TABLE IV

HEAT CONTENTS AND ENTROPIES ABOVE 298.1° K. IN CAL./G. F. W. AT 100° INTERVALS

Temp., °K.	Mn₃O₄ $H_T - H_{298.1}$	Mn₃O₄ $S_T - S_{298.1}$	Mn₃C $H_T - H_{298.1}$	Mn₃C $S_T - S_{298.1}$	MnSiO₃ $H_T - H_{298.1}$	MnSiO₃ $S_T - S_{298.1}$
400	3,700	10.60	2,450	7.07	2,320	6.66
500	7,500	19.26	5,020	12.79	4,800	12.19
600	11,590	26.54	7,700	17.67	7,430	16.98
700	15,760	32.96	10,490	21.96	10,200	21.24
800	19,980	38.59	13,350	25.78	13,080	25.09
900	24,230	43.59	16,300	29.25	15,980	28.50
1000	28,620	48.22	19,300	32.41	18,890	31.56
1100	33,130	52.52	22,400	35.36	21,830	34.37
1200	37,740	56.53	25,650	38.19	24,900	37.04
1300	42,620	60.43	29,200	41.03	27,950	39.45
1310			α29,550	41.30		
1310			β32,690	43.70		
1400	47,960	64.39	36,040	46.17	31,090	41.77
1445	α50,460	66.15				
1445	β54,960	69.26				
1500	57,700	71.12	39,840	48.79	34,300	43.99
1600	62,700	74.38				
1700	67,740	77.40				
1800	72,820	80.31				

This table, in combination with similar tables for oxygen, carbon, and silicon, permits ready calculation of free energies at these temperatures from whatever values of the heat of formation an investigator may select.

Summary

The heat contents of Mn₃O₄, MnSiO₃ and Mn₃C from room temperature to temperatures between 1140 and 1500° have been determined. These determinations have disclosed transitions of Mn₃O₄ at 1172° and Mn₃C at 1037°.

A table summarizing the increments in the heat contents and entropies of these substances above room temperature at 100° intervals has been prepared from these data and others in the literature.

NIAGARA FALLS, N. Y.   RECEIVED APRIL 6, 1942

Heat of Formation and High-temperature Heat Content of Manganous Oxide and Manganous Sulfate. High-temperature Heat Content of Manganese[1]

BY J. C. SOUTHARD[2] AND C. HOWARD SHOMATE[3]

The free energy of formation of manganous oxide at high temperatures has been uncertain because of the lack of satisfactory high-temperature heat content data. Further, the heat of formation of manganous oxide has been based almost entirely on heats of combustion. The combustion of manganese metal with oxygen in the bomb calorimeter does not proceed according to any definite reaction but yields a mixture of oxides assumed to be manganous oxide and manganomanganic oxide.[4,5] The mixture consists of 10 to 50 per cent. manganous oxide. The heat of formation of manganous oxide therefore has depended on the combustion of manganous oxide to manganomanganic oxide. This requires the use of paraffin oil and also yields a product of varying composition. Under these conditions the heat of reaction is only 5 per cent. of the total heat measured.[5] The heat of reaction also seemed to depend on whether the fraction converted to manganomanganic oxide was determined by increase in weight or by actual analysis.[4] Determination of the heat of formation of manganous oxide by a completely independent, more direct, method appears advantageous.

The thermodynamic properties of manganese sulfate have been studied and entropies of the substances involved already have been determined, as well as the high-temperature heat-content data, with the exception of manganous sulfate. The heat of formation of manganous sulfate has not been determined since the days of Thomsen and Berthelot, at which time pure manganese was not available.

Methods and Materials

The high-temperature heat contents were determined in an apparatus previously described.[6] The apparatus was calibrated electrically, using the relation 1 calorie = 4.1833 Int. joules. During the measurements manganous oxide and manganous sulfate were contained in a sealed platinum-alloy capsule and manganese metal in an evacuated and sealed silica-glass capsule. The heats of formation of manganous oxide and manganous sulfate

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(2) Formerly Chemist, Metallurgical Division, Bureau of Mines; present address, Titanium Alloy Mfg. Co., Niagara Falls, N. Y.

(3) Assistant Chemist, Metallurgical Division, Bureau of Mines.

(4) W. A. Roth, Z. angew. Chem., 42, 981 (1929).

(5) H. Siemonsen, Z. Elektrochem., 45, 637 (1939).

(6) J. C. Southard, THIS JOURNAL, 63, 3142 (1941).

TABLE I

HEAT OF SOLUTION OF MANGANESE, MANGANOUS OXIDE AND MANGANOUS SULFATE IN 1.006 N SULFURIC ACID

1 G. F. W. IN 100.27 KG. ACID AT 298.1° K.

	Manganese sample A, cal./g. f. w.	MnO, cal./g. f. w.	MnSO₄, cal./g. f. w.	Manganese "quenched," sample B, cal./g. f. w.
	−54,023	−30,607	−11,621	−54,081
	−54,041	−30,643	−11,644	−54,111
	−54,008	−30,653	−11,623	−54,089
				−54,075
Mean	−54,024 ± 11	−30,634 ± 18	−11,629 ± 10	−54,089 ± 11
Corrn. for evap. of water	−332			−332
Corrn. for diln. by water		2		
Corrected mean	−54,356	−30,632	−11,629	−54,421

were determined by the solution of manganese, manganous oxide and manganous sulfate in 1.006 N sulfuric acid solution in a calorimeter also described previously.[7] The time of solution was about twelve minutes for manganese and manganous sulfate and about twenty to thirty minutes for manganous oxide.
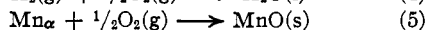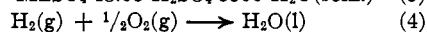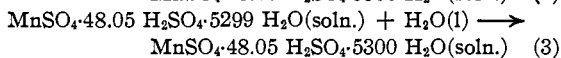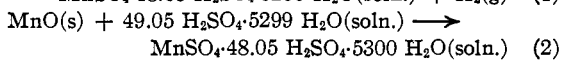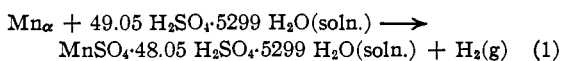
The manganese metal was an electrolytic product at least 99.9 per cent. pure. It was degassed by heating to 850° in a vacuum corresponding to 10^{-5} mm. and allowed to cool slowly (sample A). A portion of this sample was quenched from 800° in the high-temperature calorimeter (sample B) for use in certain heat-of-solution measurements. The metal was sized by passing through a 20-onto a 28-mesh screen. The manganous oxide was prepared by Millar[8] by reduction of higher oxides with hydrogen at 1100°. It was further purified for this work by removing visible particles of silica by flotation with tetrabromomethane, followed by drying in a high vacuum up to 250°. Analysis showed that it contained less than 0.04% silica and 77.42, 77.45% Mn (calcd. 77.44%). Manganese sulfate was prepared from a hydrated "C. P." preparation. It was found to contain 36.33% Mn by analysis (calcd. 36.38%). It was dried to constant weight in the capsule and bulbs at 400° before being weighed and sealed.

Results

Heat of Formation.—The heats of solution of manganese, manganous oxide, and manganous sulfate are summarized in Table I. Determinations were made at the dilution of 1 gram-atom of manganese to 100.27 kg. of acid solution. Correction for the vaporization of water by evolved hydrogen was made on the assumption that none of the hydrogen remained in solution by the time equilibrium was attained, and that it was saturated with water vapor when it left the solution. The partial pressure of water vapor over the acid solution was taken to be 23.34 mm. at 25° with a temperature coefficient of 0.14 mm. per degree. The heat of vaporization of water from 1 N sulfuric acid was taken to be 10,501 cal./g. f. w. at

25°. The final temperature lay between 25.0 and 25.2° in every case.

The heat of formation of manganous oxide, according to Eq. 5, is calculated from the heats of the following reactions, all at 298.1° K.

$$Mn_\alpha + 49.05\ H_2SO_4 \cdot 5299\ H_2O(soln.) \longrightarrow$$
$$MnSO_4 \cdot 48.05\ H_2SO_4 \cdot 5299\ H_2O(soln.) + H_2(g) \quad (1)$$
$$MnO(s) + 49.05\ H_2SO_4 \cdot 5299\ H_2O(soln.) \longrightarrow$$
$$MnSO_4 \cdot 48.05\ H_2SO_4 \cdot 5300\ H_2O(soln.) \quad (2)$$
$$MnSO_4 \cdot 48.05\ H_2SO_4 \cdot 5299\ H_2O(soln.) + H_2O(l) \longrightarrow$$
$$MnSO_4 \cdot 48.05\ H_2SO_4 \cdot 5300\ H_2O(soln.) \quad (3)$$
$$H_2(g) + {}^1/_2O_2(g) \longrightarrow H_2O(l) \quad (4)$$
$$Mn_\alpha + {}^1/_2O_2(g) \longrightarrow MnO(s) \quad (5)$$
$$\Delta H_5 = \Delta H_1 + \Delta H_4 - \Delta H_2 + \Delta H_3$$

The heats of reactions (1), (2) and (3) are given in Table I. The heat of reaction (4) was determined by Rossini[9] as −68,318 ± 9 cal./g. f. w. The heat of formation of manganous oxide from the elements at 298.1° K. is thus computed to be −92,040 ± 110 cal./g. f. w. The limits of error are estimated as the sum of the average deviations from the mean of the heats of solution of manganese and manganous oxide, plus 0.05% of the total energy measured, plus 10% of the correction for vaporization of water plus 9 calories uncertainty in the heat of formation of water. The value computed here allows the maximum correction for vaporization of water by the evolved hydrogen. Any other assumption would decrease the magnitude of the heat of formation. A comparison of the present value of the heat of formation of manganous oxide with those previously determined is given in Table II. Virtually all previous data were obtained by combustion methods from Le Chatelier's day on.

The value determined here by solution methods is believed to be more trustworthy than that obtained by combustion methods, for two reasons. (1) The combustion process does not proceed ac-

(7) J. C. Southard, *Ind. Eng. Chem.*, **32**, 442 (1940).

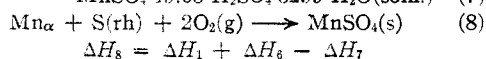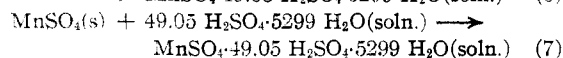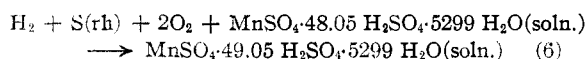(8) R. W. Millar, THIS JOURNAL, **50**, 1875 (1928).

(9) F. D. Rossini, *Bur. Standards J. Res.*, **22**, 407 (1939).

TABLE II

HEAT OF FORMATION OF MANGANOUS OXIDE

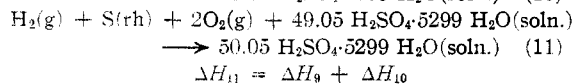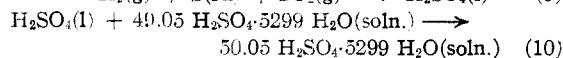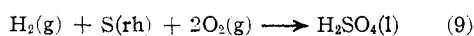|	Year	Method	$\Delta H_{298.1}$ cal./g. f. w.
Le Chatelier[10]	1896	Combustion with oxygen and charcoal	-90,900
Guntz[11]	1896	Not stated	-98,200
Roth[4]	1929	Combustion with oxygen and oil	-96,200
Siemonsen[5]	1939	Combustion with oxygen and oil	-93,100
This work	1942	Solution in 1 N sulfuric acid	-92,040 ± 110

cording to any definite reaction, while the initial and final states in the solution method are well-defined. (2) The total amount of heat per g. f. w. of manganous oxide measured in the combustion method is 5 to 7 times that measured by the solution method. The agreement between the present work and that of Siemonsen is evidence of extremely careful calorimetry on his part. The result of Roth and Müller is higher because they used a sample contaminated by silicon and aluminum and probably because it contained hydrogen.

The heat of formation of manganous sulfate from the elements (Eq. 8) is calculated from Eq. (1) above, in combination with the following reactions, all at 298.1° K.

$$H_2 + S(rh) + 2O_2 + MnSO_4 \cdot 48.05\ H_2SO_4 \cdot 5299\ H_2O(soln.)$$
$$\longrightarrow MnSO_4 \cdot 49.05\ H_2SO_4 \cdot 5299\ H_2O(soln.) \quad (6)$$
$$MnSO_4(s) + 49.05\ H_2SO_4 \cdot 5299\ H_2O(soln.) \longrightarrow$$
$$MnSO_4 \cdot 49.05\ H_2SO_4 \cdot 5299\ H_2O(soln.) \quad (7)$$
$$Mn_\alpha + S(rh) + 2O_2(g) \longrightarrow MnSO_4(s) \quad (8)$$
$$\Delta H_8 = \Delta H_1 + \Delta H_6 - \Delta H_7$$

The heat of reaction (7) is given in Table I. ΔH_6 is calculated from the heats of the reactions

$$H_2(g) + S(rh) + 2O_2(g) \longrightarrow H_2SO_4(l) \quad (9)$$
$$H_2SO_4(l) + 49.05\ H_2SO_4 \cdot 5299\ H_2O(soln.) \longrightarrow$$
$$50.05\ H_2SO_4 \cdot 5299\ H_2O(soln.) \quad (10)$$
$$H_2(g) + S(rh) + 2O_2(g) + 49.05\ H_2SO_4 \cdot 5299\ H_2O(soln.)$$
$$\longrightarrow 50.05\ H_2SO_4 \cdot 5299\ H_2O(soln.) \quad (11)$$
$$\Delta H_{11} = \Delta H_9 + \Delta H_{10}$$

The heat of reaction 9 was calculated to be -194,100 ± 100 cal./g. f. w. from the heat of formation of sulfur dioxide of Eckmann and Rossini[12] and the heat of oxidation of sulfur dioxide and heats of solution of sulfur dioxide, sulfur trioxide and sulfuric acid obtained by Roth, Grau and Meichsner.[13] It was necessary to correct some of the data to 25°. The limits of error are those set by Roth. The heat of reaction (10) has been calculated from the data of Grau and Roth[14] at about

(10) H. Le Chatelier, Compt. rend., **122**, 80 (1896).

(11) Guntz, ibid., **122**, 465 (1896).

(12) J. D. Eckmann and F. D. Rossini. Bur. Standards J. Res., **3**, 597 (1929).

(13) W. A. Roth, R. Grau and A. Meichsner, Z. anorg. Chem., **193**, 169 (1930).

(14) R. Grau and W. A. Roth, ibid., **188**, 195 (1930).

290° K. as -17,350 calories. No correction was made to 298.1° K., and the error is estimated at ±50 cal. The heat of reaction (11) must necessarily be assumed the same as that of reaction (6) but little error can arise from this source because the ionic strengths of the solutions are the same. The heat of formation of manganous sulfate from the elements is thus calculated to be -254,180 ± 250 cal./g. f. w. at 298.1° K. The limits of error are estimated as the sum of the average deviations from the mean of the heats of solution of manganese and manganous sulfate, plus 0.05% of the total energy measured, plus 10% of the correction for vaporization of water by the hydrogen in Eq. 1, plus 100 calories in the heat of formation of sulfuric acid plus 50 calories for the heat of reaction (10).

Previous determinations of the heat of formation of manganous sulfate at room temperature by Thomsen ($\Delta H = -249,730$) and Berthelot ($\Delta H = -249,400$) are discussed by Kelley.[15] Maier[16] has calculated a value of $\Delta H_{298.1} = -250,700$ from the dissociation pressure measurements of Marchal.[17] This value is not changed much by using the present high-temperature heat-content data, but may be changed by the proposed investigation of the heat of formation of mangano-manganic oxide. However, Marchal's data lead to an abnormally high entropy of manganous sulfate so that not much weight can be given to values of the heat of formation calculated from them.

The difference in the heats of solution of annealed and "quenched" manganese is computed from Table I to be 65 calories per g. f. w. This heat is required for the calculation of heat contents of manganese above the transition at 1012° K.

High-temperature Heat Contents.—The measurements of the heat content at $T°$ K., minus the heat content at 298.1° K. for manganese, manganous oxide, and manganese sulfate, are given in Tables III, IV and V. Manganous oxide and manganese sulfate show no transitions. Manganese metal shows a transition at 1012° K. Known transitions at higher temperatures could not be investigated in this work because of devitrification of the silica-glass capsule and reaction of the manganese with it. The correction of 65 cal./g. f. w. must be applied to the data of Table III above 1012° K. because the manganese did

(15) K. K. Kelley, Bur. Mines Bull., **406**, 101 (1937).

(16) C. G. Maier, Bur. Mines Inf. Circ. 6769, 68 (1934)

(17) G. Marchal, J. chim. phys., **22**, 559 (1925).

not come to the same final state in the calorimeter when dropped from temperatures above this as when dropped from temperatures below it. It is not supposed that this quantity represents the difference in heat content between α and β manganese at 298.1° K. but merely that it is a correction that must be applied to the calorimetric heat obtained when the capsule was dropped from the temperature range in which β manganese is stable.

TABLE III	
HIGH-TEMPERATUTE HEAT CONTENT OF MANGANESE (g. f. w. = 54.93)	
T, ° K.	$H_T - H_{298.1}$ cal./g. f. w.
963.8	5030
962.8	4987
925.6	4686
669.0	2622
669.3	2626
486.4	1264
481.7	1206
880.7	4307
879.2	4298
962.5	5016
1003.9	5361
977.6	5134
1027.1	6103
1071.8	6395
1075.4	6431
1013.0	5988
2d series	
855.5	4116
1153.0	7221
1161.6	7331
1260.1	8246
1264.5	8276
1307.3	8666
1307.3	8640
1105.8	6737
1379.1	9505

TABLE IV	
HIGH-TEMPERATURE HEAT CONTENT OF MANGANOUS OXIDE (g. f. w. = 70.93)	
T, ° K.	$H_T - H_{298.1}$ cal./g. f. w.
1268.6	12,050
1270.1	12,080
1041.6	8,980
1043.5	8,980
774.6	5,600
774.6	5,572
519.8	2,517
518.9	2,503
1519.0	15,490
1511.0	15,310
1153.8	10,440
1258.5	11,850
1773.4	18,980

TABLE V	
HIGH-TEMPERATURE HEAT CONTENT OF MANGANESE SULFATE (g. f. w. = 150.99)	
T, ° K.	$H_T - H_{298.1}$ cal./g. f. w.
870.3	18,180
873.5	18,250
681.5	11,620
679.9	11,480
497.0	5,520
483.3	5,070
1083.6	26,140
1082.3	26,060

The heat of transition $\alpha \rightarrow \beta$ manganese is calculated from the heat-content data to be 615 calories per g. f. w. at 1012° K. This includes the above-mentioned 65 calories. Gaylor[18] reported the transition as occurring at 1013 ± 2° K., with distilled manganese. Umino[19] observed that this transition occurred at 1108° K., accompanied by a heat effect of but 68 calories per g. f. w. Other investigators of the high-temperature heat content observed none at all. There was no evidence in

the present work of a transition reported by Gaylor at 943° K.

Previous measurements on the high-temperature heat content of manganese have been surveyed by Kelley.[20] The present work lies between that of Umino and that of Wüst, Meuthen and Durrer[21] and not far from that of Laemmel.[22] The present work is believed to be more reliable because it was done with a higher-purity sample of manganese, completely protected from oxidation, and with a higher-precision calorimeter than was previous work.

No previous determinations have been reported on the heat content of manganous oxide and manganous sulfate at high temperatures.

Table VI is a summary at 100° intervals of the heat content and entropy above 298.1° K. of manganese, manganous oxide and manganous sulfate. The 65-cal. correction to the heat content of manganese in the β range has been applied. Table VI also includes values of the free energy of formation of manganous oxide from gaseous oxygen and the form of manganese stable at the stated temperature. The present value of $-92,040$ cal./g. f. w. for the heat of formation of manganous oxide is used in conjunction with the values 7.61, 24.52 and 14.4 for the entropies of manganese, $\frac{1}{2}$ oxygen and manganous oxide, respectively,[23] to calculate a free energy of formation of manganous oxide of $-86,760$ cal./g. f. w. at 298.1° K. Values at higher temperatures were calculated with the aid of the present high-temperature heat-content data on manganese and manganous oxide and the tables of free energy of oxygen given by Johnston and Walker.[24] Comparison may be made with the experimental data of Aoyama and Oka[25] for the reaction $Mn + H_2O(g) \rightleftarrows MnO + H_2(g)$. They made five determinations in the temperature range 1,048 to 1,460° K. Their data were recalculated to the reaction $Mn + \frac{1}{2}O_2 \rightarrow MnO$ by adding the free energy of formation of water vapor, which was calculated from the tables of A. R. Gordon[26] and W. F. Giauque,[27] and the free energy of formation of water vapor at 298.1° K.

(18) M. L. V. Gaylor, J. Iron Steel Inst., 115, No. 1, 393 (1927).
(19) S. Umino, Sci. Repts. Tôhoku Imp. Univ., 16, 775 (1927).

(20) K. K. Kelley, U. S. Bur. Mines Bull., No. 371, p. 34 (1934).
(21) F. Wüst, A. Meuthen and R. Durrer, Forsch. Arb. Ver. deut. Ing., No. 204 (1918).
(22) R. Laemmel, Ann. Physik, 16, 551 (1905).
(23) K. K. Kelley, Bur. Mines Bull. 434, 115 (1941).
(24) H. L. Johnston and M. K. Walker, THIS JOURNAL, 55, 183 (1933).
(25) S. Aoyama and Y. Oka, Sci. Repts. Tôhoku Imp. Univ., 22, 824 (1933).
(26) A. R. Gordon, J. Chem. Phys., 2, 65 (1934).
(27) W. F. Giauque, THIS JOURNAL, 52, 4816 (1930).

TABLE VI

HEAT CONTENTS AND ENTROPIES OF MANGANESE AND MANGANOUS OXIDE ABOVE 298.1° K. AND THE FREE ENERGY OF FORMATION OF MANGANOUS OXIDE AT 100° INTERVALS

| T, ° K. | Mn | | MnO | | | MnSO₄ | |
	$H_T - H_{298.1}$, cal./g. f. w.	$S_T - S_{298.1}$, cal./deg. g. f. w.	$H_T - H_{298.1}$, cal./g. f. w.	$S_T - S_{298.1}$, cal./deg. g. f. w.	ΔF of formation, cal./g. f. w.	$H_T - H_{298.1}$, cal./g. f. w.	$S_T - S_{298.1}$, cal./deg. g. f. w.
298.1					−86,760		
400	660	1.89	1130	3.26	−84,970	2680	7.70
500	1364	3.46	2280	5.82	−83,240	5630	14.28
600	2100	4.80	3470	7.99	−81,520	8850	20.14
700	2874	5.99	4680	9.85	−79,820	12210	25.32
800	3668	7.05	5900	11.48	−78,120	15710	29.99
900	4480	8.00	7150	12.95	−76,430	19280	34.18
1000	5328	8.90	8430	14.30	−74,730	22970	38.07
1012α	5438	9.01					
1012β	6053	9.62					
1100	6750	10.26	9750	15.56	−73,000	26730	41.65
1200	7734	11.11	11100	16.73	−71,260		
1300	8672	11.86	12470	17.82	−69,500		
1340β	9040	12.14					
1340γ	(9220)	(12.28)					
1400	(9770)	(12.69)	13840	18.84	−67,740		
1500	(10690)	(13.33)	15210	19.79	−65,980		

given by Rossini.[9] The three lowest of Aoyama and Oka's points lie within a few hundred calories of values interpolated from Table VI, which may be said to be in good agreement. In general, however, their data give a larger ΔH and ΔS for the reaction than may be calculated from the third law.

Summary

The heat of formation of manganous oxide has been determined to be −92,040 ± 110 calories per g. f. w. and of manganous sulfate to be −254,180 ± 250 calories per g. f. w. at 25°.

The heat contents of manganese, manganous oxide, and manganous sulfate from room temperature to temperatures between 811 and 1500° have been determined. These observations have disclosed a transition in manganese at 739°.

A table summarizing increments of heat contents, entropies and free energies at 100° intervals has been prepared from these data and others in the literature.

Isomers of Crystal Violet Ion. Their Absorption and Re-emission of Light

BY GILBERT N. LEWIS, THEODORE T. MAGEL AND DAVID LIPKIN

The possibility of a new type of isomerism in such substances as triphenylmethyl and its ions was pointed out recently.[1] An extensive investigation of the light absorption of the free radicals has not given us positive evidence of such isomerism.[2] On the other hand, in the derivatives of triphenylmethyl ion we have sought, and believe to have found, these isomers.

It is often observed that the absorption curve of what is apparently a single substance, such as the ion of crystal violet (tris-(dimethyl-p-aminophenyl)-methyl ion, Fig. 6) as it exists in neutral or alkaline solution, has a shoulder as seen in Fig. 1. This shoulder suggests the superposition of two neighboring bands, which might result from (1) a partial resolution of the vibrational structure belonging to a single electronic level, which, according to the work of Dr. Goldschmid,[2] seems to be the explanation of a similar shoulder in the adsorption curve of methylene blue, or (2) two neigh-

(1) Lewis and Calvin, Chem. Rev., 25, 273 (1939).

(2) The two absorption bands of triphenylmethyl in the visible which were obtained by Meyer and Wieland [Ber., 44, 2557 (1911)] and which were resolved into three bands by Anderson [THIS JOURNAL, 57, 1673 (1935)] were shown by Dr. O. Goldschmid [Ph.D. Thesis, University of California (1939)] to be vibrational bands belonging to a single electronic band. This was shown by comparison of the absorption and fluorescence spectra of triphenylmethyl. We have further confirmed his results, but with a very high resolution we have found a much more intricate structure. This will be discussed in another place.