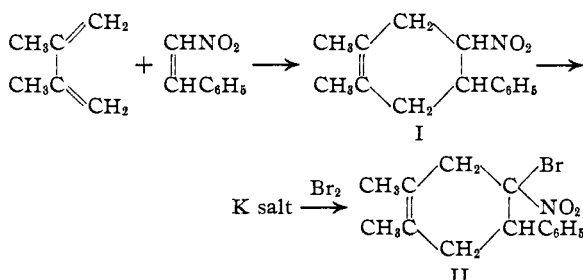


TABLE I
PROPERTIES OF THE (ADDITION) PRODUCTS

Addend	Yield, %	M. p., °C.	Formula	Calcd., %			Found, %		
				C	H	N	C	H	N
2,3-Dimethylbutadiene	82	96	C ₁₄ H ₁₇ O ₂ N	73.2	7.4		72.9	7.4	
Isoprene	7	52	C ₁₈ H ₁₆ O ₂ N	71.9	7.0	6.5	72.4	7.1	6.2
2,3-Diphenylbutadiene ^{a,b}	9	175	C ₂₄ H ₂₁ O ₂ N	81.1	5.9	3.9	81.2	6.0	3.8
1,4-Diphenylbutadiene	40	130	C ₂₄ H ₂₁ O ₂ N	81.1	5.9	3.9	80.9	5.8	4.2
Methyleneanthrone ^{a,c,d}	3	255	C ₂₈ H ₁₈ O ₈ N	78.6	3.7	4.0	78.6	3.7	4.1
Tetracyclone ^{a,e}									
B. p.									
Phellandrene	45	190/1 mm.	C ₁₈ H ₂₈ O ₂ N	75.8	8.4	4.9	76.3	8.1	4.5
Cyclopentadiene	95	145/1 mm.	C ₁₈ H ₁₆ O ₂ N	72.6	6.1	6.5	72.6	6.1	6.4
Cyclohexadiene	20	138-142/1 mm.	C ₁₄ H ₁₆ O ₂ N	73.3	6.6	6.1	72.9	6.1	6.4

^a Oxides of nitrogen evolved. ^b 5% yield of a hydrocarbon, C₂₄H₂₀, m. p. 77°. Calcd. C, 93.5; H, 6.5. Found: C, 93.0; H, 6.7. ^c 25% yield of *Bz*-1-phenylbenzanthrone. ^d On oxidation, the product yielded α -benzoylanthraquinone, hence it is *Bz*-1-phenyl-*bz*-2-nitrobenzanthrone. ^e Gave only pentaphenylbenzene, m. p. 246°, mixed m. p. 246°.

tion, they dissolve in alkaline solutions, and the latter take up bromine. Substance I does not decolorize bromine.



Anal. Calcd. for C₁₄H₁₆O₂NBr (II): C, 54.2; H, 5.2; N, 4.5. Found: C, 54.2; H, 5.1; N, 4.3.

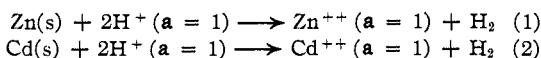
EASTMAN KODAK COMPANY
ROCHESTER, N. Y.

RECEIVED JANUARY 6, 1939

The Entropies of Aqueous Zinc and Cadmium Ions. The Heat Capacity of Zinc Ion

BY ROGER G. BATES¹

Recent studies by the writer have shown² that the standard electromotive forces, E^0 , of the reactions



may be expressed by the equations

$$E_{\text{Zn}}^0 = 0.76274 - 0.0001(t - 25) - 0.00000031(t - 25)^2 \quad (3)$$

$$E_{\text{Cd}}^0 = 0.40178 + 0.000089(t - 25) + 0.00000081(t - 25)^2 + 0.00000075(t - 25)^3 \quad (4)$$

(1) Sterling Fellow.

(2) Bates, *THIS JOURNAL*, **60**, 2983 (1938); **61**, 308 (1939).

(3) Precise measurements of this cell between 0 and 30° were made by Parks and La Mer, *ibid.*, **56**, 90 (1934). The result of Getman, *ibid.*, **39**, 1806 (1917), at 35° does not agree sufficiently well with the value calculated from the equation of Parks and La Mer to justify extending the range of validity of equation (4) to that temperature.

where t is the temperature in degrees C.

Equation (3) is valid over the temperature range 5 to 40°, but the upper temperature limit for equation (4) must be set at 30°, above which consistent measurements of the cell³ Cd(Hg)/Cd⁺⁺/Cd(s) have not been made.

By the application of the usual thermodynamic relationships to equations (3) and (4), ΔF^0 , ΔH^0 , ΔS^0 and ΔC_p^0 for reactions (1) and (2) may be computed. The values of these quantities for reaction (1) at 15, 25 and 35° and for reaction (2) at 15 and 25° are summarized in Table I. Uncertainties in d^2E^0/dT^2 from equation (4) are sufficiently large to render ΔC_p^0 for reaction (2) useless for the calculation of ionic heat capacities; ΔC_p^0 for this reaction has therefore been omitted from Table I.

TABLE I
THERMODYNAMIC QUANTITIES FOR REACTIONS (1) AND (2)

t	E^0	ΔF^0	ΔH^0	ΔS^0	ΔC_p^0
Reaction (1)					
15	0.76371	-35,244	-36,491	-4.34	-8.24
25	.76274	-35,199	-36,575	-4.61	-8.53
35	.76171	-35,151	-36,661	-4.90	-8.82
Reaction (2)					
15	0.40089	-18,500	-17,233	4.40	
25	.40178	-18,541	-17,317	4.11	

Standard entropies and heat capacities of hydrogen and zinc and the entropy of cadmium are listed in Table II. Values at 25° for zinc and cadmium and for the entropy of hydrogen were taken from the summary of Kelley.⁴ The heat capacity of hydrogen at all three temperatures and the temperature coefficient of the heat ca-

(4) Kelley, Bureau of Mines, Bull. 394, U. S. Government Printing Office, Washington, D. C., 1936.

TABLE II
THERMODYNAMIC DATA FOR H₂, Zn AND Cd

<i>t</i>	H ₂	S ⁰ Zn(s)	Cd(s)	H ₂ C _p ⁰	Zn(s)
15	31.00	9.74	12.1	6.86	6.05
25	31.23	9.95	12.3	6.86	6.07
35	31.46	10.15		6.88	6.10

capacity of zinc were taken from the equations of Kelley⁵ for these elements. Entropies at 15 and 35° were computed from S_{298.1}⁰ and the specific heat equations, corrected to conform with revised C_p⁰ values at 298.1°K.⁶

The entropies of aqueous zinc and cadmium ions and the heat capacity of zinc ion are listed in Table III in calories per degree per mole. As is customary, the standard entropy and heat capacity of aqueous hydrogen ion have been considered zero at all temperatures.

TABLE III
RELATIVE ENTROPIES OF ZINC AND CADMIUM IONS.
RELATIVE HEAT CAPACITY OF ZINC ION

	Zn ⁺⁺	Cd ⁺⁺	C _p ⁰ Zn ⁺⁺
15	-25.60	-14.50	-9.05
25	-25.89	-14.82	-9.32
35	-26.21		-9.60

It is probable that the accuracy of the entropy of zinc ion is of the order of ± 0.5 cal./deg. mole. The value for the entropy of cadmium ion is subject to the combined uncertainties inherent in the work of the author and of Parks and La Mer, but it is thought to be correct to about ± 1 cal./deg. mole.

Latimer, Pitzer and Smith,⁷ in their recent review of ionic entropies, list -25.7 ± 1 and -16.4 ± 1.5 for zinc and cadmium ions, respectively. The value for the standard entropy of cadmium ion computed from equation (4) lies just outside the limit of accuracy estimated by these authors. For zinc ion the agreement is excellent.

(5) Kelley, Bureau of Mines, Bull. 371, 1934.

(6) See footnote 23 of the paper by Owen and Brinkley, THIS JOURNAL, 60, 2233 (1938).

(7) Latimer, Pitzer and Smith, *ibid.*, 60, 1829 (1938).

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RECEIVED NOVEMBER 8, 1938

The Aldehydic Constituents from the Ethanolsis of Spruce and Maple Woods

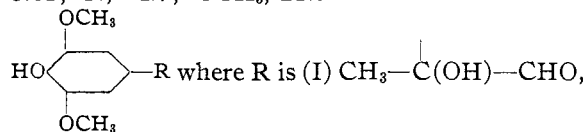
BY LEO BRICKMAN, JAMES J. PYLE AND HAROLD HIBBERT

In accompanying communications¹ from these Laboratories the occurrence has been reported of

(1) Cramer, Hunter and Hibbert, THIS JOURNAL, 61, 509 (1939); Hunter, Cramer and Hibbert, *ibid.*, 61, 516 (1939).

aldehydic constituents among the ethanolsis products of spruce and maple woods. The aldehyde fraction of the latter readily yields a crystalline semicarbazone, m. p. 210–210.5°, analysis of which points to a structural formula for the aldehyde corresponding to either I, II, III, IV or V.

Anal. Calcd. for C₁₂H₁₇O₅N₃ (I, II, III): C, 50.87; H, 6.05; N, 14.8; OCH₃, 21.9. Calcd. for C₁₂H₁₅O₅N₃ (IV and V): C, 51.24; H, 5.37; N, 14.9; OCH₃, 22.0. Found: C, 51.61; H, 5.61; N, 14.7; OCH₃, 21.9.



where R is (I) CH₃—C(OH)—CHO, (II)—CH(OH)CH₂CHO, (III)—CH₂CH(OH)CHO, (IV)—COCH₂CHO and (V)—CH₂COCHO. The experimental data are somewhat in favor of IV or V but nevertheless in good agreement with all five structures.

A similar semicarbazone has also been isolated from the ethanolsis aldehyde fraction of spruce wood and the investigation of both products is in progress.

The relation of both to the structure of lignin is discussed in the accompanying *communication* by one of us (H. H.)

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RECEIVED DECEMBER 19, 1938

The Phosphorescence of Tetraphenylmethane and Certain Related Substances

BY DANIEL B. CLAPP

Upon irradiation of solid crystalline tetraphenylmethane and certain of its derivatives with ultraviolet light from a Hanovia quartz mercury vapor cold-discharge lamp, it was noted that the substances exhibit marked luminescence after extinction of the exciting light. Tetraphenylmethane,¹ m. p. 281.5–282°, which was purified by distillation, sublimation, and recrystallization, shows a brilliant blue-green after-glow, with a visible duration at room temperature of about twenty-three seconds. The duration of the phosphorescence is dependent upon temperature; at 130° the duration is so short that no after-glow is visible; at 125° it persists for about two seconds, at 80°

(1) Prepared both according to Ullmann and Münzhuber, *Ber.*, 36, 404 (1903), and to Schoepfle and Trepp, THIS JOURNAL, 58, 794 (1936).