Summary

A rubidium molybdotellurate, $3Rb_2O \cdot TeO_3 \cdot 6MoO_3 \cdot 6H_2O$, and a cesium molybdotellurate, $3Cs_2O \cdot TeO_3 \cdot 6MoO_3 \cdot 7H_2O$, have been isolated and analyzed for the first time. The sodium molybdotellurate described by Thomsen has again been prepared and its composition verified. The alkali metal molybdotellurates form a corresponding series with the general formula $3M_2O \cdot TeO_3 \cdot 6MoO_3 \cdot nH_2O$, perhaps to be written as $M_6[Te(MoO_4)_6] \cdot nH_2O$.

Molecular and Cybotactic Weight Measurements of Resinous and Crystalline Materials[1]

BY HOWARD L. BENDER

Introduction

In the analytical determination of molecular weight numbers for phenol-formaldehyde resins, for crystalline abietic acid, and for some crystalline materials used as standards, irregularities were noted in the boiling points of their solutions. These changes are considered as a function of the time and of the initial temperature used in making the solutions. The molecular weights calculated from the boiling points of the solutions thus showed wide fluctuations. It is not considered that actual molecular structures are varying to the extent shown by these measured changes.

Irregular variations occur in resin solutions as shown[2] by increasing and decreasing viscosity measurements on the same solution held under constant conditions. Also thixotropic and similar structural changes occur under experimental variations.

These changing viscosity data imply a very puzzling shift in the determined molecular weight where the Staudinger viscosity rule is used to calculate the magnitude of the chemical molecules.

For solutions of resins, these calculated "molecular weights" shift with change of time conditions, even though boiling point temperature measurements were made with the same solvent, same resin sample and same temperature conditions. Thus for such solutions, analytical molecular weight values are an uncertain foundation upon which to build structural molecular formulas.

Stewart[3] has coined an apt term for application to changing liquid particles to meet such a diffi-

culty of stability phenomena in the field of pure liquids. According to this concept, the term "cybotaxis" is applied to describe the state wherein easily changed cybotactic groups of molecules are changing in particle size from dimolecules to a factor of approximately one thousand molecules. By Stewart's theory, when liquid molecules collide they temporarily adhere into groups but move from group to group so rapidly that actual particle detection is very difficult in low viscosity liquids.

It is now suggested that this term cybotaxis gives an apt and convenient term to describe the unstability state manifested by the unstability of supercooled liquid particles. Measurements are here given for this type material suspended in solvent solutions. The term cybotactic weight is thus proposed to replace the molecular weight number calculated from the effect of such resinous particles in solution. The proposed cybotactic analytical weight is thus a determined but transitory average value obtained by the use of ordinary molecular weight constants. Hence choice of terms between molecular weight and cybotactic weight depends upon a factor of constancy over an extended time period. This cybotactic weight value thus is a convenient analytical method for expressing the momentarily average particle size of an easily changed particle which will vary directly with the average disintegration of the mass in the solvent medium used. The values found for resins will vary with the conditions used for the determination so the conditions, including time, should always be carefully stated. The term cybotactic weight thus emphasizes the supercooled liquid state of resins. The high viscosity of undercooled liquids at the temperature of solidi-

(1) Delivered at the Baltimore Meeting of the A. C. S. Paint and Varnish Division, April, 1939.

(2) Alexander, "Colloid Chemistry," Vol. IV, The Chemical Catalog Company, New York, N. Y., 1926, p. 360.

(3) C. W. Stewart, *Trans. Faraday Soc.*, **33**, 238 (1937).

fication implies slow change and one expects to find such supercooled liquid groups to be slow in measured changes when compared to low viscosity liquids. Thus solid cybotactic groups of resins should be, even in solvent suspension, capable of measurement both as to average size and as to comparative change in size with time. This paper deals with measurements of change in comparative sizes rather than with their absolute size values.

A very great variety of data are available to show a type of slow change which such undercooled particles undergo. The data include variations from Staudinger's reported "Molecular Weights" of styrene polymers[4] which are reduced in value by simple passage through an orifice, from consideration of the time change of viscosity[5] in resin solution on standing, to the purposeful reduction of particle size[6] in the cellulose derivative field and in the synthetic resin masses.[7]

Speaking of ordinary pure liquids and crystalline solids, Stewart draws a clear working picture in the statement: "The melting point and likewise the boiling point depend directly and indirectly upon the forces which are responsible for the crystalline and liquid states. . . that these characteristics are carried over from the solid to the liquid up to the boiling point. This makes reasonable also characteristic structural differences in the liquid state." This theory of liquid structure gives a concept for ordinary liquids which clears up many of the past difficulties and conveniently may be carried over into the field of undercooled liquids with modification for an expected equilibrium rate change.

Puzzling data as to shifting molecular weight values have been reported previously. The clearest case so far noted has been the data by McMaster,[8] who has kindly furnished us some data in addition to those published. With a freezing point method for determination of molecular weight of a crystalline material in camphor, he obtained two values depending on rapidity of cooling. The values also varied with different solvents.

Other reports show that various rubbers differ as to the effect of heating on the viscosity. Some

increase and others decrease in polymer number.[9] Also pH has been reported to affect the polymer number of cellulose derivatives much the same as the well-known effect of pH on proteins.[10] The time cycle disintegration and aggregation of cellulose derivatives as measured by solubilities and viscosities have been reported.[11]

The polymerization of acetic acid is said to be affected by heat, by some solvents and by traces of water.[12]

Additional quantitative numerical data applying directly to such a concept of cybotactic, that is, to easily changed oriented groups of molecules for supercooled liquids, are now reported.

Under some conditions, the fluctuation in boiling point of a dilute solution of resin in solvent seems to be due to fluctuations in size (and hence in numbers) of the resin masses present in the solution. Thus, under certain conditions, no means were found for obtaining continued constant boiling points even though all the known mechanical aids to reduce superheating were used. These aids included the vapor pumps, roughened glass surfaces, added particles and the very rapid vibration obtained on a 60-cycle per second shaking machine. These data seem to give emphasis to the "micro-crystalline hypothesis" (that is, the actual existence of oriented small groups of molecules) as distinguished from the "quasi-crystalline hypothesis" which is a mere statistical characterization favored by Prins.[13] These data show that the cybotactic weight of a resin changes with time at any one temperature and changes with temperature on any one time cycle. We have previously reported boiling point determinations of molecular weight on a phenol-formaldehyde Novolak resin and have obtained values of 200 to 300.[14] Other reports in the literature show generally higher values so that one wonders at the variation of data. Lignin[15] has lately been reported as having two sets of molecular weights by use of two different methods. In fact, agreement as to resin molecular weights by two different methods is the exception rather than the rule. This condition has caused us to reexamine the analytical determination of the mo-

(4) Staudinger and Heuer. Ber., 67B, 1159 (1934).
(5) Bender, Wakefield and Hoffman, Chem. Rev., 15, 123 (1934).
(6) Malm and Gardner, U. S. Patent 2,080,054; C. A., 31, 4816 (1937).
(7) Bender, U. S. Patent, 2,136,329 (1938); C. A., 33, 4812 (1939).
(8) L. McMaster, THIS JOURNAL, 56, 204 (1934).

(9) Kirchhof, Kautschuk, 8, 137 (1932).
(10) Hess and Ulmann, Naturwissenschaften, 20, 296 (1932).
(11) McBain and Scott, Ind. Eng. Chem., 28, 470 (1936).
(12) P. Koteswaram, Z. Physik, 110, 118 (1938).
(13) Prins, "Structure and Molecular Forces," The Faraday Society, London, 1936, p. 265.
(14) Baekeland and Bender, Ind. Eng. Chem., 17, 225 (1925).
(15) Loughborough and Stamm, J. Phys. Chem., 40, 1113 (1936).

lecular weight number for phenol-formaldehyde resins.

The data indicate that many of the past determined molecular weight numbers for resins are simply arbitrary numbers dependent upon the method of measurement and no present scheme of selection is capable of evaluating the true molecular weight, unless one relies upon the minimum weight as determined by all known methods for indicating the true molecule. The data indicate that present methods are measuring changing particles which vary in size with at least three factors and perhaps more. The factors which always vary the determined numbers are temperature, time and the previous treatment of the sample.

Bernal[16] notes the changing configuration of a liquid as a function of temperature and pressure. To this he adds that changes which require increased energy, such as high viscosity, favor the formation of glasses. "A glass being defined as a supercooled liquid in which the viscosity has become so high that the configuration remains fixed at a state not corresponding to the equilibrium configuration but one determined by the heat treatment and the time elapsed." From the present data, the conclusion is drawn that the undercooled liquid average particle is not constant in size but that such size is a function of present temperature and previous treatment. McBain[17] reports that tested high viscosity solvent solutions of cellulose derivatives are disintegrating to end at low viscosity solutions as a function of time and of solvent power. This seems to make the supposed molecular size and shape of cellulose directly dependent upon a factor of time.

In classifying the various solvents as to their various viscosity effects, those which cause swelling cause higher viscosity.[18]

This known difference of solvent effect makes necessary a choice of solvents in the Staudinger viscosity method for determining weight numbers. No good way is known to bridge the gap between solvent choice and solvent effect except the arbitrary statement that this class of solvent may be used and that one may not be used unless one uses a compensating factor. Such methods of choice simply predetermine the molecular weight numbers to agree with wished-for results. For instance, using the case of styrene polymers in

(16) J. D. Bernal. *Trans. Faraday Soc.*, **33**. 27 (1937).
(17) McBain, Harvey and Smith. *J. Phys. Chem.*, **30**, 342 (1926).
(18) Staudinger and Huseman. *Ber.*, **68B**, 1618 (1935).

solvents, the reason given by Staudinger for the preferred use of non-polar solvents is that the values obtained from the group of non-polar solvents agree well among themselves yet different values are obtained from the group of polar solvents. We now find that in use of a single solvent those conditions which favor swelling favor high number values for the so-called molecular weights.

Experimental

In the following data, wherever molecular weight methods give variations of over $\pm 5\%$ we shall call the values obtained cybotactic weights. Yet even cybotactic weights may be closely checked at a desired number by proper control of experimental conditions. The ability to check arbitrary number values is the first requisite to their use for analytical control, but the fact that arbitrary values may be checked under arbitrary conditions does not impart an absolute significance to such obtained values. As shown by Table I, some but not all crystalline materials will give constant values.

TABLE I

STANDARDIZATION DATA. MENZIES–WRIGHT METHOD[19]

Concentration limits 0.5 to 1.0%

Substance	Theory	Found High	Low	Av.	Remarks Solvent acetone
p-Dihydroxydiphenyldimethylmethane	228	231	229	229	Vibrated 60 cycles per sec. $K = 17.2$
p-Hydroxy diphenylmethane	170	172	168	171	$K = 17.2$ Vibrated
Benzidine	184.1	187	177	184	$K = 17.2$ Vibrated

The above results indicate molecular weights.

Abietic acid (crystalline)	302	400	359	378	$K = 17.2$ Vibrated
% variation		+32	+19	+25	Above theory
From av.		+5.8	−5.0		Range 10.8% for abietic acid indicates cybotaxis

These abietic acid values are thus uncertain and are called cybotactic weights. They may be varied at will as shown later.

A sample, No. 1, of well-washed phenol-formaldehyde fusible resin was held for one hour under 1 mm. vacuum at 240° to free from low boiling solvents, and this was tested for molecular weight effects under the same conditions. The values obtained as shown in Table II are more variable than those for the crystalline abietic acid.

The problem, then, was to find a reason for and control of these fluctuations. There was a suspicion in these data that the way in which the sample was first mixed with the solvent might in-

(19) Menzies and Wright. THIS JOURNAL. **43**, 2309 (1921).

TABLE II

CYBOTACTIC WEIGHTS. VARIATIONS WITH DIFFERENT OPERATORS

Same conditions specified. Solvent acetone, $K = 17.2$. Sample of purified phenol-formaldehyde fusible resin No. 1.

Operator	Theory 212 Monomer	High	Low	Av.
A		684	597	644
B		925	788	847
C		1195	874	965
D		822	698	732
E		705	587	661
F		718	678	705
	Deviation	+57%	−23%	762 gen. av.

fluence the determined value. This effect is shown by the data of Table III.

TABLE III

EFFECT OF MANNER OF SOLUTION IN ACETONE, DETERMINED AT B. P.

Substance	Theory	Cybotactic weights High	Low	Av.	Remarks, dissolved
Abietic acid	302	400	359	378	Hot
Abietic acid	302	530	410	458	Cold
Benzidene	184	178.1	177.9	178	Hot
Benzidene	184	187.5	184	185	Cold
Sample No. 1	..	822	698	732	Hot
Sample No. 1	..	1276	1241	1253	Cold

These variations seemed significant, so were applied to other resin determinations and results are illustrated by the data in Table IV.

TABLE IV

CYBOTACTIC WEIGHT VARIATIONS

Sample 4 phenol-formaldehyde fusible resin

	Solvent	High	Low	Av.	Remarks
A	Hot acetone	790	674	743	$K = 17.2$
B	Hot ethyl acetate	820	755	766	$K = 27.9$
C	Hot methyl alcohol	840	810	820	$K = 8.8$
D	Cold acetone, detd. b. p.	1190	1080	1135	$K = 17.2$
E	Cold ethyl ether, detn. hot	..	..	1082	$K = 21.6$
F	Hot ethyl ether	..	..	720	

On Curve 1, the effect of the original solution temperature is seen to persist in determinations of weight numbers made by the Menzies–Wright method at the boiling point of acetone. These determinations were all made after boiling for five minutes in acetone.

In attempting to use quinine sulfate as a standard to determine K for ethyl alcohol, we were able to get checking curves using $K = 11.7$, where the cybotactic values start at 470 and fall when read over five-minute time intervals until 370 is reached, when the values again rise steadily until
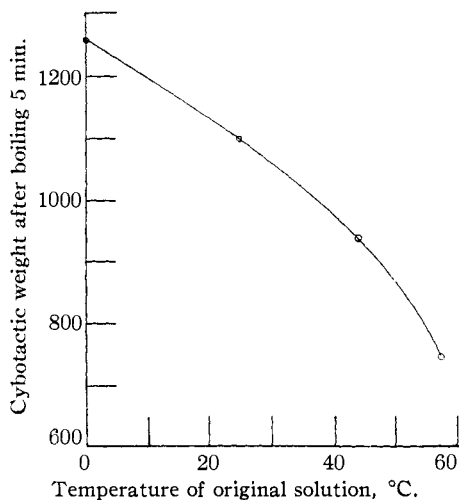

Fig. 1.—Effect of original solution temperature on cybotactic weight determinations by boiling point method. Sample, phenol–formaldehyde fusible resin and solvent acetone; $K = 17.2$.

about four constant readings may be obtained at around 600. The drop and rise cycle is completed in about one hour. Thus even crystalline standards may vary with the time factor of determination.

Curve 2 is a curve of change with time of continued reflux. At first the values drop rapidly, then after a fairly level period begin to rise. At present both the drop and rise in boiling phenomena are considered the result of change in size of the dissolved particles of a supercooled liquid. We have no present reason for attributing the changes to the acetone itself.

This Curve 2 is considered as a composite of three parts. Portion A is a curve of disintegration with time. Portion B is a curve of aggregation or growth with time. Portion C is the numerical resultant of these two factors. The intercept with the weight axis of an extension of B considered as a straight line is about 210 value. This intercept is considered as the more probable molecular weight value from these data. All values above 210 are considered as changing cybotactic weights. On this basis, solution is found as complete after two hundred and fifty minutes of reflux at $56°$. In this connection, the data of McBain[17] on the viscosity drop of cellulose nitrate solutions with time of exposure at $55°$ are of interest.

A Cottrell[20] apparatus was assembled and mo-

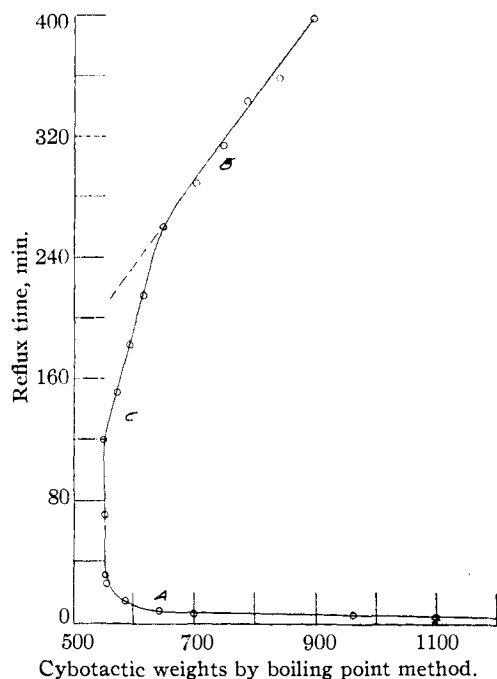(20) Cottrell, THIS JOURNAL, **41**, 729 (1919).

Fig. 2.—Change of weight values with continued reflux time: phenol–formaldehyde fusible resin in acetone, determination made by five-minute boiling periods.
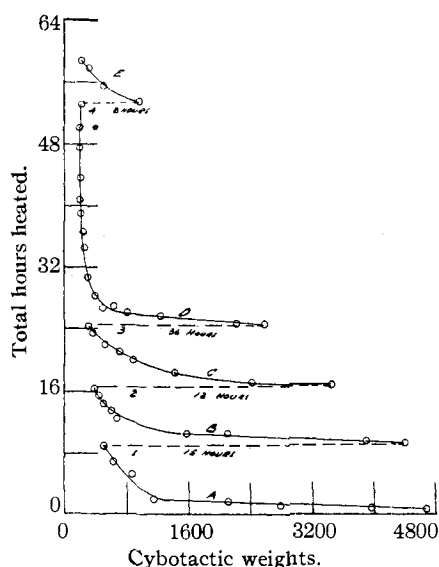

Fig. 3.—Changes in cybotactic weights on heating and on standing cold: Solvent, acetic acid; sample, phenol–formaldehyde fusible resin; $K = 30.7$. Sections A, B, C, D and E heated at 116° as indicated on scale. Sections 1, 2, 3 and 4 standing cold as marked.

lecular weight determinations made to establish a constant $K = 30.7$ for acetic acid. The apparatus was then refilled and sample of Novolak resin no. 1 placed therein. It was then closed with drying tubes and all other known precautions to avoid outside influences. Over a hundred readings of the variations of the cybotactic weights under various conditions were taken and are given on the curve. All points off the average curve are indicated.

Curve 3 shows the changes in determined values of one sample in a protected solvent system as a function of both time and temperature with actual reversal in curve direction at some undetermined temperature between the tested points of 25 and 116°. However, the decay rate at the boiling point of acetic acid was sufficiently slow to enable boiling point measurements to be made and rechecked.

Summary

The structural group in resin solutions may be

varied so easily that it seems undesirable to designate such shifting particles as chemical molecules. Nor, in fact, should their weight expressions be confused with true chemical molecular weights.

The determined molecular weight numbers of a resin in solvent are shown to be changing quantities with the temporary equilibrium numerical values shifting many fold as conditions change. Any molecular weight number determined for resins is defined as an arbitrary number and considered as a cybotactic particle value, the magnitude of which value is dependent upon the conditions under which the analytical determinations are made. These measurements of what seem to be actual cybotactic particles in the resinous state change slowly in this supercooled liquid condition.

The data obtained are interpreted as in line with the expectations of the cybotactic theory as applied to glassy polymers and are contrary to the expectations of the chain molecular theory of polymeric materials.