

course of the specific-heat curve for nearly all the organic solids ever measured, can be predicted from the degrees of freedom and the frequencies of vibration of the different atoms, as calculated from band spectra and melting points.

These are some of the questions on which it is hoped further measurements will throw more light. At present the specific heats of the nitroanilines are being measured from 110° to 2°K. in order to get more complete knowledge of the typical curve; it is hoped that when this is done the work with the conduction calorimeter may be extended to a larger number of compounds.

The author wishes to thank Professor G. N. Lewis and the University of California for the privileges of association with the department of chemistry while performing this research, and to express appreciation of the valuable assistance of Mr. Arthur H. Mendonca in taking the measurements.

Summary

1. A new type of calorimeter has been constructed employing the method of calibrated heat conduction, which in simplicity, speed of manipulation and range of temperature appears to be an improvement over previous methods where an accuracy within one or two per cent. suffices.

2. The specific heats of eleven isomers of the type *ortho*, *meta* and *para* C₆H₄XY have been measured from 110° to 340°K.

3. The specific heat seems to be a linear function of the temperature from 110° to about 320°K. and is but slightly changed by the difference in structure between the *ortho*, *meta* and *para* isomers.

BERKELEY, CALIFORNIA

NOTES

The Mechanism of Ammonia Synthesis in Low-Voltage Arcs.—

The formation of ammonia from gaseous mixtures of nitrogen and hydrogen by means of slowly moving electrons was studied by Storch and Olson.¹ They determined the rate of the reaction by pressure methods and the products of the reaction by chemical indicators. From their experiments ammonia forms when the applied potential is 17 volts, the rate of formation then remains constant until the potential reaches 23 volts, at which point an abrupt increase in ammonia synthesis occurs.

Recently Kwei² published a spectroscopic study of low-voltage arcs in nitrogen-hydrogen mixtures. He detected the ammonia bands at 23 volts, thus confirming Storch and Olson's second point, but failed to notice these bands at the 17-volt stage. Kwei advances the following two explanations of the discrepancy: (1) associated molecules are formed as the

¹ Storch and Olson, *THIS JOURNAL*, **45**, 1605 (1923).

² Kwei, *Phys. Rev.*, **26**, 537 (1925).

primary step which by dissociation give ammonia; (2) difference of sensitivity of the two methods. It seems probable to the author that recent work on nitrogen and on collisions of the second kind furnishes an insight into the mechanisms occurring at these two voltages.

Smyth³ and Hogness and Lunn⁴ have shown by positive-ray analysis that N_2^+ only is found at 17 volts, and that both N^+ and N_2^+ are present at 23 volts. The dissociation potential of nitrogen gas has been determined by Sponer⁵ to be about 11.5 volts.

If we now consider the well-known Cario and Franck reaction $Hg^* + H_2 = 2H + Hg + KE$,⁶ we see that a similar reaction can be written for nitrogen at 17 volts. Then $N_2^+ + \ominus \rightarrow N_2^*$, and $N^* + N_2 \rightarrow N_2 + 2N + KE$. Also $N_2^* + H_2 \rightarrow 2N + 2H + KE$, since N_2^* in the higher states of excitation has sufficient energy to dissociate both the hydrogen and itself. At 17 volts, therefore, normal atoms of both nitrogen and hydrogen must be present. Excited atoms of nitrogen could occur only as a secondary process. The main synthesis of ammonia at this voltage is, therefore, $N + 3H \rightarrow NH_3 + \text{heat}$, or $N + 3/2H_2 \rightarrow NH_3 + \text{heat}$; but at 23 volts, we have in addition $N^+ + 3/2H_2 \rightarrow NH_3^+$. If the NH_3^+ is necessary for the ammonia bands it follows that Kwei should have observed them at the 23-volt but not at the 17-volt point.

CONTRIBUTION FROM THE CHEMICAL
LABORATORY OF THE UNIVERSITY OF CALIFORNIA,
BERKELEY, CALIFORNIA

A. R. OLSON

RECEIVED DECEMBER 21, 1925
PUBLISHED MAY 5, 1926

Preparation of Starch Solution for Use in Iodimetric Titrations.— Since early in the nineteenth century investigators at various times have reported that starch that has been ground yields to water a small amount of soluble starch. These observations have not attracted attention. The writers have found¹ that starch that has been ground in a pebble mill disperses very largely in cold water. From these colloidal solutions, water-clear aqueous solutions of starch that keep for many months may be obtained. The writers are using these solutions as the point of departure for studies upon the chemical and physical properties of starch. They have found the solutions superior to starch paste or Lintner's soluble starch for use as an indicator. They believe that others will find them equally useful, and hence present in this note a convenient method for their preparation.

³ Smyth, *Proc. Roy. Soc.*, **104A**, 121 (1923).

⁴ Hogness and Lunn, *Phys. Rev.*, **26**, 786 (1925).

⁵ Sponer, *Z. Physik*, **34**, 622 (1925).

⁶ The symbol Hg^* indicates an activated mercury atom.

¹ Alsberg and Perry, *Proc. Soc. Expl. Biol. Med.*, **22**, 60 (1924).

Dry starch is ground in an ordinary pebble mill until under the microscope most of the granules are found to be cracked or frayed. Under the polarizing microscope the starch, mounted in some anhydrous medium such as glycerol or cedar oil, will no longer show the black cross in most of the granules. The length of the grinding required varies with the size of the mill, with its charge, its speed and with the starch variety. Under the conditions employed by the writers, 122 hours was ample for wheat starch and 70 hours for potato starch. A single grinding should prepare enough starch to last a laboratory for many years.

About 2% of ground starch is sifted slowly into distilled water that is being agitated by an electrical stirring device. The stirring is continued for about an hour. The liquid is then centrifuged at about 2000 r.p.m. for one-half to one hour, and the supernatant solution decanted and stored in an ordinary bottle with enough toluene to cover the surface.

When wheat starch has been used, the solution is water-clear. When potato starch has been used, the supernatant liquid after centrifugation is opalescent. If this opalescence is objectionable, it is best to use wheat starch. When no commercial wheat starch is available it may easily be prepared by making flour into dough, washing out the starch by kneading in a stream of water, collecting the starch from the wash waters by decantation, washing by decantation and drying with alcohol and ether;² or the opalescence can be removed from the potato starch solutions by filtering repeatedly through a 1-cm. layer of diatomaceous earth, using a Büchner funnel with suction.

The solutions show little or no Tyndall effect, contain from 0.1 to 0.5% of starch, and remain clear for months, since retrogradation is extremely slow.

CONTRIBUTION FROM THE
FOOD RESEARCH INSTITUTE
AND DEPARTMENT OF CHEMISTRY,
STANFORD UNIVERSITY, CALIFORNIA

RECEIVED FEBRUARY 15, 1926
PUBLISHED MAY 5, 1926

C. L. ALSBERG,
E. P. GRIFFING AND J. FIELD, 2ND

² Compare Rask and Alsberg, *Cereal Chem.*, 1, 7 (1924).