The chlorine, bromine and iodine derivatives were prepared by the action of hydrogen halides on the pure active negative rotating 2-methylbutanol (1), whereas the negative rotating fluorine derivative was prepared from the bromine derivative by the action of silver fluoride, as will be described in detail later. The similar procedure used for preparing the chlorine, bromine and iodine derivatives makes it very probable that these derivatives are of the same form whether or not a Walden inversion is involved in their preparation. It is immaterial for our present purpose whether this form fits into any particular scheme of classification as a *d*-form or as an *l*-form. In the case of the fluorine derivative, however, it is not certain whether the *negative* rotating form must be classified with the other halogen derivatives, which are positive rotating (Possibility I), or whether the *positive* rotating one must be taken (Possibility II). If we test both possibilities in regard to the above stated atomic dimension relationship we obtain, using the molecular rotations, for the ratio Cl-F, Br-Cl and I-Br for the first possibility, 41:18.1:21.6. This agrees very well with the ratio for the respective atomic diameters. For the second possibility no regularity is obtainable if the fluorine derivative is included. This will be observed from the rotations given above which show first a decrease and then an increase in value. Further work will be done in connection with the conclusion that the negative rotating fluorine derivative is of the same form as the positive rotating chlorine, bromine and iodine derivatives.

Further, it is obvious from these data that the ratio for the differences in weight (Guye's hypothesis) does not fit in both possibilities, as theory would require for Cl-F, Br-Cl and I-Br the ratio 16.5:44.4:47.0. This differs greatly from the observed ratios. The results of an investigation of the halogen derivatives of methylpropylcarbinol will be given in the near future. This will be of interest in connection with the present subject as the possibility exists that the relationship which involves the specific rotations is due to the arrangement of the asymmetric carbons in a ring.

BUREAU OF STANDARDS D. H. BRAUNS
WASHINGTON, D. C.

RECEIVED APRIL 14, 1934

THE BIOLOGICAL SEPARATION OF HEAVY WATER

Sir:

Eyring and Sherman [*J. Chem. Physics*, **1**, 345 (1933)] have pointed out that reactions in biological processes may fractionate the isotopes of hydrogen. In view of this, we considered that the concentrations of heavy water in the urine and in the milk of the same animal might possibly be different from each other and from that of normal water.

We have compared, by the method of the temperature of floating equilibrium [Richards and Harris, THIS JOURNAL, **38**, 1000 (1916)], the specific gravities at 24.50° of water prepared from cow's milk and from urine, with that of pure tap water. The samples of water were obtained by distilling a liquid fraction from four liters of milk, of urine and of the control water, until the dry residue of solids was left. The liquid fractions, including some volatile organic material which had been carried over during the first distillations, were distilled successively from acid and alkaline permanganate, leaving in each case approximately the same volume as residue at the end of each distillation. After six distillations, the distillates were refluxed for twenty-four hours in the presence of alkaline permanganate and finally distilled carefully through a block-tin condenser fitted with a specially constructed spray trap.

The temperature of the thermostat could be controlled to within ±0.001°. The movement of the thin-walled glass float, 6.24 ml., was observed with a reading telescope. The correction to the temperature of floating equilibrium due to changing barometric pressure was determined by artificially adjusting the pressure over a sample of water containing the float and Beckmann thermometer. This was found to be −0.001° per cm. change in pressure.

The temperatures of floating equilibrium in water from milk, tap water and urine were identical to within a maximum deviation of ±0.001°. The pressure corrections to the temperatures were negligible, as the maximum variation in atmospheric pressure during the measurements was 0.74 cm. From these results it can be concluded definitely that the isotopic concentration of deuterium in the samples of water obtained from the liquid fraction of milk and urine does not differ from that of normal water.

We appreciate the fact that the isotopic composition of the total hydrogen in milk and in urine may not be identical, as a considerable portion of the hydrogen was left in the first organic 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
MACDONALD COLLEGE
MCGILL UNIVERSITY, CANADA
W. W. STEWART
R. HOLCOMB

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.

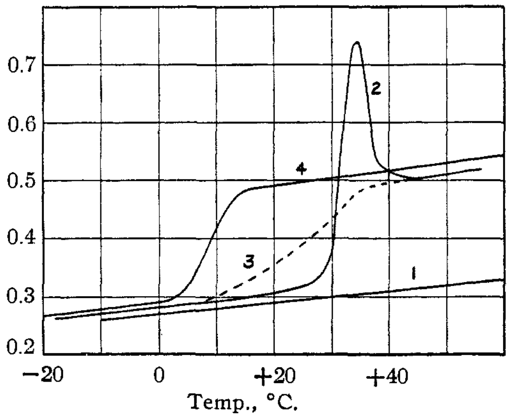

Fig. 1.

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%.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIF.
GEORGE S. PARKS
S. BENSON THOMAS

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