

TABLE II

Expt. No.	1	2	3	4
Wt. sodium oxalate, g.....	0.2000	0.2000	0.2000	0.2000
Temp. at start of run.....	70°	22.5°	22.5°	22.5°
Vol. catalyst soln. used, cc.....	0	0	5	10
Vol. KMnO_4 required, cc.....	33.90	33.87	33.85	33.85
Time for 1 cc.....	1 min. (—)	4 min. 11 sec.	1 min.	45 sec.
Time for entire titration.....	Moderately rapid	1 hr. (approx.)	9 min. 30 sec.	6 min.

masses during the course of the process. In this run the permanganate was added several drops at a time with constant agitation, as rapidly as the solution cleared, each addition being made while the solution was still faintly pink. The acidity was about 1 per cent H_2SO_4 , but as it was not controlled as carefully as in the preceding case, and as this, as well as the mass of KMnO_4 , affects the rate, the time for these runs

was taken for the entire titration, and was not so accurately observed as in the preceding experiment. Nevertheless, Table II shows an effect similar to that already shown.

CONCLUSION

These experiments indicate that the addition of MnSO_4 solution to permanganate titrations is a practicable method of increasing reaction velocity, in that the time of the peroxide-permanganate titration can by this means be reduced from about 35 min. to 8 sec., and that of the cold oxalate-permanganate titration from over an hour to 6 min. for the entire titration. The use of the catalyst does not affect the accuracy of the end-point.

LABORATORY AND PLANT

THE PRESERVATION OF BAGASSE IN SUGAR-CANE MILL CONTROL¹

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A review in the March 1920 issue of the *International Sugar Journal*, page 169, calls attention to the deterioration of bagasse composite samples as regards sucrose content. In this review two chemists report decomposition even in the presence of formaldehyde or chloroform, and a third chemist's experiments show no loss of sugar after 8 hrs. storage in a stoppered bottle without antiseptic.

The writer began the use of formaldehyde as a preservative of samples in the laboratory, and of juices and meladura in the factory in the season of 1903 to 1904 in Cuba. He abandoned its use except for very short storage periods for juices (1 hr.) and bagasse (6 hrs.), on account of inversion of sucrose by the plant acids and not on account of ferments. At that time, however, experiments indicated formaldehyde to be a fairly safe preservative for bagasse for short periods. Formaldehyde is extensively used, and is without a rival in the protection of juice and meladura, during forced stoppages of the factory, though loss by inversion is known to occur. It is possible that the present very heavy milling with long trains of mills and with large use of maceration water, as compared with the conditions of a few years ago, may be in part causes of the unsatisfactory results now obtained with formaldehyde.

In accounting for irregularities in bagasse tests, the writer recently found these to be due to the inefficiency of formaldehyde in protecting the samples. There was usually no evidence of fermentation, and it is probable that the loss of sucrose was due to inversion. This led to renewed experimentation with strong ammonia, as proposed and practiced in Egypt by the late Henri Pellet.

The bagasse is collected in covered cans in a very strong atmosphere of ammonia. Cotton, saturated with strong ammonium hydroxide, is placed in perforated tin boxes at the top and bottom of the bagasse

container. The ammonia thoroughly permeates the bagasse, saturates the acids, and imparts a characteristic yellow color to the sample. The analysis of the bagasse is conducted as usual, except that no sodium carbonate need be added in the digestion, and the water extract must be acidulated with acetic acid prior to clarification with subacetate of lead.

In comparative tests of finely comminuted bagasse, the samples were analyzed immediately, after storage with formaldehyde, and after storage with ammonia, for periods of 3 and 6 hrs. The formaldehyde sample showed a loss after 3 hrs. and a considerable loss after 6 hrs. The ammonia sample lost 0.1 per cent sucrose in 6 hrs. The sample originally contained 3 per cent of sucrose. Therefore, formaldehyde is not apparently a safe preservative for bagasse.

It is the writer's expectation to have made many comparative tests, using ammonia in preserving bagasse samples, with a view to arriving at more definite information. A combination of ammonia for saturating the plant acids and an antiseptic for preventing fermentation is desirable. Preliminary experiments indicate that bagasse may be preserved for periods of several hours in an atmosphere of ammonia and chloroform. This is also effective in preserving filter press-cakes.

THE SPECIFIC HEAT OF PETROLEUM AT DIFFERENT TEMPERATURES¹

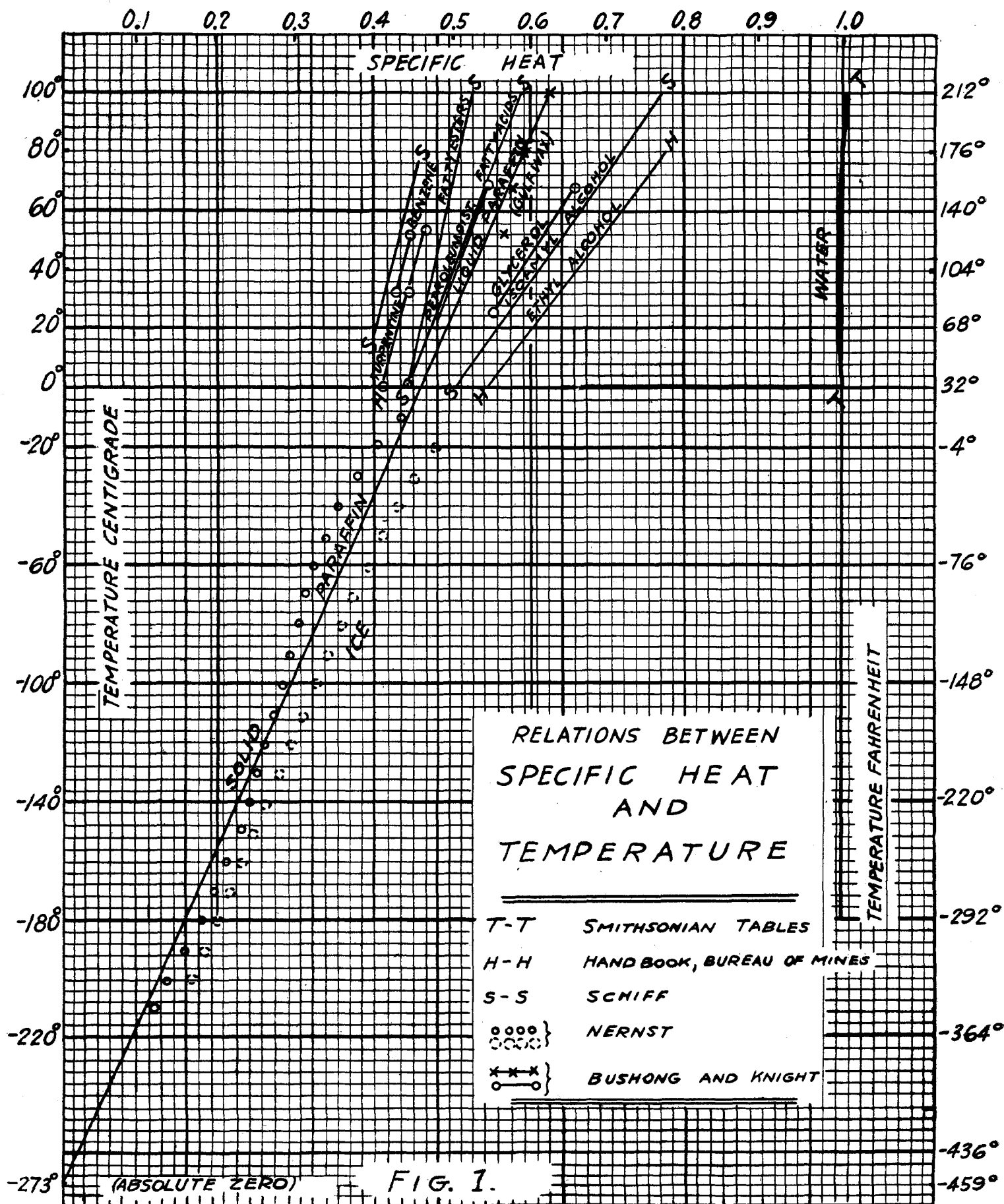
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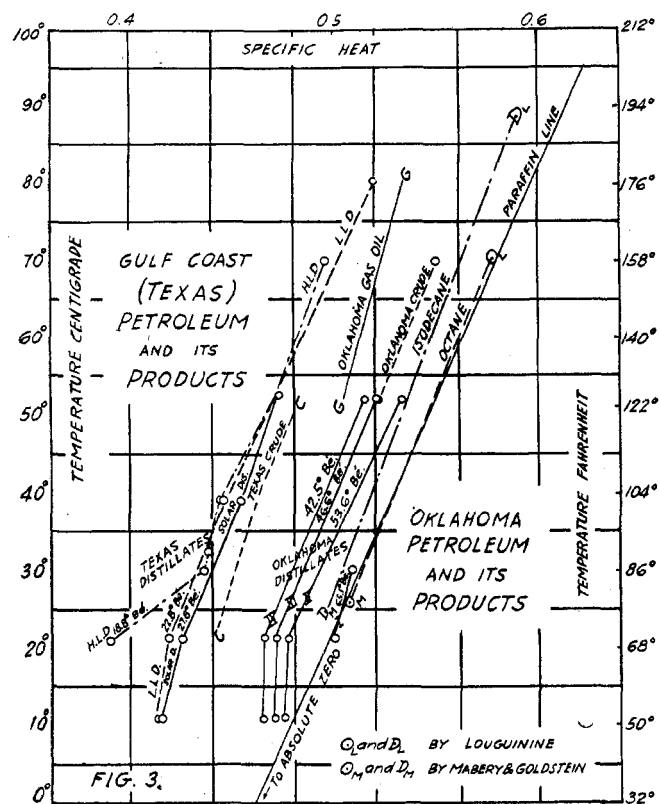
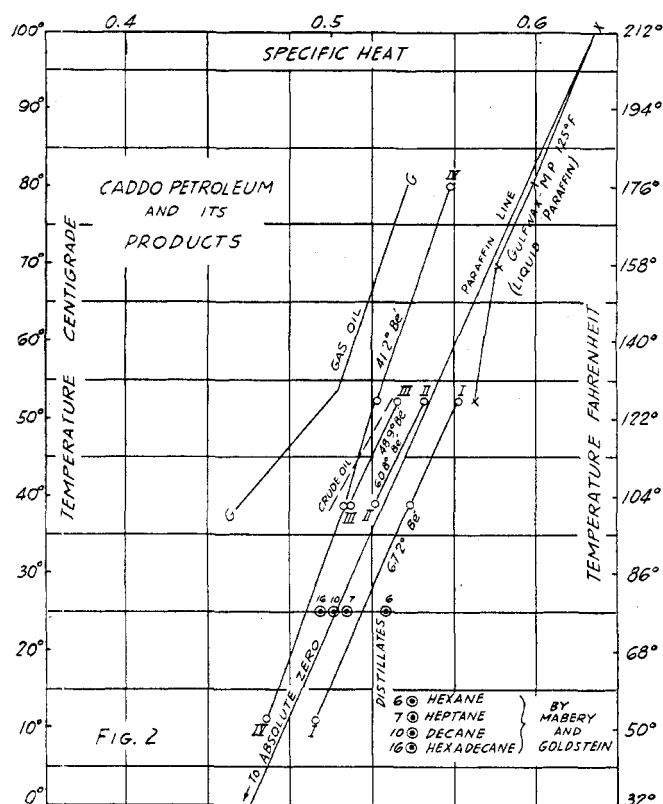
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The work herein described was undertaken to determine the rate of increase in the specific heat of petroleum with rise in temperature. The apparatus employed was the Parr standard calorimeter, which gave results of sufficient accuracy for technical work. The bomb was charged with benzoic acid, as recommended for the standardization of the instrument, and the oil or other liquid under examination was employed as the calorimeter fluid.

¹ Presented before the Division of Industrial and Engineering Chemistry at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

¹ Presented before the Section of Sugar Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.





In determinations or standardizations made with the calorimeter fluid one or two degrees below room temperature, the calculations were made in accordance with the directions furnished with the calorimeter. At other temperatures it was necessary to take into account the rates of radiation established before the ignition of the charge and after the maximum rise. These rates were laid off on coordinate paper against the observed rise, and the points representing them were joined by a straight line upon which one-minute intervals were laid off. The sum of the temperature values apportioned to the minute intervals was applied as a radiation correction to the observed rise. The specific heat was calculated as follows:

The number of calories absorbed by the apparatus was found by multiplying the water equivalent (123.3 g.) by the corrected rise. This was deducted from the heat generated in the bomb (4869 cal. in case of the usual charge), giving the number of calories absorbed by the oil. By dividing this number by the corrected rise and by the weight of the oil (in grams), the specific heat was obtained.

For the standardization of the method, water was employed up to 105° F. At higher temperatures the heat losses due to evaporation of water were so great as to introduce considerable errors. Similarly in making determinations below room temperature, errors due to condensation were introduced. High viscosity is an unavoidable source of error which cannot be neglected in the consideration of the results.

Schiff has shown that the effect of temperature upon specific heat is the same for organic liquids of the same

chemical nature, specific heat being a linear function of temperature. Curves representing the specific heat of the different members of a given class are, therefore, parallel straight lines.

The results obtained by the method just described, together with those taken from chemical literature, are presented in the form of curves.

They show that the specific heat of the petroleum hydrocarbons, including paraffin, is proportional to,

DATA FOR FIG. 1				
Temperature ° C.	Water Sp. Ht.	Liquid Paraffin Sp. Ht.	Ethyl alcohol Sp. Ht.	
110	1.0116		0° C.	0.5475
100	1.0065	0.6307	80° C.	0.7694
80	1.0024	0.5974		
68		0.5798	Isoamyl alcohol	
65	1.0000		0° C.	0.5012
52		0.5700	100° C.	0.7712
30	0.9974			
15	1.0000		Glycerol	
0	1.0087		26.5° C.	0.5523
			68.0° C.	0.6541
	Ice	Solid Paraffin	Petroleum distillates—Mean ¹	
0	0.535	0.47	21.1° C.	0.4703
-10	0.538	0.43	68.0° C.	0.5420
-20	0.478	0.40		
-30	0.450	0.375	Fatty acids	
-40	0.428	0.35	0° C.	0.4440
-50	0.409	0.34	100° C.	0.5858
-60	0.392	0.32		
-70	0.374	0.31	Fatty esters	
-80	0.358	0.30	0° C.	0.4416
-90	0.341	0.29	100° C.	0.5296
-100	0.325	0.28		
-110	0.307	0.27	Turpentine	
-120	0.293	0.26	0° C.	0.4110
-130	0.277	0.25	33° C.	0.4414
-140	0.262	0.24	53° C.	0.4639
-150	0.245	0.23		
-160	0.230	0.21	Benzene	
-170	0.215	0.20	32.2° C.	0.4247
-180	0.199	0.18	52.2° C.	0.4449
-190	0.183	0.16	Benzene and homologs	
-200	0.168	0.14	20° C.	0.4042
-210		0.12	80° C.	0.4668

¹ This is the mean derived from about 200 determinations on distillates obtained from the various oils examined by the authors. Rate of increase 0.00153 per degree C.