.01230	1225	1220	1215	1210	1205	1200	1195	1190	1185	5
57	0.01180	1175	1170	1166	1161	1156	1152	1148	1143	1138	5
58	0.01133	1128	1124	1119	1115	1110	1106	1102	1097	1092	4
59	0.01087	1083	1079	1075	1071	1067	1063	1058	1054	1049	4
60	0.01045	1041	1037	1033	1029	1025	1021	1017	1013	1009	4
61	0.001005	1001	9968	9928	9890	9851	9813	9772	9734	9696	
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	

[2] Cf. Menzies, This Journal, **43**, 852 (1921).

TABLE I (*Continued*).

°C.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	Diff.
62	0.009658	9620	9583	9545	9508	9470	9432	9396	9359	9322	37
63	0.009285	9249	9212	9177	9141	9105	9069	9034	8999	8963	35
64	0.008931	8896	8861	8826	8792	8758	8725	8692	8658	8624	34
65	0.008592	8559	8527	8494	8461	8428	8397	8365	8333	8301	32
66	0.008269	8237	8207	8175	8145	8114	8083	8052	8022	7991	31
67	0.007960	7930	7900	7870	7840	7810	7780	7750	7721	7691	30
68	0.007663	7633	7605	7575	7548	7519	7491	7463	7435	7406	29
69	0.007379	7352	7324	7297	7269	7242	7214	7188	7161	7135	27
70	0.007109	7083	7057	7031	7005	6979	6953	6928	6902	6877	26
71	0.006852	6826	6801	6776	6751	6727	6702	6677	6653	6629	25
72	0.006606	6582	6557	6533	6509	6485	6462	6439	6415	6392	24
73	0.006369	6346	6323	6301	6277	6255	6232	6210	6187	6165	23
74	0.006144	6121	6099	6077	6055	6033	6011	5989	5969	5947	22
75	0.005927	5906	5884	5863	5842	5822	5801	5781	5760	5740	21
76	0.005719	5698	5676	5657	5637	5618	5598	5578	5558	5539	20
77	0.005520	5499	5480	5461	5442	5423	5404	5384	5365	5347	19
78	0.005328	5310	5291	5273	5254	5236	5218	5200	5182	5163	18
79	0.005145	5127	5109	5091	5074	5056	5039	5021	5003	4986	18
80	0.004969	4952	4935	4918	4901	4884	4867	4851	4834	4817	17
81	0.004800	4784	4767	4751	4735	4719	4702	4686	4670	4654	16
82	0.004638	4623	4607	4592	4576	4560	4545	4530	4514	4499	15
83	0.004484	4469	4453	4438	4423	4408	4393	4378	4363	4349	15
84	0.004334	4319	4305	4290	4276	4262	4248	4234	4220	4206	14
85	0.004192	4178	4165	4151	4137	4124	4111	4097	4083	4069	14
86	0.004055	4042	4029	4016	4002	3989	3976	3963	3950	3937	13
87	0.003923	3910	3897	3885	3873	3860	3847	3834	3821	3809	13
88	0.003796	3784	3771	3759	3747	3735	3723	3711	3698	3686	12
89	0.003675	3663	3651	3639	3627	3616	3604	3592	3581	3569	12
90	0.003557	3546	3535	3524	3513	3500	3488	3477	3465	3454	11
91	0.003443	3433	3422	3410	3399	3388	3378	3367	3356	3345	11
92	0.003334	3323	3313	3302	3292	3281	3271	3260	3249	3239	10
93	0.003229	3219	3209	3200	3189	3179	3169	3159	3149	3138	10
94	0.003128	3118	3109	3099	3089	3080	3070	3060	3051	3041	10
95	0.003032	3022	3013	3004	2994	2985	2976	2967	2957	2948	9
96	0.002939	2930	2921	2912	2903	2894	2885	2876	2867	2858	9
97	0.002849	2841	2832	2823	2815	2806	2798	2789	2781	2772	9
98	0.002764	2755	2747	2738	2730	2722	2713	2705	2697	2689	8
99	0.002680	2672	2664	2656	2647	2639	2631	2623	2615	2607	8
100	0.002599	2592	2584	2576	2568	2561	2554	2546	2538	2530	8
101	0.002523	2516	2508	2501	2494	2486	2478	2471	2463	2456	7
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	

Although the thermometers are of different general types, as indicated above, it is of interest to compare this differential thermometer with the Cavendish-Walferdin[3] metastatic type as elaborated by Beckmann,[4] and as applied in the same field, for example that of ebullioscopy. With regard to length of scale per degree, the Beckmann mercurial type is

[3] Cavendish, *Trans. Roy. Soc. London*, **50**, 300 (1757). Walferdin, *Bull. soc. geol. France*, **13**, 113 (1841–2).

[4] Beckmann, *Z. physik. Chem.*, **2**, 644 (1888); **51**, 329 (1905).

limited by the usable size of bulb, and by the permissible narrowness of the capillary, so that a centigrade degree corresponds customarily to 40 or 50 mm. movement of the mercurial thread. The type here described is not thus limited in this respect, for a very low-boiling liquid may be used for filling. In both types the length of degree varies with the actual temperature. As to range, the Beckmann type is restricted to that between $-39°$ and $+250°$.[5] While this is a much larger range than can be conveniently covered by the use of a single chosen liquid in the newer type, the simplicity of construction makes possible such a wide choice of filling liquids that a much wider range is easily available in the direction of lower as well as of higher temperatures. In comparing precision, one has to bear in mind, for the Beckmann type, possibilities of error due to (1) lack of uniformity of bore, (2) hysteresis in change of volume of bulb, (3) effect of pressure on volume of bulb, (4) sticking of mercury in capillary, (5) exposed thread, (6) difference of radiation to and from bulb, (7) departure of apparent degree from true degree. For the type here described, no one of the first six of these sources of error is important, for reasons that will be sufficiently obvious. In regard to (6), it may perhaps be said that error due to the change with environment of radiation loss suffered by a Beckmann thermometer at temperatures far from room temperature is here largely eliminated because suffered alike by upper and lower bulb. With regard to (7), it is indeed most necessary to employ a factor, different for each temperature, to convert observed readings to temperature; and this factor may be criticized as inconvenient to use, inaccurate in value and laborious of computation. But the use of a similar factor is likewise necessary, although frequently neglected, in the case of the Beckmann thermometer, whose degree, if true at $0°$, is, for example, about 3% in error at $80°$.[6] The accuracy of the conversion factor for the newer type is dependent in part on the accuracy with which the vapor pressure of the filling liquid is known. For such liquids as would be employed, and within the ranges of temperature that come in question here, this quantity, the vapor pressure, can now be measured to better than one part in 1000.[7] The process of computing factors for, perhaps, each tenth part of a degree over a considerable range of temperature may indeed be laborious; but, once published, the factor table may be used by every one. This inconvenience, therefore, is shifted from the shoulders of the user of the thermometer to those of him who first computed the table.

The Beckmann type is considerably more cumbrous as well as very much more fragile than the type here described, which one constructs from stout-

[5] Cf. Staehler, "Arbeitsmethoden in der Anorg. Chemie," Veit and Co., Leipzig, 1913, part 3, vol. 1, i, p. 106.

[6] Staehler, *op. cit.*, p. 108.

[7] Cf. THIS JOURNAL, **32**, 1412 (1910).

walled Pyrex tubing. In connection with fragility, it may be added that no "setting" of the thermometer for different temperatures is required, for its zero reading for uniform temperature automatically adjusts itself near the bottom of the stem, thus leaving the major portion of the scale available throughout its whole length.

In certain respects, therefore, it would appear that this type of differential thermometer has advantages over the Walferdin metastatic type as elaborated by Beckmann; and the question arises as to whether such other factors as are peculiar to a given application are favorable to its use. In studying its application in ebullioscopy, for example, as outlined in the article following, one finds that the important disturbing factor, peculiar to ebullioscopy in its incidence, of barometric fluctuation does not measurably affect the readings of the newer type, while such pressure fluctuations are among the chief outstanding sources of error when the metastatic type is used. Another application in a different field may be described in the near future.

Summary.

A very simple form of differential thermometer has been described whose indications depend on the registration by a column of manometric liquid in a U-tube of differences of vapor pressure of this liquid in opposite limbs. A table is given for use when the filling liquid is water; and mention is made of certain advantages of this type over the metastatic type of thermometer.

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THE APPLICATION OF A DIFFERENTIAL THERMOMETER IN EBULLIOSCOPY.

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For purposes of molecular weight determination of dissolved substances, the ebullioscopic procedure has certain advantages over the method of cryoscopy. Since, to use the latter, one must for convenience employ solvents whose freezing points lie at easily accessible temperatures, it comes about that water, benzene and acetic acid have been commonly preferred. To obtain satisfactory values for the molecular weight of a solute, it is best to choose a solvent so like it chemically that compound formation shall be at a minimum. To be so closely restricted in the choice of solvents is therefore a disadvantage. Boiling temperatures are, in general, preferable to freezing temperatures as unfavorable to the formation of exothermic compounds. A majority of organic compounds boil normally below 300°. If, as is true, the solvent should differ by at least 150 degrees in boiling point from the solute in order that the volatility of the latter may