An Investigation of Polarized-Proton Target Materials
by Differential Calorimetry - Preliminary Results*

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An investigation of polarized proton target materials by differential calorimetry - preliminary results

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Abstract

We have designed and operated a simple differential calorimeter for an investigation of the thermodynamic properties of polarized target materials. The calibration and use of the calorimeter are discussed, after a brief exposition of our motivation for this work. We present the results of a preliminary study of target materials with emphasis on the relevance of the glass state to dynamic polarization in chemically-doped targets.

1. INTRODUCTION

In polarized targets, nuclear spin polarization is enhanced by microwave contact of the nuclei with easily polarized paramagnetic centers which are introduced into the target material as a dilute dopant. Since high nuclear densities are desirable for most scattering experiments, and since low temperatures are advantageous to produce high polarization, most polarized targets are solid under the conditions of use. Another desirable feature of a polarized proton target is that it be as rich in hydrogen as possible. As a result, present-day target materials and prospective materials tend to be liquids or even gases at ordinary temperatures.

Two different approaches have been used, historically, to make the paramagnetically doped solid. The first approach is to freeze the starting

material (if it is not a solid at ordinary temperatures) and then to subject it to radiation to produce radiolytic paramagnetic centers. The second approach is to chemically dope the starting material with a stable paramagnet (often, a free radical) and then to crystallize the mixture from a solution, or, directly freeze the mixture. The second approach has generally been more successful, mainly owing to the greater control over paramagnetic properties and concentrations that it offers.

Since the magnetic interactions that serve to polarize the target protons are effective only over distances of about 10^{-6} cm or less, the dopant must be fairly uniformly dispersed, on a microscopic scale, in the host target material matrix. In the radiolytic approach this condition is often easily satisfied, inasmuch as radiation-damage effects tend to be distributive on a microscopic scale. Even so, the tendency of radiolytic centers to cluster along primary radiation paths might sometimes pose a problem. With the chemical-doping approach the problem is evidently more serious. If the host is crystalline, uniform dispersal implies that the dopant must be capable of co-crystallizing with the host, that is, the dopant molecules must have a high probability of being accepted into the host lattice, as that lattice forms. It has long been suspected by some of us working toward improved target materials that the failure of some otherwise promising combinations to polarize well might be traceable to a failure of the dopant to co-crystallize. In fact, the ability of random mixtures to co-crystallize on a microscopic scale tends to be the exceptional case, rather than the rule.

On the other hand, if the host forms as a disordered or vitreous solid upon freezing from the melt, the probability that the dopant will remain uniformly dispersed upon freezing of the mixture is evidently much greater.¹ That is, it seems plausible that the desirable characteristic of the liquid solution of the paramagnet, namely the uniform dispersion of the dopant molecules, is more likely to carry over into the frozen "solid solution" if the host solvent freezes to a glass.² Indeed, some of us in the field have suspected that the principal materials now used for polarized targets, 1-butanol, ethylene glycol, and 1,2-propanediol, are easy glass-formers and that this property has contributed in some measure to their success. It is, of course, possible that there are ways in which a glassy matrix benefits the dynamics of the nuclear polarization other than through the uniformity of the dispersed dopant.³

Various aspects of the physics of polarized targets have been much studied,⁴ particularly the influence of the properties of the paramagnet on the spin dynamics. However, the physical structure of the host matrix -- the presence or absence of lattice order -- has not been systematically examined for its effect on the dynamic polarization. The above-mentioned suppositions about the relevance of the glass state have, to date, been based mainly on visual observations and a few random references in the physical chemistry literature. The present study has been undertaken to explore the application of differential calorimetry to the question.

With differential calorimetry one can measure the transition enthalpies of the liquid-solid and solid-solid phase transitions, and the specific heats

of the different phases. These measurements are relatively simple and quick, and in many cases suffice to describe the type of order present, at least on a gross scale. There are many other methods available for determining the structure of solids, involving the analysis of scattering of various types of radiation or particle. These methods give more detailed information than calorimetry, especially about the very short-range order, but they are less accessible to the non-specialist, involve the use of special facilities, and generally are not suitable for canvassing a large number of samples.

The main objective of this study is to find out what associations and correlations exist between the degree of glassiness of various frozen matrix materials and the ability of dynamic polarization to polarize the hydrogen nuclei of the matrix. There are two secondary objectives. The first is to find out which calorimetric features, if any, correlate with the "annealing temperatures" of polarized targets that have been radiation-damaged in particle beams. The second, which emanated from a certain prejudice about the outcome of the main objective, is to investigate ammonia and other hydrogen-rich substances for their glass-forming possibilities, with a view toward their use in polarized targets.

This report describes the status of this study as of August, 1980, at the end of the summer appointment of one of us (John J. Hill).

II. DIFFERENTIAL CALORIMETRY

A. General Methods

The differential calorimeter (Fig. 1) is essentially a pair of identical cups with attached thermocouples which serve to measure the temperature of one

of the cups (the sample cup) and the temperature difference between the sample cup and the other cup (the reference cup). Construction details are given in Appendix A. The calorimeter is operated in the temperature range 77 K to room temperature by varying its height above liquid nitrogen (LN) in a small dewar. Usually the calorimeter is kept fixed and the dewar position is varied by means of a jack.

In a typical measurement run, the calorimeter is first cleaned by immersing the entire housing in solvent (usually acetone), the cups are swabbed out, and the housing is allowed to dry. Then the liquid sample is placed in the sample cup with a small pipette, and the cup is covered with a disk of Kapton to reduce evaporation and absorption of water vapor. The reference cup is usually left empty. The cup capacity is approximately 27 μl . For samples which are normally gaseous, such as ammonia, the calorimeter is pre-cooled below the normal boiling point before inserting the sample. The lid is then placed on the housing, and the entire calorimeter immersed in LN (quenched) if the maximum cooling rate is desired. The maximum quench rate achievable with a calorimeter of the present geometry and mass is about 17 K/sec, which happens to be close to the quench rate commonly used in preparing frozen "beads" of polarized target materials. For slower cooling, the LN surface is simply moved more slowly up to the calorimeter. For warming the process is reversed.

The electrical schematic is shown in Fig. 2. The sample arm temperature T_A and the temperature difference ΔT are recorded on a two-channel time-base chart recorder⁵ with maximum sensitivity of 0.08 mV/inch. A differential

voltmeter⁶ is used on the ΔT channel, mainly to furnish some amplification. Typically, amplifications of 1 to 10 are used, resulting in ΔT resolution as small as ~ 25 mK. Since the calorimeter temperature is controlled manually, it was found convenient to have a thermocouple immediately outside the housing to give a fast-response indication of the LN vapor temperature there.

The theory governing the calorimeter is detailed in Appendix B.

B. Calorimeter Calibration

As shown in Appendix B, sample specific heats and transition enthalpies can be measured if the calorimeter heat transfer coefficient K_{EA} is known. The most direct method of determining K_{EA} is to measure the calorimeter response to a known heat pulse q . Since the calorimeter temperature is equal to the environment temperature, T_E , both before the pulse and sufficiently long after it, Eq. (B9) is applicable:

$$K_{EA} = q / \int_{t_1}^{t_2} \Delta T \, dt . \quad (2.1)$$

Since K_{EA} is generally temperature dependent, the pulse response must be measured over the temperature range of interest.

In the present instance, an electrical method of generating heat pulses was chosen. A slurry of glycerol and carbon black was placed in the sample cup and a fine copper wire inserted in the slurry. This provided a resistor in good thermal contact with the cup. A fifteen second pulse of known current and voltage resulted in a Joule heat pulse of known magnitude.

Since the ΔT record is in terms of voltage rather than temperature, it is convenient to convert the integral in Eq. (2.1) to a voltage integral,

$$K_{EA}/S = q/\int_{t_1}^{t_2} \Delta V dt, \quad (2.2)$$

where $S = dV/dT$ is the thermocouple sensitivity. Figure 3 is a plot of S , Fig. 4 shows the measured results for K_{EA} , and Fig. 5 shows K_{EA}/S .

The heat transfer from the cup to the environment consists of two parts: solid conduction through the constantan wire that joins the two cups, and conduction to the nitrogen vapor surrounding the cup. The first of these is easily estimated:

$$(K_{EA})_{\text{constantan}} = ka/\ell, \quad (2.3)$$

where k is the thermal conductivity of constantan, a is the wire cross-section, and ℓ is the distance from the cup to the copper support wire. Taking $k = 0.22 \text{ W/(cm}\cdot\text{K)}$ (at 150K), $a = 4.9 (10^{-3})\text{cm}^2$, $\ell = 0.7 \text{ cm}$, we find

$$(K_{EA})_{\text{constantan}} = 1.5(10^{-3}) \text{ W/K}, \quad (2.4)$$

which is to be compared to the experimental value $K_{EA} \approx 3.5(10^{-3}) \text{ W/K}$. We conclude that about 60% of the heat transfer is to the vapor. We do not attempt an estimate for that process because the geometry is complex and the degree of forced convection is unknown.

C. Relaxation Time

The decay of the response following the calibration heat pulses was found to be exponential, as expected, and yielded the measured relaxation times shown in Fig. 6. A plot of the relaxation time as predicted by Eq. (B13) is also given in Fig. 6, for which the measured values of K_{EA} were used, along

with the literature values⁷⁻⁹ of specific heat and the following mass values for the composite sample arm: mass of cup (304 SST), 0.45 g; solder, 0.07 g; and constantan, 0.05 g. The mass of the calibration slurry (75% glycerol by wt.) was assumed to be 0.055 g. The agreement between Eq. (B13) and the measured $\tau(T)$ appears to be satisfactory, considering that neither the specific heats nor K_{EA} are known to better than $\pm 5\%$.

D. Interpretation of Calorimetric Features

A typical calorimeter scan is shown in Fig. 7. The sample is ethylene glycol; the scan displays the calorimeter response during gradual warm-up following a quench in LN. This is a direct reproduction of the recorded chart, on which time proceeds from right to left. The diagonally-running trace is the direct thermocouple signal from the sample, which should be ignored. The other trace is the differential response, which shows a number of informative features. First, notice that, with the exception of the exothermic feature marked "D", the entire scan is endothermic (ΔT negative). In the intervals between the marked features this endothermy is simply a measure of the sample heat capacity [cf. Eq. (B6)].

As the temperature rises, the first feature that appears is a fairly abrupt increase in the heat capacity at ~ 160 K. This feature is marked "G" for "glass transition", and the corresponding temperature, T_G , is referred to as the "glass transition temperature". The exact nature of glass transitions is still under investigation and is a matter of some controversy.¹⁰ Heuristically, T_G is that temperature below which a "frozen", glassy solid exists and above which the molecular degrees of freedom characteristic of the

liquid state are activated. In the words of Kanno,¹⁰ "The usual interpretation of the glass transition is that at temperatures below T_G certain molecular motions are immobilized while above T_G the kinetic barriers are overcome, allowing molecules in the supercooled liquid to explore many structures over the timescale of an observation". Put even more simply (perhaps deceptively so), the glass transition is the transition from (or to) glass to (or from) supercooled liquid. The temperature T_G is not a sharply defined temperature; it is rather a loosely defined range of temperatures, depending upon heating or cooling rates, over which appear various thermophysical anomalies such as the specific heat anomaly in Fig. 7. The glass transition is often empirically characterized by a viscosity near 10^{13} poise and by the relation $T_G \sim 0.6T_M$, where T_M is the melting point of the crystalline solid.

The next feature that appears in Fig. 7 is the exothermic feature at ~ 192 K, marked "D" for "devitrification", and the corresponding temperature, T_D , is referred to as the "devitrification temperature".¹¹ At this point the sample is crystallizing and the exothermy reflects the heat of crystallization. The term "devitrification" might be considered to be somewhat of a misnomer, since the physical state immediately below T_D is presumably more accurately described as a supercooled liquid than as a vitreous solid; we might more accurately describe T_D as "that temperature at which the melt crystallizes under a regime of rising temperature". However, the distinction between supercooled liquid and glass is at best a blurred one. Also, the transition "G" is a reversible one in the sense that one can reverse the

temperature trend at a temperature between T_G and T_D and recover the glass when T has returned to a value below T_G , but the "D" transition is not reversible in that sense. Once T_D has been traversed the sample is in an equilibrium (crystalline) state; the non-equilibrium states in the vicinity of T_G can only be recovered by melting the sample and then again supercooling it at a sufficiently rapid rate. In this limited, operational sense the vitreous state still "exists" at temperatures between T_G and T_D . As in the case of T_G , T_D is not sharply defined but depends on the heating rate. In the extreme case of sufficiently rapid heating, "devitrification" may not occur at any temperature; the glass passes over into the normal liquid in just the reverse of the process which formed the glass initially.

Since the devitrification feature is central to the purposes of the present investigation, it is important to consider the following question: How can one identify such a feature and distinguish it from, say, an exothermic crystalline lattice transformation? The answer is that the identification may not always be possible, at least on the basis of purely calorimetric evidence. However, the following four indicators allow a strong presumption of a devitrification transition, especially if all four are satisfied:

- 1) The sample changes in visual appearance, usually from transparent to opaque, at T_D .
- 2) The transition is preceded by a specific heat anomaly.
- 3) The transition is not reversible.

- 4) The sample shows no exothermic feature during cooling from the normal liquid state to a temperature below T_D , i.e., there is no evidence of prior crystallization.

The next feature in Fig. 7 is the endothermic feature at ~ 260 K marked "M", the melting transition.

The small feature at ~ 273 K marked "W" is a spurious result of water ice condensate on the calorimeter cups.

Another type of transition, not shown in Fig. 7 but closely related to devitrification, is crystallization in the course of supercooling, occurring at a temperature T_C . To be precise, we will use T_C to denote "that temperature at which the melt crystallizes under a regime of falling temperature", and will refer to this as a "C" transition. In general, T_C depends on cooling rate. In some cases, T_C (and T_D) can also be influenced by extraneous factors such as the cleanliness of the sample, sample size, and even the nature of the sample container.

Figure 8 shows a scan of ethylene glycol - Cr(V), "conventional" polarized target material prepared by potassium dichromate oxidation of ethylene glycol. In addition to features analogous to those of Fig. 7, there is an unknown feature marked "U" just before the onset of melting. This may represent devitrification of a small phase-separated component, or a crystalline lattice transformation ("morphic" transition).

Figure 9 shows the way in which a transition temperature is experimentally defined relative to an observed calorimetric feature.

E. Glass Fraction

The central objective of the present study is to gain insight as to what extent, if any, the degree of glassiness of a sample matrix influences our ability to obtain high nuclear spin polarizations. We need a way to quantify the concept "degree of glassiness". The crux of our idea, which was gleaned from Ref. 11, is that the ratio of the heat of devitrification to the normal heat of fusion gives a measure of the fraction of glass present prior to devitrification. If a sample is "completely glassy", the heat released by devitrification should equal the heat required to melt the same quantity of crystalline material, i.e., the glass fraction would be unity. If a sample is "completely crystalline", no heat of devitrification is released and the glass fraction would be zero.

Actually, since devitrification and melting generally occur at different temperatures, the two transition heats cannot be equal, even for a glass. The total change of enthalpy in a closed thermodynamic cycle must be zero:

$$\oint dH = \Delta H(T) + \int_T^{T_M} C_{liq} dT - \Delta H_M - \int_T^{T_M} C_{cryst} dT = 0, \quad (2.5)$$

where $\Delta H(T)$ is the difference in heat content between liquid and crystal at a temperature $T < T_M$, ΔH_M is the heat of fusion, and C_{liq} , C_{cryst} are the liquid and crystal heat capacities. Denoting the heat of devitrification as ΔH_D , we therefore define the glass fraction f_G as

$$f_G = \Delta H_D / \Delta H(T_D)$$

$$= \Delta H_D / [\Delta H_M - \int_{T_D}^{T_M} (C_{liq} - C_{cryst}) dT] , \quad (2.6)$$

using Eq. (2.5). All quantities on the right-hand side of Eq. (2.6) are, in principle, measurable with the calorimeter.

In practice, since the heat capacities are usually not strongly temperature-dependent, average values of the heat capacities in the interval $T_D \rightarrow T_M$ are used in Eq. (2.6):

$$f_G \approx \Delta H_D / [\Delta H_M - (\bar{C}_{liq} - \bar{C}_{cryst})(T_M - T_D)] . \quad (2.7)$$

A typical run to measure f_G would consist of the following steps:

- a) The sample is prepared in the state for which one wishes to measure f_G , for example, by quenching in LN.
- b) A warming scan then yields measurements, in succession, of ΔH_D , $\bar{C}_{cryst}$, and ΔH_M .
- c) A cooling scan then yields a measure of $\bar{C}_{liq}$ below T_M , insofar as the liquid can be supercooled at the cooling rate chosen.
- d) Another warming scan to re-measure ΔH_M is then advisable, to check that the quantity of sample material in the cup has not changed substantially since step b), e.g., by evaporative loss.

If, as sometimes happens, the "D" and "M" features are not well resolved, a good melting feature and measure of $\bar{C}_{cryst}$ can usually be obtained by re-cooling the sample immediately after devitrification. A warming scan subsequent to such an annealing process will show only the "M" feature if the glass has been properly "erased".

In the event that no features other than the "G" feature can be detected, one normally concludes that the sample material is difficult to crystallize, and ipso facto, that $f_G = 1$.

F. Mixtures

Some of the phenomena discussed in the two preceding sections may be considerably more complicated if the sample is a mixture of materials. The first so-called "hydrocarbon" polarized target materials were alcohol-water mixtures; and a search for improved target materials should by no means exclude mixtures. In fact, insofar as the glass state is a relevant issue, mixtures take on added importance, since it is often true that mixtures are readier glass-formers than the separate components.

If a mixture freezes into a homogeneous solid, i.e., no phase separation occurs, we can treat it as a single material for our purposes, and the results of the preceding sections are unchanged. If phase separation occurs, however, the "sample" comprises two or more distinct parts with differing proportions of the constituents. In the case of a binary mixture, calorimetric scans may then show two transitions of each of the G, D, M, and C types. Moreover, the phase compositions may depend on the cooling and warming rates. Most of these complications can be sorted out by purely calorimetric means, but it is clearly a more laborious process than for homogeneous materials.

The glass fraction for a phase-separated mixture should evidently be defined as a linear combination of the glass fractions of each phase:

$$f_G = \sum_i w_i f_G^i, \quad (2.8)$$

where f_G^i are the individual phase fractions and the W_i are normalized weighting factors. Since we are specifically interested in polarizable protons, we choose weights of the form

$$W_i = N_i / \sum_i N_i, \quad (2.9)$$

where N_i is the number of hydrogen atoms in the i^{th} phase.

III. RESULTS

The calorimeter was used to examine various compounds that have been used in polarized targets, as well as a few other materials that might be of interest. The results are given in Tables I and II, and a summary for each material is given below. Some of the results are clearly incomplete at this point, either for lack of time or because the data were recovered from trial runs made during our learning process.

Most of the materials were used as obtained from the manufacturer. In the Tables, the symbol $\dot{T}_{\text{form}}$ refers to the cooling rate used to form the solid and $\dot{T}_{\text{meas}}$ is the subsequent scanning rate. Single-component materials are discussed first, then mixtures.

A. Toluene (8.8 wt.% H, Handbook $T_M = 178$ K)

Toluene is a material in which moderate dynamic polarization has been achieved¹²⁻¹⁵ and remains of some interest owing to its relatively high resistance to radiation damage. It is also a good test material for our type of calorimeter, having strong G, D and M features as shown in Fig. 10. A large number of runs with toluene were made in the process of debugging the

calorimeter and the operating procedures. Only a fraction of these runs are represented in Table I.

Figure 11 shows the dependence of T_D and T_G on heating rate, for toluene. In the measured range, the dependence is approximately logarithmic with a slope of ~ 6 K/decade. We note that this kind of information can be used to estimate the activation energy for the devitrification process.¹⁶

Data for two commercial brands of toluene are shown in Table I; the two seem to give similar results. Also shown are the data for toluene "beads", that is, drops of liquid frozen on the surface of LN, as in standard target preparations, and then placed in the calorimeter. In this case the apparent T_M is elevated ~ 1 deg K, probably due to the relatively poor heat contact of the beads with the cup.

Toluene showed considerable supercooling (32 deg K) before crystallizing at a cooling rate of 26 K/min., and glass formation at 83 K/min. Cooling rates between these two were not studied. In Table II these observations are summarized in the notation $\dot{T}_{\min}^G = (-26., -83.)$, i.e., the minimum cooling rate for glass formation is bracketed by these results. The measured glass fraction ranges from 0.78 at $\dot{T}_{\text{form}} = -83.$ K/min to 0.93 at $-930.$ K/min. Since the error in the measured transition enthalpies is typically $\pm 5\%$, and $\pm 15\%$ in the measured specific heats, typical errors on f_G are perhaps $\pm 10\%$. Hence, we conclude that glass formation is essentially total for $\dot{T}_{\text{form}} = -930.$ K/min, but may be incomplete at $-83.$ K/min.

Occasionally we encountered a sample of toluene that would not vitrify at the quench rate of -930 K/min. It seems likely that this is an effect of

heterogeneous nucleation on some particular sort of solid or liquid contamination. However, we were unable to reproduce the effect with the deliberate addition to the cup of room dust, water, or acetone.

B. 1,2-Propanediol (10.6 wt.% H, Handbook T_M not listed)

For the last eight years 1,2-propanediol has been a widely-used polarized target material, yielding proton polarization in excess of 80% with dichromate-produced Cr(V) doping.

We observed no transitions other than the glass transition around 170 K, and therefore assign $f_G = 1.0$.

Although we have not yet studied doped propanediol, we may safely presume that it is also an easy glass-former, by analogy with ethylene glycol (see below).

C. Pinacol (11.9 wt.% H, Handbook $T_M = 316$ K)

Pinacol was investigated some years ago¹⁷ because it is a close relative of the successful diols and a solid at room temperature. It yielded polarizations around 70% with dichromate-produced Cr(V) doping.

In a single calorimeter run, pinacol showed no C feature at -2.3 K/min, from which we conclude that $f_G \sim 1.0$ is easily achieved. The subsequent warm-up showed some very broad features which may be D and M transitions. Handling of small samples of pinacol appears to be complicated by its highly hygroscopic property. No special precautions were taken on this run to exclude water.

D. 1-Butanol (13.6 wt% H, Handbook $T_M = 183$ K)

For the last ten years or so 1-butanol has been used as a target material in situations in which its relatively high radiation resistance and low annealing temperature are advantageous. It gives polarizations around 70% when doped with water and porphyrine (see below for this mixture).

Butanol shows no C transition when cooled, even at rather low rates (-1.7 K/min). That is, it is difficult to crystallize "on the way down" but does so readily "on the way up". We have found this same paradoxical behavior in several materials. Apparently this phenomenon is well known, and in the calorimetric literature¹⁸ is explained as due to the formation of nuclei at very low temperature, which nuclei initiate crystallization upon subsequent warming.

Our measured value of $f_G = 1.01$ for butanol frozen at -2.2 K/min indicates that it is an easy glass-former. (Values of $f_G > 1$ are unphysical, of course, but our errors of the order of 10% should be remembered.) The absence of a C transition at these cooling rates leads to the same conclusion.

Our values for T_M lie 4-5 deg K below the Handbook value, which may indicate that our untreated material has significant impurities.

E. Ammonia (17.8 wt.% H, Handbook $T_M = 195$ K)

Ammonia is an attractive target material by reason of its high hydrogen content, but efforts to polarize it by means of chemical doping have been unsuccessful.¹⁹ Radiolytic doping has recently met with considerable success.²⁰

Ammonia shows no trace of G or D transitions after quenching at -1100. K/min, the maximum rate possible with this calorimeter. The M and C transitions are present, implying $f_G \sim 0$.

F. Water (11.2 wt.% H, Handbook $T_M = 273$ K)

To our knowledge, water itself has never been dynamically polarized to any appreciable degree. However, it has seen use as a small-percentage additive to polarized target materials.

In the calorimeter water behaves similarly to ammonia.

G. Ethanol (13.1 wt.% H, Handbook $T_M = 156$ K)

Ethanol was the first so-called "hydrocarbon" material found to exhibit appreciable (> 30%) dynamic polarization,¹³ when mixed with 8% water and the free radical porphyrexide.

Ethanol readily undergoes G, D, and M transitions, but shows no C transition at -3.5 K/min, the slowest cooling studied so far. From this we conclude that ethanol is an easy glass-former. A glass fraction of $f_G \gtrsim 0.68$ was calculated in one calorimeter run in which the glass was formed at -69. K/min. The ethanol runs were among the earliest done with the calorimeter, and were not very well done, so that only a lower limit on f_G was recovered. It is likely that f_G is quite close to 1.0.

As in the case of 1-butanol, the measured T_M 's are several degrees below the accepted value, and vary, suggesting varying degrees of contamination. Probably, the impurity is water vapor absorbed during handling and in the course of measurement.

H. Ethylene Glycol (9.7 wt.% H, Handbook $T_M = 262$ K)

Ethylene glycol (1,2-ethanediol) is closely related to 1,2-propanediol and gives similar polarization levels when doped with dichromate-produced Cr(V). As such, it has also been a much-used target material.

The calorimeter shows that ethylene glycol also makes a good glass, as is true of 1,2-propanediol, but the cooling rate required is much greater.

Again, our samples show a depressed T_M relative to the accepted value.

I. sec-Butylamine (15.2 wt.% H, Handbook $T_M < 201$ K)

We became interested in sec-butylamine in connection with our studies of ammonia. Since ammonia itself does not seem to form a glass easily, it is natural to ask if there are any close molecular relatives that do. The amine family is one such set of relatives; the lightest (and most hydrogen-rich) is methylamine, which does not readily form a glass according to our initial survey, but does so upon the addition of a small amount of water. Our visual survey indicated that the lightest pure amines which are easy glass-formers are sec-butylamine and iso-butylamine. A polarization of around 15% has been attained in sec-butylamine with Cr(V) doping.²¹

The calorimeter shows sec-butylamine to be a good glass with $f_G = 0.96$.

J. sec-Butylamine + Cr(V)

Upon addition of 4.0 wt.% EHBA-Cr(V)²² to sec-butylamine, the G transition remains at essentially the same temperature and the D and M transitions do not appear; i.e., the mixture is more difficult to crystallize than the pure solvent. Thus we assume $f_G \sim 1.0$.

K. Standard Target Material: Ethylene Glycol - Cr(V)

This is target material prepared in the "conventional" way: oxidation with potassium dichromate under vacuum.¹⁷ The differences from pure ethylene glycol are that T_M is depressed, T_D is elevated, and $\dot{T}_{min}^G \sim -7.5$ K/min rather than ~ -300 K/min; i.e., the oxidized material forms a glass more easily.

When a small percentage of water is added, glass formation is further facilitated, and there is some evidence that the D peak splits into two components; i.e., there may be phase separation.

L. 1-Butanol + PX (saturated)

"Butanol" polarized targets normally consist of a mixture of 1-butanol (95 wt.%) and water (5 wt.%), saturated with porphyrexide (PX). In pure 1-butanol, saturation with PX produced no significant changes in the calorimetric features. Addition of 5% water raises T_D by ~ 10 deg K, leaving T_G and T_M essentially unchanged, and $f_G \sim 1.0$ remains easily attainable at -2 K/min. No C transition is seen at these cooling rates.

When the water content is increased to 15 wt.% the behavior is quite different; evidently appreciable phase separation now occurs during cooling. A new melting feature appears at ~ 255 K in addition to the one at ~ 178 K, and a C feature appears at ~ 240 K. We tentatively associate the new features with a water-rich phase, and the feature at ~ 178 K with the butanol-rich phase. The butanol-rich phase is probably a eutectic (minimum melting point) mixture²³ and easily forms a glass. Apparently the water-rich phase does not form a glass at cooling rates up to -800 K/min. In order to measure the glass fraction of the mixture according to Eq. (2.8), more tests will be

needed to determine the phase compositions. For now we merely estimate $f_G \sim 0.75$ from the heats of fusion of the phases.

M. Ethanol + water

Some early calorimeter runs were made with ethanol-water mixtures, but these need to be repeated more carefully. The indications are that, during cooling, phase separation sets in at a composition between 5 and 20% water, and that f_G probably begins to decrease at that point. This is analogous to butanol-water in that a eutectic is known to exist at around 8 wt.% water.¹³ The glass fraction falls to an estimated 0.17 at 55 wt.% water.

N. Ammonia + Water

It would evidently be quite interesting for us if ammonia could be induced to form glass, at the available quench rates, by blending in some additive in small proportion so as to preserve the hydrogen content. Water has been suggested¹ for the purpose.

This may be the most complex mixture that we have looked at; since ammonia and water readily combine to form ammonium hydroxide, the mixture is potentially ternary. Our preliminary findings are that a small amount of glass phase is formed at 21 wt.% H_2O and that f_G increases to ~ 1.0 as the water content approaches 40%. The uncertainties of f_G quoted in Table II arise largely from difficulty in measuring the melting features; it appears that evaporation of ammonia from the calorimeter cup occurs rather quickly even at temperatures not far above the melting point. Note that we find a definite dependence of f_G on the quench rate, with 34% H_2O .

We have examined, purely visually, a number of other additives for ammonia, as follows, where the percentage admixture required for visual glass formation is given in parentheses: methanol (> 60%), ethanol (62%), 2-propanol (> 62%), 1-butanol (> 65%), tert-butanol (> 61%), tert-pentanol (> 60%), 2,3-dimethyl-2-butanol (> 62%), sec-butylamine (86%), tert-butylamine (> 68%), tert-pentylamine (> 90%), acetone (> 50%), ethylene glycol (50%), 1,2-propanediol (60%), 1,3-propanediol (43%), glycerol (45%), ammonium chloride (> 7%), ammonium bromide (> 33%). These tests were made by freezing drops of the mixtures on the surface of LN. In sum, either no glass is formed or large admixtures are required.

0. Visual Observations

In general we find that visual inspection is reliable in identifying fully glassy material; that is, drops that freeze into round, hard, transparent beads generally prove to have a calorimetric $f_G \sim 1$, and vice versa. However, partial glasses ($0 < f_G < 1$) are not reliably distinguished, visually, from fully crystalline material. And in deeply colored materials such as the standard dichromate-oxidized diols, visual transparency is difficult to judge.

The phenomenon of devitrification is also often visually detectable, but it becomes difficult when T_D is relatively close to T_M .

It is informative to observe the mechanical behavior of glassy beads at temperatures near T_D . Different materials behave differently. For example, dichromate-oxidized ethylene glycol glass beads undergoing warming through T_D soften enough at temperatures just below T_D to fuse to one another, whereas,

at similar heating rates, glassy toluene beads do not. In the first case what exists immediately above T_D (but below T_M) is an interlocking network of polycrystalline "blobs"; in the second case the polycrystalline material remains as mechanically separate spherical beads. In other words, the mechanical fate depends on the viscosity of the glass near T_D , and that viscosity can evidently vary widely between materials.

Although we have as yet no supporting calorimetric evidence, we note here that the following hydrogen-rich materials are easy glass-formers, by visual inspection: N-methylethylamine (15.3 wt.% H), methylamine + 15 wt.% water (15.5 wt.% H), 3-methylpentane (16.4 wt.% H), and 2-methylbutane (16.8 wt.% H). (That 3-methylpentane forms a glass is well known to physical chemists.) Also, we have seen some evidence that liquid propane forms a glass when quenched in liquid helium. If so, it would be the most hydrogen-rich glass (18.3 wt.% H) that we are aware of.

P. Comparison with Previous Work

In the work¹¹ which stimulated our present study, de Nordwall and Staveley examined the glass-forming properties of a number of substances in an ordinary (non-differential) calorimeter. They studied both quench-cooled bulk liquids and vapor deposits, and there were four substances in common with our study: water, ammonia, ethanol, and toluene. With water or ammonia they were able to obtain indications of a vitreous component only with the deposition method, and our results are not inconsistent with theirs. With ethanol they obtained partially vitreous deposits with $T_D \sim 121$ - 125 K and $\Delta H_D \sim 16.8$ J/g, but they quote no results for quench-cooling. With toluene they quote $T_D \sim$

123-124 K and $\Delta H_D \sim 6.4$ -20. J/g for quench-cooling. These values for T_D are somewhat less than ours, the values for ΔH_D are considerably less, and although they did not calculate glass fractions as such, the fractions would have been considerably smaller than ours. However, their calorimeter used large ($\sim 1 \text{ cm}^3$) samples. The resultant lower (and inhomogeneous) quench rates can certainly explain the differences.

In the work of Cocks et al.¹⁶ the mixtures studied (dimethyl sulfoxide or glycerol in water) are not of immediate concern to us, but it is interesting to note the motivation for this study of the role of glass-phase induction, by cryoprotective agents in frozen biological materials. It is thought that one mechanism for the action of cryoprotective agents such as glycerol is the inhibition of salt segregation and crystallization when biological materials are frozen, via the development of a glassy phase.

It is appropriate to note here the recent viscometric studies of alcohols²⁴ in which it is shown that the viscosity of 1-butanol or 1-pentanol near the melting point is greatly increased by the addition of small percentages of water or pinacol. The authors report that such additives also improve the dynamic polarization obtainable with Cr(V) doping, and suggest that the increased viscosity facilitates glass formation and inhibits crystallization of the dopant.

IV. DISCUSSION

A. Correlations between Glass Properties and Dynamic Polarization Data

1. General comments

All of the materials that we have studied that have actually been used as polarized targets have proven to be easy glass-formers, and have yielded thermodynamic glass fractions near unity, when cooled at the rates normally used. We have seen that materials like water and ammonia, which can scarcely be polarized via chemical paramagnetic doping if they are not mixed with other solvents, have glass fractions of essentially zero when quenched at accessible rates. These observations tend to endorse the "visual lore" that has grown up, that "transparent solids polarize, opaque do not", and promise to enable us to put it on a more quantitative footing.

We must stress that these considerations apply only to chemical doping situations, and are less relevant for radiolytic doping, although perhaps not entirely so inasmuch as glasses and crystals can differ generically in certain aspects of their radiation chemistry. They also clearly do not apply to systems like LMN-Nd,²⁵ the earliest polarized target material, wherein co-crystallization occurs with a certain ease.

We should also note that our initial survey has perforce focussed on a few materials which tend to make glasses rather easily, and might lend a false impression as to the prevalence of this phenomenon. In fact, while easy glass-formers are not exactly the exceptional case, they are far from being the rule among materials in general.

We now turn to some specific examples of dynamic polarization data that are clarified by the calorimetric data.

2. Alcohol-water mixtures

Figures 12 and 13 show the polarization data for ethanol-water and butanol-water mixtures saturated with PX, respectively, from the "discovery" publications.^{13,26} The samples were cooled at rates of ~ 3 K/min or greater, rates at which the pure alcohols readily form glasses according to the calorimetric results. In both alcohols the polarization shows a tendency to increase, as water is added, up to around the eutectic composition, and then decreases as further water is added. At one time it was thought that the initial increase was simply due to the increase in room-temperature solubility of PX as a little water is added, but the effect remains if a constant concentration of PX is used instead of a saturated condition. It seems that the increase in viscosity²⁴ mentioned previously, and its role in hindering segregation of the dopant, is a likely explanation. To this point the calorimeter offers little insight, since up to the eutectic point the glasses all appear to be of high thermodynamic quality (at least for butanol). However, for the higher water concentrations the decrease in polarization is evidently paralleled by a decrease in f_G , which, as we have seen, is a consequence of phase separation during cooling and the fact that one of the phases is not glassy. The authors of Ref. 26 noted some indirect evidence for phase separation in samples containing more than 10% water.

It should be educational to examine these mixtures more thoroughly with a calorimeter. A parallel behavior of f_G and the polarization would demonstrate the value of calorimetry as a diagnostic.

3. The effect of cooling rate

We are aware of a few anecdotes linking the degree of polarization attained with the rate at which the sample was cooled, but most of them are the result of uncontrolled and undocumented experiments. One exception is an account by Atsarkin et al.²⁷ involving ethylene glycol-Cr(V). Samples cooled at ~ 3.7 K/min yielded polarizations less than those quenched in LN, by factors ranging from 1.5 to 10 depending on the measurement frequency. Moreover, when 2% water was added, the cooling rate influence was eliminated. Atsarkin et al. attributed the ill effect of slow cooling to segregation of the Cr(V) complexes, and the ameliorative effect of water to the hindrance of the segregation because of "hydration of the Cr(V) complexes". We can now say that, although the first suggestion is probably correct, the effect of the water is simply the prevention of crystallization of the matrix. The calorimetric data show that, without water, ethylene glycol-Cr(V) crystallizes at cooling rates less than ~ 7.5 K/min, whereas, with 2.5% water, the critical rate is less than 2.3 K/min.

4. The effect of devitrification

There are some data that we have recovered from old ZGS-experiment log books that suggest that the polarization in ethylene glycol-Cr(V) targets decreased by factors between 4 and 40 when the target temperature was accidentally raised to values between T_D and T_M before re-cooling. These targets were not frozen beads in form, but rather were encapsulated in teflon film, so that melting, as such, should have had little effect. In two such

cases, the target was then re-warmed to ~ 280 K before again re-cooling, and the polarization recovered to within a factor of 2 of its original value.

These results are suggestive of a large effect of devitrification, and should be repeated in a controlled experiment.

B. Radiation-Damage Annealing Temperatures

One of the secondary objectives of this study is to relate the annealing temperatures (T_A) of radiation-damaged target materials to observable calorimetric features. In Table III we list the target materials for which we have both calorimetric and annealing data, albeit incomplete. It appears that the annealing temperatures consistently lie in a range which starts near T_G and runs up to somewhat below T_D . The relationship of T_A to T_G is not unexpected,³⁴ although it is gratifying to see the direct thermodynamic evidence. The apparent relationship of the upper end of the annealing range with T_D is a new observation so far as we are aware.

C. Hydrogen-Rich Glasses

We have found that there exist some additives which convert ammonia and light amines to easy glass-formers, however, the proportions required are such as to reduce the hydrogen content to around 15% in all of these polar glasses. (To date we are unable to dissolve Cr(V) in most non-polar solvents.) To summarize, the hydrogen-rich ($> 15.0\%$ H) glasses that we know of at this point are:

polar glasses:	$\text{NH}_3/\text{H}_2\text{O}$ (60/40)	- 15.1 wt.% H
	sec-Butylamine	- 15.2

	N-Methylethylamine	- 15.3
	sec-Butylamine/NH ₃ (86/14)	- 15.5
	Methylamine/H ₂ O (85/15)	- 15.5
non-polar glasses:	3-Methylpentane	- 16.4
	2-Methylbutane	- 16.8
	Propane (?)	- 18.3

There probably exist some other members of these series (e.g., ethylamine/H₂O, and branched alkanes C_nH_{n+2}, n > 6).

Higher quench rates may allow glassification of pure, bulk NH₃ in the future; however, initial trials indicate that the required rate is $\geq 10^4$ K/min.

We have mentioned in Sec. III.J that a dynamic polarization trial has already been done using sec-butylamine doped with EHBA-Cr(V), yielding only 15% polarization with indications of an inhomogeneously broadened EPR resonance.²¹ While this polarization is far better than that attained in crystalline ammonia with the same dopant, it demonstrates (if any demonstration were necessary) that a glassy matrix, by itself, is no guarantee of high polarization. The calorimeter seems to offer no clue as to what other factor is "amiss" in this system. Perhaps some of the Cr(V) is crystallizing out in spite of the glassy matrix, but it is unclear how this would lead to inhomogeneous broadening. X-ray diffraction studies of this system might be informative. Also, variation of the Cr(V) content and/or additives such as H₂O might increase the polarization in this material and shed some further light on the problem.

V. FUTURE WORK

From our results it is abundantly clear that calorimetry is a distinct aid to an understanding of several aspects of the behavior of polarized target materials. Our view of the relevance of glassy materials is reinforced, and certain areas of "black magic" are greatly illuminated, such as the implications of phase separation of mixtures and the distinctions between softening of the glass, devitrification, and crystalline melting.

For the future, it is clear that several of the tests reported here deserve a more careful repetition. In some cases we need better control of sample purity and evaporative losses. Information about the degree of reproducibility of certain results would be desirable. More thorough literature searches, and input from knowledgeable physical chemists, would undoubtedly be educational. The search for more hydrogen-rich glasses should continue. More dynamic polarization tests with the hydrogen-rich glasses should be done, as well as controlled dynamic polarization tests of individual samples before and after devitrification. It might be useful to explore the possibility of higher quench rates for bulk solutions. Our preliminary tests show that some improvement (up to $\times 10$) over the usual method is possible using sub-cooled liquids (e.g., propane) at LN temperature, or by quenching a thin layer of solution on a thin sheet of metal or plastic.

We might also consider implementing a capability of operating the calorimeter down to liquid helium temperatures or of automating the heating and cooling processes. These improvements may not be worth the effort.

APPENDIX A: CONSTRUCTION OF CALORIMETER

The differential calorimeter (Fig. 1) is constructed as follows. Two cylindrical cups of dimensions .475 cm high, .475 cm diam. with a concentric hole .300 cm deep and .325 cm diam. are made of stainless steel, for corrosion resistance. The cup size was chosen somewhat arbitrarily, large enough to allow visual judgement of the appearance and approximate volume of the sample, but as small as possible within that constraint to allow rapid cooling, and to minimize the relaxation time. The ratio of sample mass to cup mass was also rather arbitrary (volume ratio $\sim .5$), small enough to limit self-heating of the sample during exothermic transitions.

The cups are soft-soldered to the ends of a constantan wire .079 cm in diameter and 2.3 cm long. Copper-constantan thermocouple pairs, #40 gauge, are also soldered to each end of the constantan wire. The constantan wire is placed perpendicular to a heavy (.206 cm) copper support wire and their centers are soldered together. The copper support is mounted horizontally inside a copper housing (3.2 cm O.D., 2.4 cm high). Thus the center of the differential calorimeter is thermally anchored to the massive housing.

The four thermocouple wires exit through a hole in the housing and up through a stainless steel tube (0.48 cm diam., 0.025 cm wall) which is used to support the calorimeter. The T-channel reference thermocouple is threaded down through this same tube and has its junction approximately 18 cm below the housing, since it must remain immersed in the liquid nitrogen during measurements. A fourth thermocouple terminates at the end of the tube just

outside the housing and serves to monitor the vapor temperature. The electrical schematic is shown in Fig. 2.

The housing has four holes in the bottom for liquid drainage. A loose-fitting lid on the housing and a sheet of plastic over the dewar serve to reduce convection. A circular cap (0.48 cm diam., 0.013 cm thick) of Kapton H-film is used to cover the sample cup to reduce sample evaporation and contact with air.

APPENDIX B: CALORIMETER THEORY

1. Notation and Heat Balance Equation

The object of differential calorimetry is to extract the thermodynamic properties of a sample from the observed temperature difference, ΔT , between the sample and reference cups, under various regimens of heating and cooling. The relationship between ΔT and the sample properties is found by solving the heat balance equations for the two cups. We define the following terms, in which the subscript S stands for sample, A stands for sample arm, A' for reference arm, and E for environment. (The "environment" consists of the copper support wire and housing, and the nitrogen vapor inside the housing, all of which are assumed to be at the same temperature T_E .)

T_x : temperature of x; x = S, A, A', E

m_x : mass of x

c_x : specific heat of x

$C_x = m_x c_x$: heat capacity of x

K_{xy} : heat transfer coefficient between x and y

Q_x : heat content of x

Q_T : sample phase transition heat

$\dot{T}_x, \dot{Q}_x, \dot{Q}_T$: time derivative of T_x, Q_x, Q_T

The rates of heat transfer to the sample, sample arm, and reference arm are, respectively,

$$\dot{Q}_S = \dot{Q}_T + K_{SA}(T_A - T_S) + K_{ES}(T_E - T_S) = C_S \dot{T}_S, \quad (B1)$$

$$\dot{Q}_A = K_{SA}(T_S - T_A) + K_{EA}(T_E - T_A) = C_A \dot{T}_A, \quad (B2)$$

$$\dot{Q}_{A'} = K_{EA'}(T_E - T_{A'}) = C_{A'} \dot{T}_{A'}. \quad (B3)$$

Adding Eq. (B1) to Eq. (B2) and subtracting Eq. (B3) yields the heat balance equation:

$$C_A \Delta \dot{T} = \dot{Q}_T - C_S \dot{T}_S - K_{EA} \Delta T + K_{ES}(T_E - T_S) + (T_E - T_{A'}) \Delta K_{EA} - \dot{T}_{A'} \Delta C_A, \quad (B4)$$

where $\Delta T = T_A - T_{A'}$, $\Delta K_{EA} = K_{EA} - K_{EA'}$, and $\Delta C_A = C_A - C_{A'}$. Since the calorimeter is symmetrical in construction, we assume that $\Delta K_{EA} = \Delta C_A = 0$. (This can be checked by running the calorimeter with both cups empty.) We also assume that the sample has no direct thermal contact with the environment, i.e., $K_{ES} = 0$. Equation (B4) then reduces to

$$\dot{Q}_T = C_A \Delta \dot{T} + K_{EA} \Delta T + C_S \dot{T}_S. \quad (B5)$$

2. Measurement of Sample Specific Heat and Heats of Transition

In the absence of phase transitions ($\dot{Q}_T = 0$), and at a constant rate of heating or cooling ($\dot{T}_S = \text{const.}$), the calorimeter reaches a state of quasi-equilibrium ($\Delta \dot{T} \approx 0$) in which, from Eq. (B5), ΔT is proportional to the sample heat capacity:

$$\Delta T \approx - C_S \dot{T}_S / K_{EA}. \quad (B6)$$

Since $\dot{T}_S \approx \dot{T}_A$, the sample specific heat is

$$c_S \approx - K_{EA} \Delta T / m_S \dot{T}_A, \quad (B7)$$

which thus can be measured if K_{EA} is known. The sample mass is obtained either from the area of the melting curve and the known value of the heat of fusion, or from the known sample volume inserted in the cup.

If the sample undergoes a phase transition, the resulting pulse of heat to or from the sample causes ΔT to depart transiently from the above quasi-equilibrium; it returns to quasi-equilibrium, once the phase transition is complete, with a relaxation time characteristic of the calorimeter (see Sec. B.3). The area under the resulting peak in the time domain is related to the heat of the transition, as can be seen by integrating Eq. (B5):

$$\begin{aligned} Q_T &= \int_0^\infty C_A \dot{\Delta T} dt + \int_0^\infty C_S \dot{T}_S dt + \int_0^\infty K_{EA} \Delta T dt \\ &\approx \bar{C}_A \delta(\Delta T) + \bar{C}_S \delta T_S + \bar{K}_{EA} \int_{t_1}^{t_2} \Delta T dt, \end{aligned} \quad (B8)$$

where the time interval t_1, t_2 spans the period of the phase transition and calorimeter relaxation, $\delta(\Delta T) = (\Delta T)_{t_2} - (\Delta T)_{t_1}$, $\delta T_S = (T_S)_{t_2} - (T_S)_{t_1}$, and $\bar{C}_A, \bar{C}_S, \bar{K}_{EA}$ are time averages. If the heating or cooling rate is made sufficiently small, we have $\delta(\Delta T) \approx \delta T_S \approx 0$ and Eq. (B8) reduces to

$$Q_T \approx K_{EA} \int_{t_1}^{t_2} \Delta T dt, \quad (B9)$$

since K_{EA} depends only on the calorimeter temperature and not on the phase of the sample. More generally, if the heating or cooling rate is appreciable, one can compensate for the "heat capacity offsets" of ΔT by re-defining the baseline ("zero") of ΔT . Specifically, if we define a ΔT^* such that

$$\Delta T^* = \Delta T + (C_S \dot{T}_S + C_A \dot{\Delta T}) / K_{EA} , \quad (B10)$$

then

$$Q_T \approx \bar{K}_{EA} \int_{t_1}^{t_2} \Delta T^* dt . \quad (B11)$$

Note that $\Delta T - \Delta T^*$ corresponds to the response of the calorimeter in the absence of transition heat; it is not necessarily a constant offset, since C_S may differ for the two sample phases. Therefore, there is some guesswork in estimating the proper baseline of ΔT and it is preferable when possible to keep the rate and offset small, so that Eq. (B9) remains nearly correct. Figure 9(a) shows a graphic example of ΔT^* .

The calibration procedure (determination of K_{EA}) is described in Sec. 11.B.

3. Calorimeter Relaxation Time

If T_E is held fixed, both cup temperatures ultimately reach equilibrium values of T_E , as does T_S . If T_S is then perturbed by a heat pulse, it relaxes back to T_E with a relaxation time

$$\tau = -(T_S - T_E) / \dot{T}_S \approx -\Delta T / \dot{\Delta T} , \quad (B12)$$

since by assumption $T_{A1} = T_E$ and $T_S \approx T_A$. Equation (B5) then gives

$$\tau \approx (C_A + C_S) / K_{EA} . \quad (B13)$$

Since the present calorimeter design is such that $C_A \gg C_S$, τ does not vary much from sample to sample.

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References and Notes

1. See, for example, M. C. R. Symons in Proc. of the Second Workshop on Polarized Target Materials (Rutherford Laboratory, 1980) RL-80-080, pp. 27,68; also K. Guckelsberger, Nucl. Instr. and Meth. 144, 93 (1977). This view seems to be widely held, and undoubtedly is correct, but we are unaware of any quantitative studies of the phenomenon.
2. One is tempted to carry this line of reasoning one step further, to the case in which both the host and the dopant are easy glass-formers.
3. R. C. Fernow, "Report of the Workshop on Polarized Target Materials", in Proceedings of High Energy Physics with Polarized Beams and Polarized Targets (Argonne, 1978), AIP Conf. Proc. No. 51; p. 23.
4. For the most recent reviews, see A. Abragam and M. Goldman, Rep. Prog. Phys. 41, 395 (1978); and V. A. Atsarkin, Sov. Phys. Usp. 21, 725 (1978).
5. Texas Instruments, Servo/Riter II.
6. John Fluke Co., model 833 AB.
7. Handbook of Thermophysical Properties of Solid Materials, Vol. II (Macmillan Co., 1961; ed. A. Goldsmith, T. Waterman, H. Hirschhorn).
8. International Critical Tables, Vol. 5.
9. Cryogenics and Industrial Gases Data Book, 8, (1973).
10. For some recent papers on the glass transition, see M. H. Cohen and G. S. Grest, Phys. Rev. B20, 1077 (1979); G. S. Grest and M. H. Cohen, Phys. Rev. B21, 4113 (1980); H. Kanno, J. Non-Cryst. Solids 37, 203 (1980); R. Fisch, Phys. Rev. B22, 3459 (1980).
11. H. J. de Nordwall and L.A.K. Staveley, Trans. Faraday Soc. 52, 1207 (1956); also 52, 1061 (1956).
12. R. P. Haddock and R. J. Wagner in Proc. of the Internat. Conf. on Polarized Targets and Ion Sources (Saclay, 1966); p. 381.
13. M. Borghini et al. in Ref. 12, p. 387.
14. R. Fernow, Nucl. Instrum. and Meth. 159, 557 (1979).
15. D. Crabb in Ref. 1, p. 52.

16. F. H. Cocks, W. H. Hildebrandt, and M. L. Shepard, J. Appl. Phys. 46, 3444 (1975).
17. H. Glättli in Proc. of the Second Internat. Conf. on Polarized Targets (Univ. of Calif., Berkeley, 1971) LBL-500, p. 281.
18. Experimental Thermodynamics, Vol. I (Plenum Press, 1968; ed. J. P. McCullough and D. W. Scott); p. 175.
19. Ref. 3, p. 30; and D. Hill in Ref. 1, p. 67.
20. T. O. Niinikoski and J. M. Rieubland, Phys. Lett. 72A, 141 (1979); M. Seely et al., and U. Hartel et al. in Proc. of the Internat. Symp. on High Energy Physics with Pol. Beams and Pol. Targets (Lausanne, 1980), to be published.
21. D. Hill in Ref. 1, p. 66.
22. Sodium bis (2-ethyl-2-hydroxybutyrato) oxochromate (V).
23. Mixtures of glycerol-water evidently show similar phenomena, with phase separation of a eutectic phase (see Ref. 16). The enhanced ability of eutectics to form glass is discussed, for metallic alloys, by P. Chandhari and D. Turnbull, Science 199, 11 (1978); and J. Gilman, Science 208, 856 (1980).
24. T. Niinikoski in Ref. 1, p. 69.
25. Lanthanum Magnesium double-Nitrate doped with Nd.
26. S. Mango et al., Nucl. Instr. and Meth. 72, 45 (1969).
27. V. A. Atsarkin et al., Sov. Phys. - Solid State 15, 580 (1973).
28. M. Borghini et al., Nucl. Instr. and Meth. 84, 168 (1970).
29. G. Court, private communication.
30. M. Hennecke, private communication.
31. R. Fernow, private communication.
32. M. Seeley, private communication.
33. R. C. Fernow, Nucl. Instr. and Meth. 148, 311 (1978).
34. V. K. Ermolaev et al., Kinetika i Kataliz 3, 58 (1962).

Table I

Summary of Measured Transition Temperatures for the Materials Investigated.

Where two temperatures are given, the presence of two phases is suspected. A blank space indicates that the measurement has not been made, a dash indicates that the quantity is not defined or applicable.

Material	$\dot{T}_{\text{form}}$ (K/min)	$\dot{T}_{\text{meas}}$ (K/min)	T_G (K)	T_D (K)	T_C (K)	T_M (K)	T_G/T_M	T_D/T_M
Toluene ^a	-930.	+ 1.3		131	--	177		0.74
	-930.	+ 4.6	118	132	--	177	0.67	0.75
	-930.	+ 4.7		134	--	177		0.76
	-930.	+ 13.		135	--	177		0.76
	-930.	+ 17.		140	--			
Toluene ^b	-930.	+ 1.5		130	--			
	-930.	+ 3.2	119	132	--			
	-930.	+ 3.7	119	132	--	177	0.67	0.75
	-930.	+ 4.8	120	134	--	177	0.68	0.76
	-930.	+ 5.3	120	133	--	177	0.68	0.75
	-930.	+ 6.3	119	132	--			
	-930.	+ 7.		134	--	177		0.76
	-930.	+ 12.	122	134	--	177	0.69	0.76
	-930.	+ 14.	121	136	--	177	0.68	0.77
	-930.	+ 26.	125	138	--	177	0.71	0.78
	-930.	+ 32.		138	--	177		0.78

Table I (continued)

Material	$\dot{T}_{\text{form}}$ (K/min)	$\dot{T}_{\text{meas.}}$ (K/min)	T_G (K)	T_D (K)	T_C (K)	T_M (K)	T_G/T_M	T_D/T_M
(beads)		+ 5.7		132	--	178		0.74
	--	-15.	--	--	174	--	--	--
	--	-17.	--	--	173	--	--	--
	--	-26.	--	--	145	--	--	--
1,2-Propanediol ^c	- 2.3	+ 2.2	170	None	--	None	--	--
	- 6.7	+ 6.3	172	None	--	None	--	--
	--	- 2.3		--	None	--		--
Pinacol ^d	- 2.3	+ 2.4	190	?	--	?		
	--	- 2.3		--	None	--		--
1-Butanol ^e	- 2.2	+ 3.8	115	153	--	178	0.65	0.86
	- 6.3	+ 3.8		159	--			
	- 810.	+ 4.8	115	150	--	178	0.65	0.84
	- 810.	+ 7.5	119	148	--	179	0.66	0.83
	--	- 1.7		--	None	--		--
Ammonia ^f	-1050.	+ 5.2	None	None	--	193	--	--
Water	- 820.	+ 3.3	None	None	--	272	--	--

Table 1 (continued)

Material	$\dot{T}_{\text{form}}$ (K/min)	$\dot{T}_{\text{meas}}$ (K/min)	T_G (K)	T_D (K)	T_C (K)	T_M (K)	T_G/T_M	T_D/T_M
Ethanol ^g	- 68.	+ 2.8	99	138	--	~ 149	0.66	0.93
	- 53.	+ 3.3		141	--	~ 146		0.97
	- 6.7	+ 4.0	101	139	--	~ 153	0.66	0.91
	- 930.	+ 4.3	102	136	--	~ 152	0.67	0.89
	- 930.	+ 6.0		139	--	~ 152		0.91
	- 930.	+ 12.	106		--			
	- 3.5	+ 12.		144	--			
	--	- 3.5		--	None	--		--
Ethylene Glycol ^b	- 550.	+ 2.8	156	187	--	256	0.61	0.73
	- 830.	+ 4.0	157	187	--	255	0.62	0.73
	- 300.	+ 4.2	157	190	--			
	- 830.	+ 4.8	159	187	--	257	0.62	0.73
	- 500.	+ 9.5		193	--	254		0.76
	- 270.	+ 7.3	None	None	--	254		
	--	- 3.7	--	--	231	--	--	--
	--	- 180.	--	--	233	--	--	--
	--	- 270.	--	--	212	--	--	--
	--	- 300.		--	None	--		--
sec-Butylamine ^h	- 4.7	+ 0.53		149	--	168		0.89
	- 8.3	+ 1.3		147	--	166		0.89

Table I (continued)

Material	$\dot{T}_{\text{form}}$ (K/min)	$\dot{T}_{\text{meas}}$ (K/min)	T_G (K)	T_D (K)	T_C (K)	T_M (K)	T_G/T_M	T_D/T_M
	- 5.0	+ 2.7		152	--			
	- 810.	+ 5.3	117	147	--	166	0.70	0.89
	--	- 0.58		--	None	--		--
sec-Butylamine + EHBA-Cr(V) 4.0%, 5×10^{19} spins/ml)	- 810.	+ 3.0	119	None	--	None	--	--
Standard Target Mat'l. (Ethylene Glycol-Cr(V), 7×10^{19} spins/ml)	- 820.	+ 1.2		201	--	245		0.82
	- 820.	+ 2.3	159	202	--	238	0.67	0.85
	- 7.5	+ 2.3	158	203	--	241	0.66	0.84
	- 820.	+ 9.8	165	214	--	245	0.67	0.87
	- 820.	- 2.5	149	--	--	--	0.61	--
	--	- 3.5	--	--	221	--	--	--
	--	- 4.2	--	--	220	--	--	--
	--	- 7.5		--	(212)	--		--
" + 2.5% H ₂ O	- 3.3	+ 2.2		208,223	--	233		0.89,0.96
	- 2.3	+ 4.7	164	215,228	--	239	0.69	0.90,0.95
	--	- 2.3		--	None	--		--
" + 7.8% H ₂ O	- 24.	+ 0.32		None	--	None	--	--
	- 24.	+ 2.1	164		--			
	- 7.2	+ 4.7	156	None	--	None	--	--
	--	- 2.2		--	None	--		--

Table I (continued)

Material	$\dot{T}_{\text{form}}$ (K/min)	$\dot{T}_{\text{meas}}$ (K/min)	T_G (K)	T_D (K)	T_C (K)	T_M (K)	T_G/T_M	T_D/T_M
1-Butanol + PX, saturated	- 39. - 2.2 --	+ 3.4 + 4.1 - 2.2		152 149 --	-- -- None	178 178 --		0.85 0.84 --
1-Butanol + 5% H ₂ O + PX, sat.	-35. - 2.1 --	+ 1.2 + 2.4 - 2.1		160 159 --	-- -- None	178 178 --		0.90 0.89 --
1-Butanol + 15% H ₂ O + PX, sat.	- 2.5 - 810. -- --	+ 3.1 + 5.2 - 2.5 - 6.8	118,None 121,None	160,None 164,None -- --	-- -- None,243 None,239	178,256 177,254 -- --		-- --
Ethanol + 0.4% H ₂ O + 3.0% H ₂ O + 4.7% H ₂ O + 20. % H ₂ O + 30. % H ₂ O + 40. % H ₂ O + 55. % H ₂ O	- 930. - 930. - 930. - 930. - 930. - 890. - 880.	+ 8.2 + 7.7 + 5.7 + 4.2 + 10. + 9.0 + 6.8	106 107 105 109,None 108,None 129,None 136,None	138 None 140 None None 171,None 175,None	-- -- -- -- -- -- --	153 None 148 None,191 None,207 208,222 209,224	0.69 0.71 tentative	0.90 0.95

Table I (continued)

Material	$\dot{T}_{\text{form}}$ (K/min)	$\dot{T}_{\text{meas}}$ (K/min)	T_G (K)	T_D (K)	T_C (K)	T_M (K)	T_G/T_M	T_D/T_M
Ammonia + 21% H ₂ O	- 970.	+ 3.7		123, None	--	180, 185	tentative	
	- 3.3	+ 5.6		None	--			
	--	- 3.3		--	174	--		
" + 31% H ₂ O	- 950.	+ 3.7	123	130, None	--	184, 190		
	--	- 4.4		--	167	--		
" + 34% H ₂ O	- 5.9	+ 3.2		None, 158	--	185, 189		
	- 950.	+ 3.5	123	134, 159	--	185, 189		
	--	- 5.9		--	165, None	--		
	--	- 16.		--	(162), None	--		
" + 37% H ₂ O	- 910.	+ 3.5	124	144, 158	--	186, 188		
" + 40% H ₂ O (approximately)	- 860.	+ 3.7	127	152		185		

a MCB Co., spectrophotometric grade (boiling range 2°C, max. water 0.03%).

b Fisher Scientific Co., reagent (boiling range 1°C, max. water 0.01%).

c Eastman-Kodak, practical (boiling range 2°C).

d Koch-Light Lab. Ltd., practical.

e Fisher Scientific Co., spectrophotometric.

f Matheson Gas Products, electronic (99.998% min.).

g Rossville, reagent.

h J. T. Baker Co., dried and distilled.

Table II

Summary of measured properties for the materials investigated.

Material	$\uparrow_{Min}^G$ (K/min)	$\uparrow_{form}$ (K/min)	$\bar{c}_{cryst}$ (J.g ⁻¹ .K ⁻¹)	$\bar{c}_{liq}$ (J.g ⁻¹ .K ⁻¹)	ΔH_D (J/g)	ΔH_M (J/g)	f_G
Toluene ^a	(-26., -83.)	- 83. - 930. - 930.	0.93	1.20	46.5 56.5 51.8	71.8 ^b 71.8 71.8	0.78 0.93 0.87
1,2-Propanediol ^c	(0, -2.3)	- 2.3			None	None	1.0
Pinacol ^d	(0, -2.3)	- 2.3					~ 1.0
1-Butanol ^e	(0, -1.7)	- 2.2	0.74	1.95	95.6	125.2 ^f	1.01
Ammonia ^g	(-1100., -∞)	-1100.			~ 0	332.1 ^h	~ 0
Water	(- 820., -∞)	-820.			~ 0	333.4 ^f	~ 0
Ethanol ⁱ	(0, -3.5)	-69.	1.4 ^j	1.9 ^j	≥ 70.	109.0 ^f	≥ 0.68
Ethylene Glycol ^a	(-270., -300.)	- 830.	1.6	2.1	147.	181.0 ^f	0.98
sec-Butylamine ^k	(0, -0.58)	- 8.3	1.8	2.4	62.8	75.1	0.96
sec-Butylamine + EHBA - Cr(V) (4.0%, 5x10 ¹⁹ spins/ml)		-810.					~ 1.0

Table II (continued)

Material	$\uparrow_{\text{Min}}^G$ (K/min)	$\uparrow_{\text{form}}$ (K/min)	$\bar{c}_{\text{cryst}}$ (J.g ⁻¹ .K ⁻¹)	$\bar{c}_{\text{liq}}$ (J.g ⁻¹ .K ⁻¹)	ΔH_D (J/g)	ΔH_M (J/g)	f_G
Standard Target Mat'l. (Ethylene Glycol-Cr(V), 7x10 ¹⁹ spins/ml)	~ - 7.5	- 820.	1.6 ^l	2.1 ^l	155.	181.0 ^l	0.94
" + 2.5% H ₂ O	(0, - 2.3)	- 2.3					~ 1.0
" + 7.8% H ₂ O	(0, - 2.2)	- 2.2					1.0
1-Butanol + PX, sat.	(0, - 2.2)	- 2.2	0.93	1.88	105.7	125.2 ^m	1.08
1-Butanol + 5% H ₂ O + PX, sat.	(0, - 2.1)	- 2.1					~ 1.0
1-Butanol + 15% H ₂ O + PX, sat.	$\begin{cases} (0, - 2.5) \\ (- 810., - \infty) \end{cases}$	- 2.5					0.75 (est.)
Ethanol + 40% H ₂ O		- 890.					0.25 (est.)
Ethanol + 55% H ₂ O		- 880.					0.17 (est.)
Ammonia + 21% H ₂ O	$\begin{cases} (- 3.3, - 970.) \\ (- 970., - \infty) \end{cases}$	- 970.					0.09 - 0.31
" + 31% H ₂ O	$\begin{cases} (0, - 4.4) \\ (- 950., - \infty) \end{cases}$	- 950.					≥ 0.31

Table II (continued)

Material	$\uparrow_{\text{Min}}^{\text{G}}$ (K/min)	$\uparrow_{\text{form}}$ (K/min)	$\bar{c}_{\text{cryst}}$ (J.g ⁻¹ .K ⁻¹)	$\bar{c}_{\text{liq}}$ (J.g ⁻¹ .K ⁻¹)	ΔH_D (J/g)	ΔH_M (J/g)	f_G
Ammonia + 34% H ₂ O	{ (0, - 3.3) (-5.9, - 950.)	- 3.3 - 950.					~ 0.24 0.56 - 0.73
" + 40% H ₂ O (approx.)	(0, - 860.)	-860.					1.01

- a Fisher Scientific Co., reagent grade.
- b From Ref. 11.
- c Eastman-Kodak, practical.
- d Koch-Light Lab. Ltd., practical.
- e Fisher Scientific Co., spectrophotometric.
- f Handbook of Chem. and Phys.
- g Matheson Gas Products, electronic (99.998% min.)
- h From Ref. 11.
- i Rossville, reagent.
- j From Ref. 8.
- k J. T. Baker Co., dried and distilled.
- l Values for pure ethylene glycol assumed.
- m Values for pure 1-Butanol assumed.

Table III

Measured transition and radiation-damage annealing temperatures (T_A)
for polarized target materials, in Kelvins

Material	T_G	T_D	T_M	T_A
1-Butanol + 5% H ₂ O + PX, sat.	117	159	178	110-150 ^a
Ethylene Glycol - Cr(V) (7×10^{19} spins/ml)	159	202	242	160-180 ^b
1,2-Propanediol (undoped)	171			180-200 ^c
Pinacol (undoped)	190			~ 200 ^d

^a Refs. 28-32

^b Refs. 30,33

^c Refs. 30,33

^d Ref. 30

Figures

Figure 1 Differential calorimeter.

Figure 2 Calorimeter electrical schematic.

Figure 3 Copper-constantan thermocouple sensitivity as a function of temperature.

Figure 4 Measured calorimeter heat transfer coefficient as a function of temperature. The circles were obtained by starting at the lowest temperature and working in increments up to 300 K. The square was obtained at the end of the run upon returning to the lowest temperature, and gives a measure of the reproducibility.

Figure 5 Calorimeter calibration coefficient as a function of temperature.

Figure 6 Thermal relaxation time of the calorimeter as a function of temperature. The solid line is a plot of Eq. (B13).

Figure 7 Calorimeter scan of ethylene glycol quenched in LN. Note that time proceeds from right to left. The diagonal trace is the

direct thermocouple signal from the sample cup, used only to monitor the temperature. The features marked G, D, M, and W are, respectively, the glass transition, devitrification, melting, and water contamination features. The vertical sensitivity is 0.16 mV/inch. Positive-going features are exothermic and negative-going, endothermic.

Figure 8 Scan of ethylene glycol-Cr(V), conventional polarized target material, quenched in LN. The marked features are analogous to those of Fig. 7. An unknown feature, marked U, appears just before the onset of melting. The vertical sensitivity is 0.04 mV/inch.

Figure 9 Experimental definitions of transition temperature, T_t .

(a) In the case of T_M , T_C , or T_D , T_t is taken to be the intersection of the extrapolated leading edge of the feature with the extrapolated baseline. The effective deflection ΔT^* is discussed in Appendix B.

(b) T_G is taken to be that temperature at which the apparent heat capacity has undergone one-half of its total change at the glass transition.

Figure 10 Scan of toluene, quenched in LN. The vertical sensitivity is 0.04 mV/inch.

Figure 11 Observed dependence of T_D and T_G on heating rate for toluene. The dashed lines are only to guide the eye.

Figure 12 Dynamic proton polarization in ethanol-water mixtures from Ref. 13.

Figure 13 Dynamic proton polarization in 1-butanol-water mixtures from Ref. 26.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13