residues. To examine this point further, we contemplate performing complete combustions of these products.

We are glad to acknowledge our indebtedness to Dr. J. F. Snell for the facilities of these laboratories and to Dr. Darol K. Froman for his kind assistance.

DEPARTMENT OF CHEMISTRY
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RECEIVED APRIL 21, 1934

THE HEAT CAPACITIES OF CRYSTALLINE, GLASSY AND UNDERCOOLED LIQUID GLUCOSE

Sir:

The heat capacities of glucose in the crystalline α-form (Pfanstiehl Chemical Co.) and in the undercooled glassy and liquid condition have been measured with a "radiation" calorimeter, described previously by Thomas and Parks [*J. Phys. Chem.*, **35**, 2091 (1931)]. The specific heats thereby obtained, expressed in calories per gram, are represented graphically by Curves 1, 2 and 3 in the accompanying figure. Curve 1 is for the α crystals and conforms closely to the linear equation $C_p = 0.270 + 0.00092t$. These crystals decomposed slightly when heated slowly up to the melting point. A measurement of their heat of fusion gave 41.7 cal./g. at about 141°. Curve 2 was obtained on heating undercooled liquid glucose, at the rate of about 10° per hour, from the condition of a hard, brittle glass to that of a highly viscous liquid ($\eta = 10^8$ poises at 48.5°). It shows a large maximum or "hump" between 28 and 38°. Conversely, Curve 3 was obtained while this glucose sample was similarly cooling from 45 to 10° and in this case no hump appears, although the total energy changes represented under Curves 2 and 3 are approximately the same. Similar curves have been found with B_2O_3 glass.

In an earlier investigation Parks, Huffman and Cattoir [*J. Phys. Chem.*, **32**, 1366 (1928)] have measured the heat capacities of glassy and liquid glucose from −180 to +70°. Curve 4 represents their results within the temperature range of the present study. They used an aneroid calorimeter and the Nernst method, which involved the introduction of discontinuous increments of energy sufficient to raise the temperature at the rate of about 3° per hour. No hump appears in this curve but there is a 60% rise in the heat capacity between 5 and 15°.

The marked differences between Curves 2 and 4 are due to two factors: (1) the use of different samples of glucose glass, with perhaps a few tenths of one per cent. of water (as an impurity) in the material with Curve 4, and (2) the employment of very different methods in heating these samples in this transition range within which the hard glass is transformed into a pasty liquid.

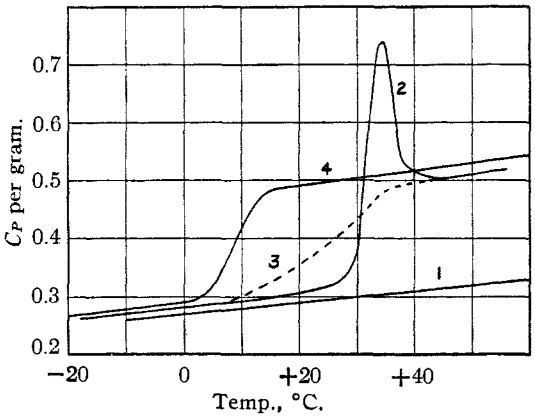

Fig. 1.

In our judgment the second factor is the more important, at least in determining the shape of the curves. In the case of Curve 4 the temperature interval from 5 to 40° was traversed discontinuously in a period of over forty-eight hours; with Curve 2 it was traversed by a continuous heating process within four hours. Curve 4 undoubtedly represents a much closer approach to a true equilibrium condition, although probably no process carried on with a glassy material within finite time can be regarded as involving complete equilibrium. Above 40° the 4% difference between Curves 2 and 4 should probably be attributed to experimental errors, as each method at this temperature may have involved absolute systematic errors of 2 or 3%.

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STANFORD UNIVERSITY, CALIF.
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RECEIVED APRIL 24, 1934

SEPARATION OF DEXTRO AND INACTIVE LUPANINES

Sir:

No convenient method has been reported for separating the mixture of optically isomeric alkaloids derived from *Lupinus albus*. Soldaini [*Arch. Pharm.*, **231** 321, (1893)], and Davis