Vol. 45

developed farther and farther apart. I shall refer to this striking phenomenon in a later paper.

Rhythmic Bands of Purple of Cassius.—Narrow but distinct rhythmic bands of purple of Cassius are obtained as follows. To 12.5 cc. of 3 Nhydrochloric acid add 1 cc. of 1% gold chloride solution. Shake the mixture vigorously while adding 12.5 cc. of water glass (d., 1.16). Allow the liquid to set in a test-tube for 3 days. Add 3 cc. of a mixture made from the equivalent of 10 g. of anhydrous stannous chloride and 0.1 g. of anhydrous stannic chloride in 90 g. of water. This mixture is turbid and, therefore, must be shaken vigorously before it is used. During the diffusion, the turbidity entirely disappears. When heavier bands are desired they may be obtained by using more concentrated solutions of gold chloride up to 10%; but when these more concentrated solutions are used the zones between the bands are not so free from residue.

Summary

1. Experiments have been performed which show that gels made with silicic acid and gold chloride are remarkably affected by light and that it is the light of short wave length which functions thus.

2. The results obtained remove Bancroft's objection to Holmes' diffusion theory of Liesegang band formation.

3. Another series of experiments has shown that there is a distinct relation between hydrogen-ion concentration and the size of "pockets" in which the gold is formed.

4. Directions are given for a striking lecture or laboratory experiment to show the influence of light on reduction.

5. Purple of Cassius was obtained in true Liesegang bands. Morgantown, West Virginia

[CONTRIBUTION FROM THE EPPLEY LABORATORY]

THE TEMPERATURE COEFFICIENTS OF UNSATURATED WESTON CELLS

By WARREN C. VOSBURGH AND MARION EPPLEY

RECEIVED JULY 3, 1923

The unsaturated Weston cell, although not a true standard cell, is widely used as a secondary standard of electromotive force because of its low temperature coefficient. Jaeger¹ stated that the electromotive force of a cell of this type with a cadmium sulfate solution saturated at 4° as the electrolyte could be regarded as practically constant at all ordinary temperatures. Dearlove² found a temperature coefficient —0.00003 volts

¹ Jaeger, "Die Normalelemente," Wilhelm Knapp, Halle a.S., 1902, p. 86.

² Dearlove, *Electrician*, **31**, 645 (1893). Dearlove does not state the concentration of cadmium sulfate in the electrolyte of his cells but the electromotive forces indicate that it was smaller than that of a solution saturated at 4° .

to -0.00007 volts per degree. The present investigation was undertaken to supply more definite information as to the magnitude of the temperature coefficient of unsaturated Weston cells.

Materials

Cadmium Sulfate.—A good grade of commercial cadmium sulfate was thrice recrystallized slowly at room temperature, or slightly above, the third time from redistilled water slightly acidified with sulfuric acid.

Mercurous Sulfate.—The mercurous sulfate designated as No. 1 was prepared electrolytically from mercury which had been purified by electrolysis. The apparatus was similar to that of Hulett,³ and the current density was 0.5 amp. per sq. dm. The amount of finely divided mercury in the mercurous sulfate was found to be dependent on the rate of stirring, a whiter product being obtained with more vigorous stirring. The mercurous sulfate was allowed to stand for several months under 0.02

M sulfuric acid solution. It was then digested for 5 days at a temperature near the boiling point with 1.8 M sulfuric acid and kept under the acid solution in the dark until used.

Mercurous sulfate No. 2 was prepared by reducing mercuric sulfate with formaldehyde.⁴ Mercuric oxide of C. P. quality was added to a large excess of hot 4 M sulfuric acid solution, an excess of formaldehyde added and the solution maintained at 100° until precipitation was complete. The precipitate was washed and maintained at boiling temperature for several hours under 1.8 M sulfuric acid solution and kept under a 1.8 M acid solution in the dark.

Mercurous sulfate No. 3 was obtained by allowing a portion of the mercuric sulfate solution used in the preparation of No. 2 to stand at room temperature after addition of formaldehyde. It was washed and kept under 1.8 M sulfuric acid solution in the dark.

Mercury.—Commercial redistilled mercury was purified by electrolysis as described by Wolff and Waters⁵ and twice redistilled by Hulett's method.⁶

Cadmium Amalgam.—Cadmium was deposited electrolytically from a concentrated solution of the purified cadmium sulfate, the cathode consisting of a weighed portion of the mercury described above. When sufficient cadmium had been deposited the amalgam was weighed, mercury added to bring the cadmium concentration to 12.5% and the amalgam melted by gentle heating

bring the cadmium concentration to 12.5%, and the amalgam melted by gentle heating and well mixed.

Vessels.—Glass H-vessels of the type shown in Fig. 1 were used.

Apparatus

Potentiometer.—The potentiometer described by Eppley and Gray⁷ was used, the working battery consisting of 2 large capacity cadmium cells. Cell comparisons with this instrument were reproducible to 1 or 2 microvolts. For measuring Cells 56–60 and the normal cells at 45° a commercial potentiometer was used. It was calibrated over the range of the other potentiometer by making cell comparisons by means of both instruments. The correction at the upper limit of this range was assumed to apply to

- ⁵ Wolff and Waters, Bur. Standards Bull., 4, 10 (1907).
- ⁶ Hulett, Phys. Rev., 33, 307 (1911).



Fig. 1.— Type of Hvessel used. The length was about 13 cm. and the inside diameter of the lower parts of the legs 1 cm.

³ Hulett, Phys. Rev., 32, 262 (1911).

⁴ Deniges, Ann. chim. phys., [7] 18, 397 (1899).

⁷ Eppley and Gray, J. Optical Soc. Am., 6, 859 (1922).

the readings of Cells 56-60, and that at the lower limit to to the readings of the normal cells. The corrected readings thus obtained must have been accurate to 0.00004 volt. The temperature coefficients should be more accurate than this, however, as readings could be duplicated to 0.00001 volt, and some errors must have been cancelled by the subtraction.

Both potentiometer systems were shielded as recommended by White.⁸

Standards.—Three well-aged, very constant, normal cells made at the National Physical Laboratory at Teddington, England, and furnished to this Laboratory through the kindness of Dr. F. E. Smith, were used as the reference standards. Their values were assumed to be such that the normal cells made in this investigation would have a value of 1.018054 volts at 25°.

Temperature Control.—Two oil thermostats, maintained constant within 0.02° , were used for regulation of the temperature. One was kept at 25° and contained the reference and working standards; the other contained the experimental cells, and its temperature was changed as desired. Temperatures were determined by means of a thermometer recently calibrated by the Bureau of Standards, and were accurate to 0.03° .

Preparation of the Cells

The platinum wires in the mercury legs of the vessels were amalgamated and the amalgam and mercury introduced as described by Wolff and Waters.⁹ A 0.015 M sulfuric acid solution, prepared from water redistilled from alkaline permanganate, was saturated with cadmium sulfate. Fifteen normal cells were prepared using this solution,¹⁰ but otherwise as described by Wolff and Waters.⁹ Cells 1 to 5 were prepared with mercurous sulfate No. 1, Cells 6 to 10 with No. 2, and Cells 11 to 15 with No. 3. For the unsaturated cells, portions of the saturated solut on were diluted with from 2.5 cc. to 50 cc. of the 0.015 M acid solution to a liter, as shown in Table I. The mercurous sulfate, No. 1, was washed well with the cadmium sulfate solution to be used in the cells and introduced into the vessels by means of a pipet. Cadmium sulfate solution was then run in until the level was above the cross-arm. The air was displaced by nitrogen which had been washed with water and concentrated cadmium sulfate solution, and the upper ends of the glass tubes hermetically sealed. Special precautions were taken to prevent evapora-

* White, This Journal, 36, 2011 (1914).

⁹ Ref. 5, p. 30.

¹⁰ Hulett [(a) Trans. Am. Electrochem. Soc., 14, 89 (1908)] found that Weston cells with acid electrolytes were remarkably constant in electromotive force, and Smith [(b) Electrician, 75, 463 (1915)] and Obata [(c) Proc. Math. Phys. Soc. Japan, 2, 232 (1920)] found that Weston normal cells were more constant if the electrolytes were acid than if they were neutral. Obata determined the relation of the electromotive force to the acid concentration, and on the basis of his results it was calculated that an electrolyte containing 0.0115 moles of sulfuric acid in a liter (resulting from the saturation of 0.015 M sulfuric acid with hydrated cadmium sulfate) would give cells with an electromotive force 20 microvolts lower than that of the neutral cell. Obata's acid cells were all more acid than this, but some experiments in this Laboratory have shown that his relationship holds for low acidities also, contrary to the statement of Hulett (Ref. 9a, p. 80).

Oet., 1923

tion of the electrolyte. The cells were mounted on racks, copper connecting wires being soldered to the platinum wires and to short copper rods¹¹ inbedded in a hard rubber plate.

The concentration of cadmium sulfate in the various solutions was determined by evaporating 3 to 5 g. samples to dryness, with the addition of a little sulfuric acid. The residue was brought to constant weight by adding 1 or 2 drops of concd. sulfuric acid, heating with a medium flame, cooling, adding more acid, and heating with a low flame until the acid was completely expelled.¹² Three determinations were made on each solution, and the average results together with the average variations are given in Table I.

TABLE I

Co	OMPOSITIO	n of Cadm	IUM SULFATE	SOLUTIONS AND EL	ECTROMOTIVE FORCES OF CELLS
	solution no,	Cells	Dil. acid added Cc.	CdSO₄ %	E.m.f. at 25° Average volts
1	1	16 - 20	None	43.22 ± 0.01	1.018270 ± 0.000008
	2	41 - 45	2.5	$43.12 \pm .03$	$1.018374 \pm .000007$
	3	21 - 25	5	$43.06 \pm .00$	$1.018548 \pm .000005$
1	4	26 - 30	9	$42.94 \pm .01$	$1.018711 \pm .000013$
	5	31-35	11	$42.90 \pm .01$	$1.018788 \pm .000007$
	6	36-4 0	15	$42.77 \pm .04$	$1.018983 \pm .000006$
	7	46 - 50	22.5	$42.63 \pm .00$	$1.019343 \pm .000007$
	8	51 - 55	30	$42.39 \pm .01$	$1,019688 \pm .000014$
	9	56 - 60	50	$41.84 \pm .02$	$1.02095 \pm .00003$

Electromotive-force Measurements

The cells were allowed to age for over a month at 25° before the final measurements were made. Preliminary measurements showed that they changed very little during that time. Measurements were then made successively at 25° , 35° , 40° , 45° , 40° , 35° , 15° , and finally at 25° again. At each temperature measurements were made on successive days until it was shown that equilibrium had been attained. At the higher temperatures equilibrium was attained within less than a day after the temperature was changed. At equilibrium measurements nearly always agreed within 1 or 2 microvolts. The results are given in Tables I, II and III.

The first values at 25° for the unsaturated cells are given in Table I, each value being the average of a group of 5 cells. The figures for the average variation from the group averages give an idea as to the reproducibility of acid cells. In the case of the normal cells, in which there were no variations due to concentration differences, the average variation was

¹¹ The lead wires to the potentiometer were attached to these rods by means of spring clips.

¹² Preliminary experiments showed that weighing after the first heating gave erratic results, due doubtless to loss of sulfur trioxide. It was considered necessary, however, for the expulsion of all the water. See Baxter and Wilson, THIS JOURNAL, 43, 1238 (1921).

7.7

Vol. 45

considerably less, 0.000002_5 volts at 25° . No cells were rejected for inconstancy or disagreement with the majority.¹³

TABLE II

	Nor	MAL CELLS			
Temp., °C.	15.00	24.98	35.03	40.03	45.04
E.m.f., Cells 1–5, volts	1.018456	1.018053	1.017492	1.017167	1.01682
E.m.f., 6–10,	1.018450	1.018052	1.017490	1.017164	1.01681
E.m.f., 11–15,		1.018056	1.017491	1.017163	1.01681
E.m.f., Cale. (Wolff),	1.018459	(1.018054)	1.017488	1.017164	· • · · •

In Table II it is shown that the temperature formula of Wolff¹⁴ expresses the relationship between temperature and electromotive force of Cells 1 to 15.¹⁵ The practically negligible differences from the calculated values in Table II are in the direction of a smaller temperature coefficient. The results in Table II indicate that mercurous sulfate No. 1, which was used in the unsaturated cells, is a normal preparation, since

TABLE III

AVERAGE ELECTROMOTIVE FORCES OF UNSATURATED CELLS AT VARIOUS TEMPERATURES

	15.00° E m f	24.98° Emf I ^a	24.98° Emf 11ª	35.03° EmfI
Cells	Volts	Volts	Volts	Volts
16-20	1.018236	1.018270	1.018264	1.018295
41 - 45	1.018346	1.018374	1.018367	1.018393
21 - 25	1.018531	1.018548	1.018541	1.018558
26 - 30	1.018703	1.018711	1.018704	1.018709
31-35	1.018784	1.018788	1.018783	1.018784
36 - 40	1.018991	1.018983	1.018978	1.018968
46 - 50	1.019369	1.019343	1.019334	1.019305
51 - 55	1.019734	1.019688	1.019679	1.019631
56 - 60	1,02108	1.02095	1.02095	1.02082
	35 03°	40 03 °	40.03°	45 04 °
Cells	E.m.f. II Volts	E.m.f. I Volts	E.m.f. II Volts	E.m.f. Volts
16 - 20	1.018292	1.018320	1,018318	1.018359
41 - 45	1.018389	1.018415	1.018413	1.018450
21 - 25	1.018554	1.018574	1.018572	1.018603
26 - 30				
	1.018707	1.018720	1.018721	1.018746
31-35	1.018707 1.018781	1.018720 1.018793	$1.018721 \\ 1.018793$	$1.018746 \\ 1.018815$
31-35 36-40	1.018707 1.018781 1.018965	1.018720 1.018793 1.018971	1.018721 1.018793 1.018970	1.018746 1.018815 1.018988
31-35 36-40 46-50	1.018707 1.018781 1.018965 1.019301	1.018720 1.018793 1.018971 1.019300	1.018721 1.018793 1.018970 1.019296	1.018746 1.018815 1.018988 1.019303
31-35 36-40 46-50 51-55	1.018707 1.018781 1.018965 1.019301 1.019626	1.018720 1.018793 1.018971 1.019300 1.019614	1.018721 1.018793 1.018970 1.019296 1.019610	$\begin{array}{c} 1.018746 \\ 1.018815 \\ 1.018988 \\ 1.019303 \\ 1.019609 \end{array}$

^a I and II indicate the first and second results at the given temperature, respectively.

18 Compare Shaw and Reilley, Trans. Roy. Soc. Canada, [iii] 13, 171 (1919).

¹⁴ Wolff, Bur. Standards Bull., 5, 326 (1908).

¹⁵ The values for Cells 11–15 are the results of the first measurements at 25° , 35° , 40° and 45° . Hysteresis interfered when the temperature was decreased. Cells 1 to 10 and the unsaturated cells showed very little hysteresis.

the saturated cells made with it agree with those made with the other mercurous sulfate preparations.¹⁶

Temperature Coefficients of Unsaturated Cells

There is an average difference of 7 microvolts between the first and second results at 25° in Table III. Smaller differences are to be noticed between the two series of results at 35° and 40° , respectively. These differences may have been caused by a decrease in electromotive force of the cells due to the reaction, $Cd + 2Hg^+ \longrightarrow Cd^{++} + 2Hg$, at the surface of the amalgam, the mercurous ion being supplied by diffusion.¹⁷ In view of the small size of the decrease and the order in which the measurements at the different temperatures were made, it was considered sufficient



Fig. 2.--Variation of electromotive force with temperature

correction for this error to use the mean values at each temperature for the comparison. The results at 15° were obtained just previous to the final ones at 25° , and so were corrected for comparison with the others by adding half the differences between the two results at 25° . The relation between electromotive force and temperature is shown graphically in Fig. 2. Curve 1 represents the average electromotive force of cells 16–20, Curve 2 that of Cells 26–30, and Curve 3 that of Cells 45–50. Curves for the other groups were similar. The electromotive force is a linear function of the temperature¹⁸ between 15° and 35° , but not between 35° and 45° .

Table IV shows that the temperature coefficient of the unsaturated

¹⁶ Lewis and Gibson {THIS JOURNAL, **39**, 2575 (1917)] and Gerke [*ibid.*, **44**, 1702 (1922)] have called attention to the possibility of differences in free energy between salts prepared by chemical and electrolytic methods, respectively.

¹⁷ After the final measurements at 25° the unsaturated cells were kept at 25° for 3 months, at room temperature for 3 months more, and then measured at 25°. The average decrease was 23 microvolts, or 0.0023%. The normal cells decreased 6 microvolts during the first 2 months and remained constant for the next 4 months.

¹⁸ Callender and Barnes [*Proc. Roy. Soc.* (London) **62**, 117 (1898)] and Jaeger (Ref. 1, p. 69) found the electromotive force of the unsaturated form of the Clark cell to be a linear function of the temperature over a wide range.

cell is not only "negligible," but at a particular cadmium sulfate concentration is zero between 15° and 35° . This is illustrated in Fig. 3 in which the straight line, expressing the relation between the electromotive

TABLE IV

TEMPERATURE COEFFICIENTS					
Cells	E.m.f. 25° Volts	$\Delta E/\Delta T$ 15-25° Mmv./deg.	$\Delta E/\Delta T$ $25-35^{\circ}$ Mmv./deg.	$\Delta E/\Delta T$ 35–40° Mmv./deg.	$\begin{array}{c} \Delta E/\Delta T\\ 40-45^{\circ}\\ \mathrm{Mmv./deg.}\end{array}$
16 - 20	1.01827	2.8	2.7	5.0	8. 1
41 - 45	1.01837	2.1	2.0	4.7	7.1
21 - 25	1.01854	1.0	1.1	3.4	5.9
26 - 30	1.01871	0.1	0.0	2.5	5.4
31–35	1.01879	- 0.1	- 0.3	2.1	4.5
36 - 40	1.01898	- 1.3	- 1.4	0.7	3.5
46 - 50	1.01934	- 3.5	- 3.6	- 0.9	0.9
51 - 55	1.01968	- 5.5	- 5.5	- 3.2	-0.6
56 - 60	1.0210	- 13	-13	-10	-8

force of the cell and its temperature coefficient, crosses the axis when the electromotive force is 1.01873 volts. The average variation of the temperature coefficients of the individual cells from the values given was about 0.1 microvolts per degree for the temperature coefficients between 15°



Fig. 3.—Variation of temperature coefficient with electromotive force. The circles represent the acid cells, and the crosses the neutral cells. (See below)

and 35° and about 0.2 mmv. per degree for the other temperature coefficients.

The temperature coefficients between 25° and 35° were measured again after the cells were about 8 months old. The electromotive forces had decreased¹⁷ a little, but the temperature coefficients, in all cases but one, came within 0.2 microvolts per degree of the curve of Fig. 3. The average temperature coefficient of Cells 46–50 was —2.5 mmv. per degree instead of —3.3 as read from the curve, and the agreement among the individual cells was not as good as before. None of the unsaturated cells showed any appreciable hysteresis when the temperature was changed.

Cells with Neutral Electrolyte

Some unsaturated cells with neutral electrolytes were prepared in order to determine if possible how much effect acid in the electrolyte had on the temperature coefficient. The materials were the same as those used in the other cells. The acid in 4 of the cadmium sulfate solutions was neutralized by means of cadmium oxide precipitated from a cadmium sulfate solution by means of ammonium hydroxide, and well washed. Four groups of 5 cells each were prepared and the electromotive forces measured at 25° and at 35°. The temperature coefficients thus obtained did not lie on a straight line or on any regular curve when plotted against electromotive force, as seen in Fig. 3. The temperature coefficient of one group was practically on the curve for the acid cells, but the coefficients of the other groups were below it. Two determinations of the temperature coefficients about a month apart, and before the cells were 3 months old, gave closely agreeing values for 3 of the groups, but for the cells of the average electromotive force of 1.01870 volts the first determination gave -1.5 mmv. per degree, and the second -2.4 mmv. per degree. The latter cells showed considerable hysteresis when the temperature was reduced. Most of the other neutral cells showed some hysteresis. It seems likely that some disturbing factor, such as hydrolysis of the mercurous sulfate, was present in varying degree in the neutral cells and absent in the acid cells.

Electromotive Force and Cadmium Sulfate Concentration

The cadmium sulfate concentrations of the electrolytes of the unsaturated cells are given in Table I. When the concentrations are plotted against the electromotive force of the corresponding cells, all the points, except that for Solution 9, the most dilute one, lie on a straight line. The concentration in a cell having the electromotive force of the normal cell at a certain temperature gives the solubility of hydrated cadmium sulfate in a 0.015 M sulfuric acid solution at that temperature. By plotting the concentrations given in Table I against the electromotive forces at 15°, 18° and 25°, the solubilities calculated as percentages of anhydrous cadmium sulfate were found to be 43.08%, 43.14%, and 43.32%, respectively, the last value requiring a short extrapolation. These values are 0.13%, 0.13% and 0.12% lower, respectively, than the values given by Steinwehr¹⁹ for neutral solutions.

A cell with a zero temperature coefficient, which would have an electromotive force of 1.01873 volts, would require an electrolyte containing 42.93% cadmium sulfate. If the effect of acid on the solubility of cadmium sulfate is the same at lower temperatures as between 15° and 25° the electrolyte of the cell with zero temperature coefficient would be saturated at the same temperature as a 43.06% neutral solution, namely at about 4° .

¹⁹ Steinwehr, Z. physik. Chem., 94, 6 (1920).

Differential Heat of Solution of Cadmium Sulfate

The differential heat of solution of hydrated cadmium sulfate in its saturated solution, q', can be calculated by means of the equation²⁰

$$q' = 46148 \frac{m - 2.67}{m} T_0 \left[\frac{\mathrm{d}E_1}{\mathrm{d}T} - \frac{\mathrm{d}E_2}{\mathrm{d}T} \right]$$

where m is the number of moles of water per mole of cadmium sulfate in the saturated solution, E_1 is the electromotive force of the normal cell, E_2 that of a cell with saturated electrolyte but without crystals, and T_0 is the temperature. The results of this calculation are given in Table V. The temperature coefficients for the normal cell were obtained by differentiating Wolff's formula,¹⁴ and those for the cells without crystals from curves similar to Fig. 3 drawn for the temperatures 15°, 18° and 25°. The values of m were calculated from the solubilities given above of hydrated cadmium sulfate in a 0.015 M sulfuric acid solution.

TABLE V

DIFFERENTIAL HEAT OF SOLUTION OF HYDRATED CADMIUM SULFATE IN A SATURATED SOLUTION CONTAINING 0.012 MOLE OF SULFURIC ACID IN A LITER

Temp. °C.	m Moles	dE_1/dT Volts/deg.	dE_2/dT Volts/deg.	q' Cal./mole
15	15.27	-0.00003057	0.0000153	-352
18	15.23	00003686	.00000205	-431
25	15.12	- :00004945	.00000392	-605

If it is assumed that the temperature coefficient of neutral unsaturated cells is the same as for the acid ones of the same electromotive force, the heats of solution in Table V apply to neutral solutions as well as to the slightly acid ones for which they were calculated. For neutral solutions the values for dE_1/dT would be the same, since Wolff's formula, although derived for neutral cells, has been shown to hold for the acid cells. The values of m would be 3 to 4 parts in a thousand lower for neutral solutions, but an examination of the above equation shows that the values of q' would be in error by only a small part of this.

The differential heat of solution at 18° as determined in the above manner is less than half the value found by Steinwehr²¹ by a different method. The temperature coefficient of q' in the vicinity of 18° is -25 cal. per degree according to the above results while Steinwehr¹⁹ calculated -63 to -78 cal. per degree.

Summary

1. The electromotive force of unsaturated Weston cells increased in an approximately linear manner as the cadmium sulfate concentration decreased.

2. The electromotive forces were linear functions of the temperatures between 15° and 35° but were not linear functions between 35° and 45° .

²⁰ Jaeger, Ref. 1, p. 36. Verhdl. Deutsch. Phys. Ges., 3, 50 (1901). Ref. 19, p. 14.
²¹ Steinwehr, Z. physik. Chem., 88, 245 (1914).

4. Normal cells with electrolytes made by saturating a 0.015 M sulfuric acid solution with hydrated cadmium sulfate behaved in accordance with Wolff's temperature formula.

5. Mercurous sulfate prepared by reduction of mercuric sulfate with formaldehyde at 100° was no different in its behavior in normal cells from the electroltyic salt.

6. The differential heat of solution of hydrated cadmium sulfate in a slightly acid saturated solution was calculated.

NEWPORT, RHODE ISLAND

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 30]

THE ENTROPY OF DIATOMIC GASES AND ROTATIONAL SPECIFIC HEAT

BY RICHARD C. TOLMAN AND RICHARD M. BADGER

Received July 3, 1923

I. Introduction

Assuming the rigid "dumb-bell" model, the entropy of a diatomic gas at temperatures high enough so that the specific heat at constant pressure has become 7/2 R, is given by the equation

 $S = \frac{7}{2} R \ln T - R \ln p + \frac{3}{2} R \ln M + R \ln J + S_2$ (1)

where T is the absolute temperature, p is the pressure, M the molecular weight, J the moment of inertia of the molecule and S_2 a constant which has the same value for all diatomic gases composed of molecules of the assumed model. This equation has been derived by Tetrode,¹ Sackur² and Schames³ on the basis of the quantum theory and by Tolman⁴ from the theory of similitude or relativity of size, and using kinetic-theory data for calculating moments of inertia, has been shown⁴ to agree with the available experimental data.

An important advance in the use of Equation 1 has been made by Urey.⁵ In the first place he has used moments of inertia obtained from spectral data instead of kinetic-theory data in testing the equation,⁶ and in the

¹ Tetrode, Ann. Physik, 38, 434 (1912).

² Sackur, *ibid.*, **40**, 87 (1913).

³ Schames, Physik. Z., 21, 38 (1920).

⁴ Tolman, THIS JOURNAL, **43**, 866 (1921).

⁵ Urey, *ibid.*, **45**, 1445 (1923).

⁶ Compare also Eucken, Jahrb. Radioakt. Elektronik, 16, 361 (1920); Z. Elektrochem. 26, 377 (1920).