the end-point for ammonia corresponds to about 0.38 volt, but the curve is steep between 0.25 volt and 0.53 volt. Evidently, therefore, bromophenol blue, changing at 0.34 volt, or resorcin blue, changing at 0.39 volt, should give a sharp end-point in the titration of ammonia.

Summary.

Hydrogen-electrode titration-curves are given for a number of reactions in the ethyl alcohol system, together with a table of indicators for use in such reactions. The possible applications of the data obtained are illustrated by the titration of a fatty acid in the presence of its glyceride.

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NOTE.

The Relation Between Entropy and Probability.[1] The Integration of the Entropy Equation.—The rate of increase of the specific heat with the entropy of a given element or compound depends upon the probability of the randomness of the individual particles. At the absolute zero, or at the point of zero kinetic energy we are quite certain that each particle will remain in a fixed position. The probability, therefore, will be unity. At relatively high temperatures the probability of that state prevailing is very nearly zero. Now, the mathematical expression of the above statements may be assumed to be proportional to the term, $\dfrac{C_\infty - C}{C_\infty}$,

which at the absolute zero is unity and at relatively high temperatures approaches zero, or,

$$\frac{dC}{dS} = K \left\{ \frac{C_\infty - C}{C_\infty} \right\} \tag{1}$$

Assuming that when C is zero S is also zero, Equation 1 on integration gives,

$$S = \frac{C_\infty}{K} \log \frac{C_\infty}{C_\infty - C} \tag{2}$$

The value of K may be readily obtained by substituting in Equation 1 $C dT/T$ for its equal dS and integrating. Thus,

$$\frac{dC}{dT} = \frac{K(C_\infty - C)C}{C_\infty \ T}. \tag{3}$$

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[1] The specific heats of all solid substances decrease with the temperature and approach zero as the absolute temperature approaches zero. This experimental fact led to the assumption that at the absolute zero of temperature the specific heat of all substances is actually zero. Following this announcement many attempts were made, notably by Einstein, (*Ann. Physik*, [4] **22**, 180 (1907)), Nernst and Lindemann, (*Sitzt. Akad. Wiss. Berlin.*, 494, **1911**), Debye, (*Ann. Physik,* [4] **39,** 789 (1912)), and by Planck, "Theorie der Wärmestrahlung," to express the specific heat as a simple function of the absolute temperature, but with no success.

Whence,

$$\log \frac{C}{C\infty - C} = K \log T + \log k \qquad (4)$$

In the straight line equation (4) K is the slope, and $\log k$ is the intercept on the ordinate.[2] This equation may of course be written in the simpler form,

$$C = \frac{C\infty\, kT^K}{kT^K + 1}. \qquad (5)$$

Equation 4 or 5 reproduces the experimental data, within the probable error, for the specific heats of all substances thus far obtained by thermoelectric methods.

The following table giving the results for copper demonstrates this.

TABLE I

CALCULATIONS OF THE SPECIFIC HEAT OF COPPER AT DIFFERENT TEMPERATURES BY

THE FORMULA $C = \dfrac{C\infty\, kT^K}{kT^K + 1}$

1	2	3	4	1	2	3	4
T	C_p (obs.)	C_v Calc.	Diff.	T	C_p (obs.)	C_v Calc.	Diff.
Dutch (Leyden Laboratory)				English			
14.51	0.04	0.04	0.00	50.00	1.32	1.28	+0.04
15.59	0.05	0.05	0.00	90.00	3.98	3.57	+0.41
17.17	0.07	0.07	0.00	130.00	4.78	4.84	−0.06
20.19	0.11	0.11	0.00	170.00	5.23	5.39	−0.16
20.74	0.12	0.12	0.00	210.00	5.50	5.64	−0.14
25.37	0.23	0.22	+0.01	250.00	5.70	5.77	−0.07
29.73	0.38	0.34	+0.04	290.00	5.83	5.83	0.00
40.22	0.83	0.75	+0.08	390.00	6.09	....	......
50.04	1.43	1.28	+0.15	German (Nernst Laboratory)			
59.75	2.06	1.86	+0.20	23.5	0.22	0.18	+0.04
60.33	2.08	1.90	+0.18	27.7	0.32	0.28	+0.04
69.66	2.59	2.47	+0.12	33.4	0.54	0.46	+0.04
80.32	3.05	3.08	−0.05	87.0	3.33	3.43	−0.10
88.86	3.37	3.50	−0.13	88.0	3.38	3.47	−0.09
89.39	3.44	3.55	−0.11	137.0	4.57	4.98	−0.41
				234.0	5.59	5.72	−0.13
				290.0	5.79	5.83	−0.04
				323.0	5.90	5.87	+0.03

$$C\infty = 3\ R = 5.966$$
$$\log k = -5.4955$$
$$K = 2.900$$

The figures of Cols. 1 and 2 were collected by Dr. Latimer, Gilman Hall, University of California.

In the table following are given in the second and third columns, the values for K and for K_1, or $\log k$, obtained from the straight line experimental plots according to Equation 4; in the fourth column are given the

[2] Actually, the raw experimental C_p values were used in the straight line plots, as the increase in volume is negligibly small up to 100° A. and in some cases even up to 200° A.

specific heats per gram atom for constant volume, calculated from the values of K and K_1 with the aid of Equation 4 or 5. In the fifth column are given the entropies per gram atom or mol, calculated by means of Equation 2, and in the sixth column are given the values for the entropies obtained by Lewis and Gibson[3] by a graphical method.

Since Lewis and Gibson state that their calculated values are accurate to from 0.3 to 2.0 units of entropy the agreement between the two columns is entirely satisfactory. However, the values obtained by means of Equation 2 are slightly but consistently higher in most cases. This is due to the fact that for very low temperatures for which there are no available data Lewis and Gibson join to their graphical method the equation,

$$C = aT^3, \text{ whence } S = \frac{1}{3} C.$$

This is equivalent to the assumption that in Equation 1 $(C\infty - C)/C\infty$ remains unity at very low temperature and that $K = 3$ which is evidently not true, as a glance at the table will show.

TABLE II
ENTROPIES AT CONSTANT VOLUME

	K	K_1	C_v (298)	S_v (298) Calc. (Eq. 2)	S_v (298) Lewis & Gibson
Al	2.90	−5.6985	5.774	7.07	6.7
Cu	2.90	−5.4955	5.844	8.00	7.8
C, diamond	2.80	−7.4088	1.482	0.61	0.6
C, graphite	1.83	−4.7946	2.093	1.41	1.3
KCl	2.47	−4.3320	5.870	19.90	19.4
NaCl	2.94	−5.4008	5.887	17.55	17.2
PdCl₂	1.88	−3.1133	5.798	33.99	33.2
Na	2.334	−3.7157	5.916	12.23	11.7
I	1.84	−2.5074	5.911	15.20	14.8
Pb	2.18	−2.9652	5.943	15.21	15.0
S, rhombic	1.23	−2.4418	4.771	7.80	7.4
S, monocl.	1.30	−2.5627	4.882	7.83	7.6
Sn, gray	2.24	−4.0162	5.794	9.23	....
Sn, white	2.79	−4.7626	5.922	10.50	....
Cd	6.00	−10.2960	5.965	8.65	....
Ca	2.53	−4.3570	5.892	10.35	10.3
HgCl	1.60	−2.6235	5.702	23.26	23.2
Zn	2.40	−4.2204	5.880	10.54	9.7
Ag	2.36	−4.0875	5.862	10.24	9.9
Mg	2.57	−4.8409	5.790	8.18	8.1
CO(NH₂)₂	0.705	−1.7485	2.969	46.62	41.0 ±2[a]

[a] This value is taken from a paper by Gibson, Latimer and Parks, (THIS JOURNAL, 42, 1541 (1920)). On plotting the values of C_v, calculated by means of Equation 5, and also the experimental values for C_p against log T, the difference was found to be 8(0.035), whence $S_p(298) = 46.9$.

[3] Lewis and Gibson, THIS JOURNAL, 39, 2554 (1917), Tables VI, VIII.