solvent used (ethyl alcohol, acetone, methyl ethyl ketone, toluene, and mixtures of these). The separation resulted in small amounts of pure 2-*p*-cymylmercuric chloride being separated from the minimum melting mixture (126–127°). It was found that by conversion into the dicymylmercury compounds the relative solubilities were greatly changed. The 2-di-*p*-cymylmercury is much less soluble than the 2-*p*-cymylmercuric chloride, while the 3-di-*p*-cymylmercury is more soluble than the 2-*p*-cymylmercuric chloride. This causes a greater difference in solubility between the 2- and 3-derivatives, so that the 2-di-*p*-cymylmercury was almost completely removed when the alcoholic sodium iodide solution cooled. No separation was effected by simple distillation.

The orientation in the *p*-cymene molecule has been the subject of some discussion.[4] Early workers reported that the entering group went into the 2-position. However, there is a very close agreement in the physical properties for the 2- and 3-derivatives, other than mercury derivatives, so that the two can easily be confused. The correct relationships have been shown for sulfonation by Phillips[1] and LeFèvre,[2] and for nitration, chlorination and bromination by LeFèvre.[4] The orientation in the present work can be found from the data given in Fig. 1. The mixture of mono isomers melted at 127° and as this was fractionally crystallized to give pure 2-*p*-cymylmercuric chloride and the minimum melting mixture, this melting point corresponds to approximately 60% of 2-*p*-cymylmercuric chloride and 40% of 3-*p*-cymylmercuric chloride. These figures were approximately checked by a weight balance when this mixture was separated. These results may be compared with the data obtained for other substitution reagents.

Method	2-sub., %	3-sub., %	Ref.
Sulfonation	90	5	2
	85	15	1
Nitration	87	..	4
Chlorination	63	..	4
Bromination	57	..	4
Mercuration	60	40	

This comparison shows that mercuration produces a larger proportion of the 3-derivative than any of the reactions previously investigated.

This work will be continued for the purpose of identifying and synthesizing derivatives.

Summary

1. *p*-Cymene has been directly mercurated with a 64% yield of mono-mercurated compounds.

2. A method of separation of the two mono derivatives is given, based on the great difference in solubility of the di-cymylmercury compounds.

3. 3-Di-*p*-cymylmercury and 3-*p*-cymylmercuric chloride are identified.

Seattle, Washington Received March 11, 1935

[Contribution from the School of Chemistry and Physics of the Pennsylvania State College]

Heat Capacities and Entropies of Organic Compounds. I. A Thermodynamic Temperature Scale in Terms of the Copper–Constantan Thermocouple from 12 to 273°K.[1]

By J. G. Aston, Eugene Willihnganz and George H. Messerly

Introduction

For measurements in progress in this Laboratory of heat capacities from 11°K. to room temperatures, it was necessary to establish a temperature scale over this range. As Giauque and coworkers[2a b] had obtained satisfactory results in terms of the copper–constantan couple over this same range, it was decided to establish the scale on essentially the same terms. The present paper contains a portion of the results of the comparison of copper–constantan couples with a helium thermometer.

Recently Southard and Andrews[3] have calibrated a copper–constantan thermocouple against a resistance thermometer down to 85°K. They used constantan wire which was quite different from that of G., B. and S.,[2a] but which was so like our wire that the difference corresponded to only 0.9° at 85°K. Experience has shown that most of the constantan wire now available is quite similar to that of S. and A.[3] and to our own. A

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[1] Submitted by Eugene Willihnganz in partial fulfilment of the requirements for the Ph.D. degree.

[2] (a) Giauque, Buffington and Schulze, This Journal, **49**, 2353 (1927); (b) Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

[3] Southard and Andrews, *J. Franklin Inst.*, **207**, 323 (1929).

thermocouple reference table from 12 to 90°K. is therefore given to supplement that of S. and A.[3] which is intended for use in interpreting calibration data when only a few points are available (*e. g.*, from vapor pressure comparisons).

As a check on our scale a comparison has been made with the Leiden scale using hydrogen and oxygen vapor pressures. The agreement was satisfactory.

The results of G., B. and S.,[2a] which were obtained with a hydrogen gas thermometer, show discrepancies below 30°K., which they attributed to adsorption of hydrogen on the walls of the Pyrex thermometer bulb. That that explanation is correct seems probable because the results of the present investigation, where helium replaced hydrogen in an exactly similar apparatus showed no such effects.

Experimental Method and Results

Thermocouples.—Nine thermocouples were constructed similar to those used by G., B. and S.[2a] Eight of them (S-1 to S-8) had five parallel No. 30 B. and S. constantan wires while S-9 had three such wires.[4] Each of the couples had a single No. 36 B. and S. copper wire going to both junctions. Each couple was 320 cm. long. The thermocouples were located for intercomparison and for comparison with the gas thermometer in the same manner in which they were to be located in the calorimetric apparatus. Sixty-four cm. was wrapped around the cylinder whose temperature was being measured to prevent heat leak to the junction and 8 cm. passed through the block of copper and lead above[2a] which was at essentially the same temperature. The same 138 cm. was in the temperature gradient in every case.

Comparison of Thermocouples.—All the couples were compared with S-5 from 15°K. to room temperature by the method described by G., B., and S.[2a] The maximum difference between the groups of constantan wires of the various thermocouples was 7.5 μv., while those of S-2, S-5 and S-6 differed at the most by 0.5 μv.; the reproducibility was 0.2 μv. The results for the copper wires were similar to those of G., B. and S.[2a]

The Helium Thermometer.—This was in every respect similar to the hydrogen thermometer described by G., B. and S.[2a] The helium pressure between the 126-cc. Pyrex thermometer bulb and the case of lead and copper was kept within 1 cm. of that within the bulb to prevent diffusion of helium through the bulb as well as distortion. The total obnoxious volume was 0.77 cc. (0.23 cc. in the temperature gradient and the rest at room temperature).

Purification of Helium and Filling the Thermometer.—The helium was purified by passing slowly first over activated charcoal cooled by liquid air and then over activated charcoal cooled by liquid hydrogen. (In each case about 200 cc. of freshly degassed charcoal was used and the helium passed at a rate of 250 cc. per hour.) It was stored over mercury for one hundred and sixteen days in a system which had previously been evacuated for several weeks. Contamination due to this standing was negligible as ascertained by a leak rate, taken with a McLeod gage prior to filling but as a safeguard the helium was passed slowly over charcoal cooled by liquid air before filling the degassed thermometer.

Comparison of the Thermocouple with the Helium Thermometer from 12°K. to the Ice Point.—S-6 was compared with the helium thermometer over this range in the manner described by G., B. and S.[2a] However, use of a manometer similar to that of Cath and Kamerlingh Onnes[5] prevented any chance of even minute contamination or loss of gas. At each temperature, two complete sets of readings were taken on the thermocouple and gas thermometer at about ten minutes apart. In only two cases did the temperature change by more than 0.02° in this interval. In these two cases the change was slightly less than 0.05°. A single measurement took about five minutes.

The Thermocouple Reference Table.—The temperatures were calculated from the pressure readings as described by G., B. and S.[2a] using a pressure coefficient corresponding to 273.16°K. for the melting point of ice.[6] In correcting the results for the deviation of helium from the perfect gas law the results of Cath and Kamerlingh Onnes[5] were used. From the results, a table of temperatures corresponding to rounded e. m. f. readings of S-6 was computed up to 100°K. using the procedure of G., B. and S.[2a] modified to suit the transposed nature of our table. Above 90°K. the table was obtained with the help of a deviation plot from the table of Southard and Andrews.[3] Finally the second differences of both sections were smoothed and slight corrections applied to make a single table.

The section of this table up to 90°K. is given in Table I. The third decimal place is significant only for interpolation or where differences are involved. This table may be used to supplement that of S. and A., the two overlapping sufficiently for the purpose.

Figure 1 is a graph showing the deviations (Δ) of the temperatures calculated from the thermocouple readings using the final reference table, (T_E), from those observed with the helium thermometer (T_G), ($\Delta = T_E - T_G$), over the range 12 to 273°K. The average deviation is 0.015°. The maximum deviation is 0.06°, occurring in one of the points at 40°K. It is, therefore, believed that this table is accurate to within 0.05°.

Comparison with Vapor Pressure Thermometers.—A comparison was made with the Leiden thermodynamic scale at liquid hydrogen and liquid oxygen temperatures with the aid of hydrogen and oxygen vapor pressures. For this

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(4) All from one spool obtained from the Leeds and Northrup Company. A sample from it showed a maximum e. m. f. of 1.3 μv. in a loop test through liquid air.

(5) Cath and Kamerlingh Onnes, *Communications Phys. Lab. Univ. Leiden*, 156a (1922).

(6) Heuse and Otto, *Ann. Physik*, [5] **2**, 1012 (1929).

Table I

The Reference Table for S-6 (0°C. = 273.16°K.)

E. m. f., μ v.	°K.	Diff.	E. m. f., μ v.	°K.	Diff.
5200	90.206	571	5	55.734	393
10	89.635	573	30	55.341	395
20	89.062	576	5	54.946	396
30	88.486	578	40	54.550	399
40	87.908	581	5	54.151	400
50	87.327	584	50	53.751	403
60	86.743	586	5	53.348	404
70	86.157	589	60	52.944	407
80	85.568	590	5	52.537	408
90	84.978	594	70	52.129	410
5300	84.384	596	5	51.719	412
10	83.788	599	80	51.307	415
20	83.189	602	5	50.892	416
30	82.587	605	90	50.476	419
40	81.982	608	5	50.057	421
50	81.374	611	5800	49.636	423
60	80.763	613	5	49.213	425
70	80.150	617	10	48.788	429
80	79.533	620	5	48.359	430
90	78.913	623	20	47.929	432
5400	78.290	626	5	47.497	435
10	77.664	629	30	47.062	438
20	77.035	633	5	46.624	441
30	76.402	636	40	46.183	444
40	75.766	638	5	45.739	446
50	75.128	643	5850	45.293	450
60	74.485	648	5	44.843	452
70	73.837	650	60	44.391	456
80	73.187	655	5	43.935	459
90	72.532	660	70	43.476	463
5500	71.872	662	5	43.013	467
10	71.210	667	80	42.546	471
20	70.543	671	5	42.075	475
30	69.872	676	90	41.600	480
40	69.195	681	5	41.120	483
50	68.515	686	5900	40.637	489
60	67.829	690		40.148	494
70	67.139	694	10	39.654	499
80	66.445	700		39.155	503
90	65.745	706	20	38.652	510
5600	65.039	710		38.142	515
10	64.329	717	30	37.627	522
20	63.612	720		37.105	527
30	62.892	727	40	36.578	535
40	62.165	733		36.043	540
50	61.432	741	50	35.503	549
60	60.691	745		34.954	555
70	59.946	751	60	34.399	564
80	59.195	757		33.835	571
90	58.438	764	70	33.264	580
5700	57.674	385		32.684	589
5	57.289	386	80	32.095	598
10	56.903	388		31.497	609
5	56.515	390	90	30.888	620
20	56.125	391		30.268	631
6000	29.637	125	6050	590	160
1	512	128	1	430	160
2	384	128	2	270	161
3	256	129	3	109	162
4	127	129	4	21.947	163
5	28.998	129	5	784	165
6	869	130	6	619	165
7	739	131	7	454	166
8	608	131	8	288	167
9	477	131	9	121	169
6010	346	132	6060	20.952	170
1	214	133	1	782	171
2	081	133	2	611	172
3	27.948	133	3	439	174
4	815	134	4	265	175
6015	681	135	5	090	178
6	546	135	6	19.912	178
7	411	136	7	734	180
8	275	136	8	554	181
9	139	137	9	373	183
6020	002	137	6070	190	185
1	26.865	138	1	005	187
2	727	139	2	18.818	189
3	588	139	3	629	191
4	449	140	4	438	193
5	309	140	5	245	195
6	169	141	6	050	198
7	028	142	7	17.852	201
8	25.886	142	8	651	203
9	744	143	9	448	206
6030	601	144	6080	242	208
1	457	144	1	034	211
2	313	145	2	16.823	214
3	168	146	3	609	217
4	022	146	4	392	221
5	24.876	147	5	171	224
6	729	148	6	15.947	227
7	581	148	7	720	231
8	433	149	8	489	234
9	284	150	9	255	238
6040	134	151	6090	017	241
1	23.983	151	1	14.776	245
2	832	153	2	531	249
3	679	153	3	282	254
4	526	154	4	028	258
5	372	154	5	13.770	262
6	218	156	6	508	266
7	062	157	7	242	271
8	22.905	157	8	12.971	275
9	748	158			

purpose our calorimetric apparatus, which was in general similar to that of Giauque and Wiebe,[7] was used as described by Giauque, Johnston and Kelley.[2b] The calorimeter which served as the thermometer bulb was of gold-plated copper and will be described in a forthcoming paper on the heat capacity of tetramethylmethane. The

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(7) Giauque and Wiebe, This Journal, **50**, 101 (1928).

manometer was similar to that of Cath.[8] In correcting the readings to international cm. the gravitational constant for State College was taken as 980.124.[9]

Couple S-2 was used in all vapor pressure measurements.

The hydrogen used had previously been purified for liquefaction. It originally contained 0.039% of nitrogen. Before condensing in the bulb it was passed slowly through 300 cc. of degassed charcoal cooled to liquid air temperatures to remove the last traces of nitrogen.

The results of the hydrogen vapor pressure measurements are given in Table II. Column 1 gives the temperature calculated from the thermocouple readings using Table I. Column 2 gives the pressure. Column 3 gives the temperature calculated from the vapor pressures using the equations of Keesom, Bijl and van der Horst for normal and para hydrogen.[10]

$$t = -260.865 + 1.0619 \log_{10} p + 1.7233 \log_{10}^2 p \quad (1)$$

$$t = -260.937 + 1.0270 \log_{10} p + 1.7303 \log_{10}^2 p \quad (2)$$

TABLE II

HYDROGEN VAPOR PRESSURES, MARCH 28, 1935

T., obs., °K.	Pressure (obs.), international mm.	T., calcd., °K.	ΔT Obsd. − calcd.
18.02	343.2	17.95	+0.07
19.92	650.5	19.85	+ .07
20.25	720.7	20.19	+ .06
20.65	813.9	20.59	+ .06

(1) refers to normal and (2) to para hydrogen, the temperature is in degrees C., and the pressure in cm. In the calculation a 50% mixture of ortho and para hydrogen was assumed,[11a,b] taking the temperature as a linear function of the composition. The temperatures have been converted to °K. for comparison by the addition of 273.16° since the equations are based on a pressure coefficient the same as our own. The deviations in column 4 show a satisfactory agreement.

For the oxygen vapor pressure measurements, oxygen was prepared and purified by the method of von Siemens.[12] Typical results are given in Table III. Column 1 gives the temperature calculated from the thermocouple readings, using Table I and corrected to the basis of the pressure coefficient used for the Leiden Scale (corresponding to 273.09°K. for the ice point) by multiplying by 273.09/273.16. Column 2 gives the pressure calculated from the equation of Cath[8]

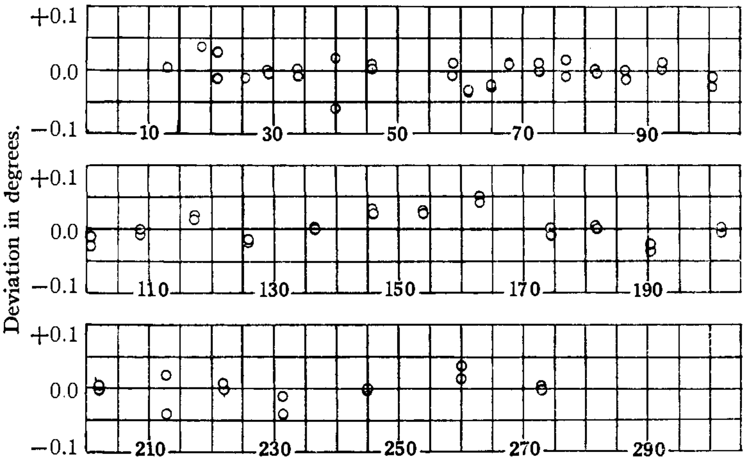

Fig. 1.—Deviation plot for gas thermometer, comparisons of May 1–10, 1934.

$$\log_{10} P_{\text{atm.}} = -(419.31/T) + 5.2365 - 0.00648T \quad (3)$$

TABLE III

OXYGEN VAPOR PRESSURES

Date April, 1935	T, obs., °K.	P, calcd. international mm.	P, obsd., international mm.	ΔT
19	63.051	11.45	11.28	+0.065
19	67.463	29.16	28.61	+ .095
15	71.196	58.41	57.68	+ .079
17	73.342	134.94	133.25	+ .076
17	80.010	228.12	225.62	+ .081
17	85.692	466.49	462.51	+ .073
17	90.029	752.56	746.70	+ .075
16	78.610	187.88	184.64	+ .112[a]

[a] Temperature gradients smaller than usual.

Column 3 gives the observed pressure and column 4 the temperature deviation corresponding to the pressure difference. Other measurements, not included, agreed with those tabulated to 0.02°. The result marked (*a*) was obtained with the temperature gradient in the couple quite different from that in normal use. The results show a satisfactory agreement with the Leiden scale.

The result in Table III at 746.70 mm. is in excellent agreement with the value of Heuse and Otto (Reichsanstalt) for the normal boiling point of oxygen.[13] Using their equation to calculate

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(8) Cath, *Communications Phys. Lab. Univ. Leiden*, 152d (1918).

(9) "International Critical Tables," Vol. I, p. 396.

(10) Keesom, Bijl and van der Horst, *Communications Phys. Lab. Univ. Leiden*, 217a (1931).

(11) (a) Bonhoeffer and Harteck, *Z. physik. Chem.*, **B4**, 113 (1929); (b) Eucken and Hiller, *ibid.*, **B4**, 142 (1929).

(12) Von Siemens, *Ann. Physik*, [4] **42**, 871 (1913).

(13) Heuse and Otto, *Ann. Physik*, **9**, 486 (1931).

the boiling point of oxygen at this pressure one obtains 90.029°K. based on 273.16°K. for the ice point. This, corrected to the pressure coefficient used by Cath,[8] is 90.006°K. as compared with our value, on the same basis, of 90.029°K.

Acknowledgments.—The authors wish to thank the National Research Council for Grants-in-Aid, without which this investigation would have been impossible. They are indebted to Mr. M. G. Mayberry and Dr. P. A. Lasselle, who kindly helped with the measurements. The Linde Company lightened our task considerably by supplying us willingly with pure hydrogen suitable for liquefaction purposes. The help and advice of Mr. J. E. Key of the Industrial Engineering Department and of Mr. G. F. Nelson of the University of California in connection with the mechanical construction of the apparatus has been invaluable. Especially we wish to thank Professor W. F. Giauque of the University of California for encouragement and advice which have contributed much to the success of the work.

Summary

1. The establishment of a temperature scale from 12–273°K. in terms of the copper–constantan thermocouple, using a helium thermometer, is described.

2. An e. m. f. temperature reference table is given from 12–90°K.

3. The scale is compared with the Leiden scale, using hydrogen and oxygen vapor pressure thermometers.

STATE COLLEGE, PA. RECEIVED MAY 3, 1935

[CONTRIBUTION FROM THE NICHOLS LABORATORY OF NEW YORK UNIVERSITY]

Condensations of Benzoylformanilide with Cyano-activated Methylene Compounds[1]

BY JOHN V. SCUDI[2] AND H. G. LINDWALL

This paper is a further report on a series of studies of condensation reactions of alpha-ketoamides as exemplified by isatin and benzoylformanilide. The reactions of the latter with acetophenone give rise to the formation of pyrrolone structures.[3]

Benzoylformanilide reacts with malonitrile (Chart A) to yield an orange-red compound (1-phenyl - 1 - formanilido - 2,2 - dicyanoethylene) (I), which on treatment with hydrochloric acid is hydrolyzed to the corresponding di-amide (II). Reduction products III and IV, obtained from I and II, respectively, give phenylsuccinic acid (V) upon hydrolysis, identified by melting point methods and by conversion to phenylsuccinanil.

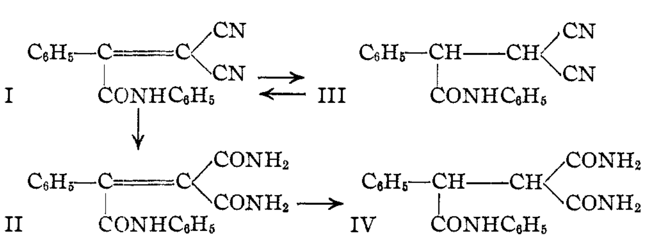

CHART A

Compound III gives positive Tollens' and Fehling's tests. Heating III in alcohol causes solution with an accompanying production of color and an 80% yield of I is obtained.

Cyanacetamide condenses with benzoylformanilide (Chart B) to yield VI which exhibits typical imide properties, liberating ammonia upon treatment with alkali, and giving VII under the influence of hydrochloric acid. The amide (VII) forms the corresponding nitrile (VIII) upon distillation from phosphorus pentoxide. Both VII and VIII undergo interesting addition reactions; VIII reacts with ammonia at zero degrees in moist ether giving VI, and VII reacts with diethylamine under the same conditions to yield an addition product (VII-A) for which no structure is postulated at present. Compound VII is regenerated from VII-A by heating with concentrated hydrochloric acid.

Further, the amide (VII) yields upon reduction the formamido substituted phenylsuccinanil (IX), which is hydrolyzed and subsequently decarboxylated by hot mineral acid to give phenylsuccinic acid. Compound IX gives a dibasic acid (X), as a result of careful alkaline hydrolysis, which is converted to phenylsuccinanil by

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[1] Presented in part at the New York Meeting of the American Chemical Society, April, 1935.

[2] From a dissertation presented by John V. Scudi in partial satisfaction of the requirements for the Ph.D. degree at New York University.

[3] Bashour and Lindwall, THIS JOURNAL, **57**, 178 (1935).