

[CONTRIBUTION FROM THE EUREKA JUNIOR COLLEGE, SCIENCE DEPARTMENT]

CORRELATION OF ENTROPY AND PROBABILITY

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In a recent article¹ two equations are given, one connecting entropy and probability, and the other, specific heats and temperature. These equations are

$$S = \frac{C \infty}{K} \log \frac{C \infty}{C \infty - C} \quad (2)$$

$$C = \frac{C \infty k T^K}{k T^K + 1} \quad (5)^2$$

In the article just cited the validity of Equation 2 is amply substantiated by a comparison of the calculated entropies for 18 substances with the values obtained for the same substances by a graphical method. For Equation 5, however, only one set of calculated values is given, namely, those for the specific heats of copper. The purpose of the present article is to show that this equation which is based upon the laws of entropy and probability holds for the specific heats of all substances thus far obtained by thermo-electric methods. It will be seen that in all cases where check values are given (see silver chloride and aluminum) the deviations from the values calculated by means of Equation 5 are far less than the variations among the experimental values themselves. Most of these data have been obtained in Nernst's Laboratory³ and are scattered all through the literature in fragments, each writer smoothing, readjusting and generally vitiating the experimental data to suit his particular empirical equations. In the present paper are given presumably only the actually "observed" values. These have been subjected to the treatment described in the article previously cited. The results with the 31 substances, with the exception of those for ice and silver iodide, leave nothing to be desired. The data for the specific heats of these two compounds seem to be quite erroneous.

In conclusion it may be pointed out that from the results obtained with the aid of Equations 2 and 5 the values for Sp can in every case be found as follows: Calculate $Sv(298)$ by means of Equation 2, then with the aid

¹ Linhart, *THIS JOURNAL*, **44**, 140 (1922).

² Here, as in the article cited above, C denotes the average gram atomic heat at any temperature, T ; $C \infty$ equals $3R$, equals 5.966 cal.; k and K are constants. For convenience of computation and tabulation, $\log k$ is given instead of k and is denoted by K' . Where the values for K and K' are omitted in the present article they may be found in Table II of the article cited.

³ The data for Na, Mg, Ca, Cd, $TiCl_4$, CCl_4 , $SiCl_4$, $SnCl_4$, $HCOOH$, $CO(NH_2)_2$ were obtained in the Chemical Laboratory of the University of California and have been published in *THIS JOURNAL* within the past 5 years.

of two or three calculated C_v values, from the point where C_p begins definitely to exceed C_v ,⁴ sketch C_p and C_v against $\log T$ on uniform tracing paper or cloth, cut out the segment thus obtained and weigh it. Having previously determined the relation between a unit of entropy and a square unit of the tracing cloth, the difference between S_p and S_v is very accurately obtained, provided, of course, the substance does not undergo a modification in form or a change of state for the chosen temperature interval.

TABLES

Sodium				Calcium			
T	C_p (obs.)	C_v (calc.)	Diff.	T	C_p (obs.)	C_v (calc.)	Diff.
64.6	4.52	4.54	-0.02	80.6	4.42	4.44	-0.02
67.9	4.66	4.66	0.00	92.7	4.81	4.81	0.00
71.1	4.77	4.77	0.00	94.9	4.92	4.86	+0.06
74.2	4.81	4.86	-0.05	103.4	5.07	5.04	+0.03
84.6	5.08	5.11	-0.03				----- ^a
94.8	5.30	5.29	+0.01	141.4	5.70	5.51	+0.19
156.8	6.02	143.3	5.68	5.52	+0.16
Silver				145.2	5.75	5.54	+0.19
35.0	1.58	1.58	0.00	163.2	5.97	5.64	+0.16
39.1	1.90	1.90	0.00	198.5	6.36
42.9	2.26	2.19	+0.07	Cadmium			
45.5	2.47	2.50	-0.03	68.4	4.98	5.00	-0.02
51.4	2.81	2.81	0.00	70.7	5.20	5.15	+0.05
53.8	2.90	2.97	-0.07	72.5	5.29	5.25	+0.04
77.0	4.07	4.17	-0.10	74.8	5.25	5.36	-0.11
100.0	4.86	4.84	+0.02	75.7	5.36	5.40	-0.04
			----- ^a	76.8	5.45	5.44	+0.01
200.0	5.78	5.71	+0.07	78.8	5.32	5.51	-0.19
273.0	6.00	79.1	5.56	5.52	+0.04
331.0	6.01	80.7	5.49	5.51	-0.08
535.0	6.46	81.8	5.65	5.60	+0.05
589.0	6.64	84.2	5.71	5.65	+0.06
Magnesium				86.2	5.63	5.69	-0.06
74.9	2.90	2.90	0.00	87.0	5.67	5.70	-0.03
78.3	3.03	3.08	-0.05	88.4	5.74	5.73	+0.01
83.5	3.33	3.32	+0.01	90.0	5.78	5.75	+0.03
92.1	3.61	3.68	-0.05	92.5	5.73	5.78	-0.05
101.5	3.99	4.04	-0.05	298.0	6.35
114.5	4.47	4.41	+0.06	Mercury			
115.8	4.44	4.44	0.00	$K = 2.07$			
132.7	4.77	4.80	-0.03	$K' = -2.8050$			
155.2	5.08	4.96	+0.12	31.1	3.89	3.93	-0.04
172.4	5.31	5.31	0.00	36.6	4.36	4.35	+0.01

⁴ This is due to an increase in atomic or molecular volume. For the elements and compounds here presented this phenomenon begins to appear at about 100°Å , except for Cu, Al, diamond, graphite, HCOOH and $\text{CO}(\text{NH}_2)_2$. For some of these substances the increase in volume does not seem to be appreciable even up to room temperature.

			----- ^a	43.0	4.70	4.71	-0.01
192.6	5.55	5.46	+0.09	62.0	5.34	5.31	+0.03
220.0	5.82	5.59	+0.23	65.0	5.37	5.36	+0.01
237.3	5.83	5.66	+0.17	69.0	5.43	5.43	0.00
253.5	5.98	5.70	+0.28				----- ^a
255.2	5.86	5.71	+0.15	80.5	5.58	5.56	+0.02
288.5	6.11	86.0	5.66	5.61	+0.05
Calcium				92.0	5.79	5.65	+0.14
67.6	3.93	3.89	+0.04	164.0	6.26
70.4	4.02	4.03	-0.01	168.0	6.29
73.3	4.16	4.16	0.00	201.0	6.42
76.2	4.28	4.28	0.00	207.0	6.48

^a These lines indicate approximately where the increase in volume begins to be appreciable and, with the exception of a few substances, this is approximately at about 100° Å.

Mercury			
T	Cp(obs.)	Cv(calc.)	Diff.
213.0	6.58
214.0	6.58
229.0	6.62
232.0	6.70

Zinc			
33.1	1.25	1.26	-0.01
34.3	1.32	1.34	-0.02
36.3	1.71	1.49	+0.22
41.0	1.60	1.84	-0.24
43.7	2.17	2.04	+0.13
61.8	3.25	3.25	0.00
64.0	3.51	3.37	+0.14
68.0	3.59	3.59	0.00
75.0	3.95	3.91	+0.04
80.0	4.17	4.11	+0.06
85.0	4.24	4.29	-0.05
89.0	4.39	4.42	-0.03
89.3	4.32	4.44	-0.12
94.0	4.55	4.57	-0.02

			----- ^a
207.0	5.83	5.70	+0.13
274.0	5.90	5.83	+0.07
290.0	6.03
366.0	6.20
395.0	6.28

Aluminum			
19.1	0.07	0.06	+0.01
23.6	0.11	0.11	0.00
27.2	0.16	0.17	-0.01
33.5	0.30	0.30	0.00
37.1	0.40	0.40	0.00
41.9	0.60	0.55	+0.05
49.6	0.90	0.85	+0.05
53.4	1.11	1.02	+0.09
62.4	1.55	1.45	+0.10

Diamond			
T	Cp(obs.)	Cv(calc.)	Diff.
88	(0.03)	0.064
92	(0.03)	0.073
205	0.62	0.62	0.00
209	0.66	0.65	+0.01
220	0.72	0.74	-0.02
222	0.76	0.75	+0.01
232	0.86	0.84	+0.02
243	0.95	0.94	+0.01
262	1.14	1.12	+0.02
284	1.35	1.34	+0.01
306	1.58	1.57	+0.01
331	1.84	1.83	+0.01
358	2.12	2.12	0.00
413	2.66	2.70	-0.04
1169	(5.45)	5.60	(-0.15)

Graphite			
28.7	0.06	0.04	+0.02
38.1	0.07	0.07	0.00
44.1	0.10	0.10	0.00
58.8	0.14	0.16	-0.02
85.0	0.31	0.31	0.00
137	0.69	0.69	0.00
232	1.50	1.52	-0.02
284	1.92	1.98	-0.06
334	2.39	2.39	0.00
412	3.04	2.95	+0.09
622	4.00	4.03	-0.03

1095	5.45	5.10	+0.35
1250	5.60	5.26	+0.34

Tin (white)			
79.8	4.68	4.64	0.00
87.3	4.87	4.88	-0.01
94.8	5.07	5.07	0.00
194.9	6.20

TABLES (Continued)

Mercury				Diamond			
T	Cp(obs.)	Cv(calc.)	Diff.	T	Cp(obs.)	Cv(calc.)	Diff.
73.4	2.08	2.03	+0.05	197.2	6.23
79.1	2.36	2.32	+0.04	205.2	6.25
32.4	0.25	0.27	-0.02	248.4	6.36
35.1	0.33	0.34	-0.01	256.4	6.37
83.0	2.41	2.53	-0.12	264.3	6.38
86.0	2.52	2.68	-0.16	273.0	6.39
88.3	2.62	2.79	-0.17	288.1	6.40
137.0	3.97	4.53	-0.56	Tin (gray)			
235.0	5.32	5.60	-0.28	79.8	3.80	3.80	0.00
331.0	5.82	5.82	0.00	87.3	4.07	4.07	0.00
433.0	6.10	94.8	4.30	4.30	0.00
555.0	6.48	194.9	5.66
Tin (gray) (cont.)				Iodine			
T	Cp(obs.)	Cv(calc.)	Diff.	T	Cp(obs.)	Cv(calc.)	Diff.
197.2	5.71	28.3	3.78	3.54	+0.24
205.2	5.75	33.5	3.97	3.97	0.00
248.4	5.87	36.5	4.17	4.17	0.00
256.4	5.88	77.0	5.38	5.38	0.00
264.3	5.89	<hr/>			
273.0	5.90	186.0	5.92	5.84	+0.08
288.1	5.91	235.0	6.36
Lead				298.0	6.64
23.0	2.96	3.00	-0.04	Sodium chloride			
28.3	3.92	3.66	+0.26	25.0	0.29	0.30	-0.01
36.8	4.40	4.40	0.00	25.5	0.31	0.31	0.00
38.1	4.45	4.49	-0.04	28.0	0.40	0.40	0.00
85.5	5.65	5.65	0.00	67.5	3.06	2.90	+0.16
90.2	5.71	5.68	+0.03	69.0	3.13	3.00	+0.13
200.0	6.13	81.4	3.54	3.72	-0.18
290.0	6.33	83.4	3.75	3.81	-0.06
332.0	6.41	138.0	(3.87)?	5.29
409.0	6.61	235.0	(5.76)?	5.81	-0.05
Sulfur (rhombic)				Potassium chloride			
22.7	0.96	0.86	+0.10	22.8	0.58	0.57	+0.01
25.9	0.99	0.99	0.00	26.9	0.76	0.82	-0.06
27.5	1.04	1.05	-0.01	30.1	0.98	1.01	-0.03
28.3	1.08	1.08	0.00	33.7	1.25	1.30	-0.05
29.9	1.14	1.14	0.00	39.0	1.83	1.70	+0.13
57.0	2.06	2.05	+0.01	48.3	2.85	2.40	+0.45
69.0	2.29	2.37	-0.08	52.8	2.80	2.72	+0.08
83.0	2.70	2.70	0.00	57.6	3.06	3.04	+0.02
93.0	2.93	2.91	+0.02	63.2	3.36	3.37	-0.01
138.0	3.63	3.63	0.00	70.0	3.79	3.74	+0.05
<hr/>				76.6	4.11	4.04	+0.07
198.0	4.72	4.22	+0.50	86.0	4.36	4.40	-0.04
235.0	4.93	4.47	+0.46	137.0	5.25?	5.36	-0.11
297.0	5.47	4.77	+0.70	235.0	5.89?	5.79	+0.10

Sulfur (monocl.)			
83.0	2.75	2.75	0.00
87.0	2.82	2.84	-0.02
87.0	2.90	2.84	+0.06
89.0	2.90	2.88	+0.02
91.0	2.95	2.93	-0.02
96.0	2.97	3.03	-0.03
102.0	3.15	3.15	0.00
194.0	4.92	4.30	+0.62
200.0	5.00	4.35	+0.65
201.0	4.81	4.35	+0.46

Silver chloride			
<i>T</i>	<i>Cp</i> (obs.)	<i>Cv</i> (calc.)	Diff.
23.5	1.49	1.49	0.00
26.4	1.72	1.75	-0.03
32.8	2.40	2.28	+0.12
45.6	3.63	3.18	+0.45
87.0	4.87	4.72	+0.15
116.0	5.17	5.16	+0.01
207.5	5.90	5.66	+0.24
330.0	6.51
405.0	6.80
430.0	6.86

Thallium chloride			
$K = 1.90$			
$K' = -2.8838$			
23.1	1.89	2.02	-0.13
26.7	2.32	2.40	-0.08
29.7	2.69	2.69	0.00
32.4	2.95	2.94	+0.01
36.3	3.22	3.25	-0.03
40.9	3.53	3.59	-0.06
44.8	3.79	3.83	-0.04
50.1	4.03	4.11	-0.08
90.4	5.20	5.20	0.00
94.0	5.25	5.25	0.00
138.0	5.62	5.60	+0.02
236.0	6.02
297.0	6.34

Mercurous chloride			
23.0	1.56	1.58	-0.02
25.7	1.74	1.79	-0.05
29.0	2.18	2.01	+0.17
34.5	2.54	2.43	+0.11
75.0	4.20	4.20	0.00
83.0	4.40	4.40	0.00

331.0	6.16
416.0	6.36
550.0	6.54
Silver chloride			
22.5	1.39	1.40	-0.01
26.6	1.73	1.77	-0.04
31.3	1.99	2.16	-0.17
43.1	2.75	3.02	-0.27
68.0	4.20	4.20	0.00
72.2	4.32	4.34	-0.02
81.3	4.60	4.58	+0.02
91.4	4.91	4.80	+0.11

Titanium tetrachloride (cont.)			
<i>T</i>	<i>Cp</i> (obs.)	<i>Cv</i> (calc.)	Diff.
99.3	4.54	4.54	0.00
194.6	6.19	5.45

Carbon tetrachloride			
$K = 2.92$			
$K' = -5.605$			
39.1	0.60	0.59	+0.01
40.7	0.65	0.67	-0.02
63.8	2.05	1.89	+0.16
79.6	2.81	2.80	+0.01
91.0	3.40	3.38	+0.02
95.0	3.57	3.56	+0.01
99.5	3.60	3.75	-0.15
199.5	5.84	5.54	+0.30
204.1	5.90	5.56	+0.34
208.0	5.90	5.58	+0.32
229.4	6.20

Silicon tetrachloride			
$K = 1.89$			
$K' = -3.3882$			
77.4	3.60	3.60	0.00
81.8	3.70	3.75	-0.05
86.6	3.83	3.90	-0.07
94.8	4.14	4.12	+0.02
131.3	4.80	4.80	0.00
168.6	5.68	5.18	+0.50
181.0	5.95	5.27	+0.68
185.8	6.08

Tin tetrachloride			
$K = 2.25$			
$K' = -3.8800$			
89.0	4.59	4.55	+0.04
89.5	4.53	4.55	-0.02
95.0	4.73	4.70	+0.03

TABLES (Concluded)

Silver chloride				Titanium tetrachloride (cont.)			
<i>T</i>	<i>Cp</i> (obs.)	<i>Cv</i> (calc.)	Diff.	<i>T</i>	<i>Cp</i> (obs.)	<i>Cv</i> (calc.)	Diff.
84.0	4.43	4.42	+0.01	95.9	4.71	4.72	-0.01
86.0	4.46	4.46	0.00				
89.0	4.52	4.52	0.00	161.2	5.89	5.51	+0.38
				200.5	6.32
198.0	5.69	5.44	+0.25	Lead chloride			
326.0	6.12	15.6	0.72	0.71	+0.01
331.0	6.24	19.8	1.03	1.04	-0.01
Titanium tetrachloride				24.0	1.17	1.39	-0.22
$K = 1.79$				27.0	1.63	1.63	0.00
$K' = -3.0725$				54.9	3.49	3.52	-0.03
86.7	4.26	4.26	0.00	61.5	3.91	3.82	+0.09
92.8	4.40	4.40	0.00	84.4	4.46	4.55	-0.09
Lead chloride				Formic acid (cont.)			
<i>T</i>	<i>Cp</i> (obs.)	<i>Cv</i> (calc.)	Diff.	<i>T</i>	<i>Cp</i> (obs.)	<i>Cv</i> (calc.)	Diff.
87.7	4.52	4.63	-0.11	205.0	2.73	2.70	+0.03
106.5	4.97	4.97	0.00				
				237.0	3.02	2.89	+0.13
205.5	5.80	5.64	+0.16	243.2	3.12	2.92	+0.20
330.0	6.17	Urea			
405.0	6.32	86.4	1.79	1.75	+0.04
430.0	6.42	90.0	1.76	1.78	-0.02
Formic acid				90.0	1.83	1.78	+0.05
$K = 0.90$				90.3	1.82	1.79	+0.03
$K' = -2.1650$				96.5	1.89	1.84	+0.05
71.0	1.45	1.44	+0.01	97.0	1.83	1.85	-0.02
73.3	1.50	1.47	-0.03	104.0	1.87	1.91	-0.04
76.6	1.50	1.51	-0.01	107.5	1.94	1.94	0.00
77.7	1.52	1.52	0.00	128.1	2.13	2.11	+0.02
82.0	1.55	1.58	-0.03	198.5	2.57	2.54	+0.03
86.0	1.60	1.63	-0.03	199.5	2.55	2.55	0.00
89.0	1.60	1.67	-0.07	201.4	2.54	2.56	-0.02
90.0	1.66	1.68	-0.02	204.7	2.59	2.58	+0.01
90.3	1.68	1.69	-0.01	208.2	2.58	2.59	+0.01
94.0	1.73	1.73	0.00				
176.3	2.48	2.49	-0.01	223.9	2.83	2.67	+0.16
180.0	2.51	2.52	-0.01	244.2	2.87	2.76	+0.11
184.5	2.59	2.56	+0.03	274.0	3.21	2.88	+0.33
196.0	2.69	2.63	+0.06				

EUREKA, CALIFORNIA