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 (15) Polarizability, rotatory power, anisotropies, Kerr specific. All calculation being complete, the S_k expression we have adopted is $S_k = (22.7244/M)(4.62 + 1232\gamma^2 + 24316\theta) \times 10^{-14}$ esu cgs.
 (16) This comparison is only a reminder, as the "old method" is incomparably easier to implement.
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Glass Transition Temperatures for Simple Molecular Liquids and Their Binary Solutions

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Glass transition temperatures have been measured at 20 mol % intervals in 55 binary molecular liquid systems and the results used as a basis for (a) estimating by extrapolations the glass transition temperatures of many common organic liquids which do not vitrify in the pure state and thereby (b) identifying the various structural features of a molecule which collectively determine the magnitude of its T_g . In most cases, simple linear composition dependences are observed for T_g . The thermodynamic significance of dT_g/dx is discussed. In the case of cyclohexanol T_g estimated for the liquid exceeds the known value of " T_g " for the plastic crystal phase by some 10 °C. The T_g estimated for CCl_4 and CHCl_3 exceed by large intervals the T_g values reported for vapor-deposited amorphous phases of these substances.

In recent years there has been increasing utilization, in solutions research, of solvents which fail to crystallize and consequently solidify continuously on cooling (i.e., which vitrify). This has been particularly marked in radiation chemistry where the glassy matrix is utilized to trap radiolysis products for subsequent EPR or visible spectroscopic examination and, on subsequent annealing at T_g , to study recombination kinetics.¹ There has also been interest in noncrystallizing solvents in low temperature electrochemical studies^{2,3} and in the investigation of structural and dielectric relaxation processes.⁴⁻⁶

In such studies it is obviously desirable to have available a range of solvents with different annealing points and chemical properties and also some means of predicting the

properties of mixed solvents from the known properties of possible components. However, there has been little systematic work, prior to the recent papers of Lesikar,⁷⁻⁹ on the glass transition temperatures of mixed molecular solvents, or on assessments of the extent to which known vitrifiable solvents can be diluted with nonvitrifying solvents without loss of glass-forming capability. The present paper represents a modest attempt to provide representative information on this problem.

The information acquired in these studies makes it possible to obtain, by reasonable linear extrapolations, the glass transition temperatures for a number of simple liquids which are not glass-forming in normal cooling or even fast quenching experiments. The glass transition tem-

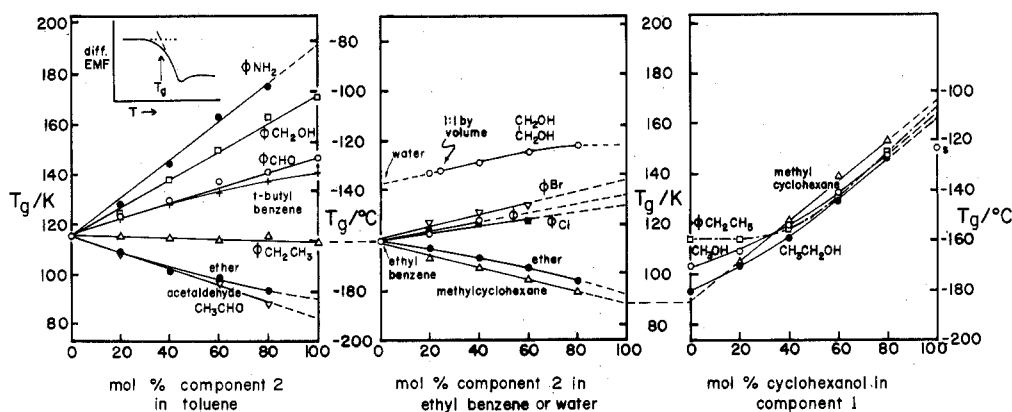


Figure 1. T_g -composition relations for a selection of binary molecular liquid systems showing predominantly linear variations, and also estimates by extrapolation of T_g for nonvitrifying constituents.

peratures, at which liquids fall out of internal equilibrium, provide rather direct information on the magnitude of interparticle interactions and hence are very useful for diagnosing the effect of chemical constitution on liquid properties.⁷⁻¹² Their utility in revealing molecular structure-liquid property relations is partly due to the fact that the measurement is made at the low temperature limit of liquid-state behavior so that the masking of structural effects by temperature-induced disordering, i.e., entropy effects, is minimized.

Estimates of the temperature at which simple liquids would enter the vitreous state if crystallization were precluded are of special interest currently because of the unexpected differences they show from the glass transition temperatures recently measured for vitreous forms of the same substances prepared by low-temperature deposition from the vapor state.

Experimental Section

The experimental aspects of this study are very simple. Solutions of binary solvent systems of interest were prepared at 20 mol % composition intervals by weighing of reagent grade components. Their glass-forming capability was assessed by quenching test tubes containing ~ 2 cm³ of solution into liquid nitrogen. This yields a cooling rate of approximately 20 °C/min. In those cases where crystallization was totally suppressed, the glass transition temperature, determined at a heating rate of 8 °C/min, was measured by a simple differential thermal analysis procedure using two pen recording described in a previous paper.¹³ Other work¹⁴ has shown that T_g determined on this time scale and defined as indicated in Figure 1 (inset) corresponds to the temperature at which the viscosity, η , is $\sim 10^{11}$ P. According to the Maxwell relation

$$\eta = G_{\infty} \langle \tau_s \rangle \quad (1)$$

a viscosity of this magnitude implies an average shear relaxation time (τ_s) of 1–5 s, since G_{∞} , the high frequency shear modulus for molecular liquids, is consistently in the range $0.5\text{--}4 \times 10^{11}$ dyn cm⁻². The bulk structural relaxation time will, however, generally be longer, e.g., 5–200 s.¹⁴

T_g was always determined on the same volume of solution using the same thermocouple position, so that the magnitude of the differential pen deflection caused by the transition gave a means of qualitatively comparing the change in heat capacity of the solution as it passed from the vitreous to the supercooled liquid condition.

Most measurements were made on solutions in which the first component was either toluene, ethylbenzene, ethanol, or cyclohexanol. The first three are strongly glass

forming in the pure state and their use ensured a reasonably broad composition range of glass-forming binary solutions. The particular one of the three chosen for measurements involving a given second component depended on the chemical character of the second component. Generally, it was desirable to choose chemically similar components in order that glass temperatures varied approximately linearly with composition thereby permitting reliable extrapolations to the T_g of the pure second component.

Results

In all, some 55 binary systems were studied, each at 20 mol % composition intervals.

Some typical sets of results are shown in Figure 1a, in which toluene serves as the first component for binary solutions with various benzene derivatives, ether, and acetaldehyde. It is seen that except for *tert*-butylbenzene and ether the T_g vs. composition relation is almost linear, and extrapolations to give T_g of, for instance, aniline and acetaldehyde (which differ in T_g by more than 100 °C) would appear to be fairly reliable. In Figure 1b one of the second components of Figure 1a, ethylbenzene, serves as solvent for benzene and two halo-substituted benzenes, ether, and methylcyclohexane. The results for the ether solutions in Figures 1a and 1b serve to point up the dangers of uncritical linear extrapolations because the extrapolated glass transitions in that case would differ by some 7 °C. In fact the binary solutions show small negative deviations from linearity in the first case and small positive deviations in the second case which must be recognized if the extrapolations are to be reliable. Finally in Figure 1c methylcyclohexane, one of the second components of Figure 1b, carries over as the solvent in the "best-behaved" of several binary systems containing cyclohexanol which were examined in order to estimate the T_g value for the latter substance (see below).

In Figure 2, ethylbenzene serves as first component for binary solutions involving three chloromethanes, methylcyclohexane, and two methylbutanes. It appears that methylene dichloride, a useful solvent in low temperature electrochemical studies,² is almost glass forming by itself, and may be characterized by a glass transition temperature of -172 °C.

Several cases, of which ethylbenzene + 2-methylbutane is one example, were encountered in which opalescent glasses were formed at intermediate compositions. This is evidently a result of liquid-liquid phase separation (a manifestation of excessive positive deviations from ideal mixing due to too-great differences in internal pressures¹⁵) occurring at temperatures where the viscosity is too great

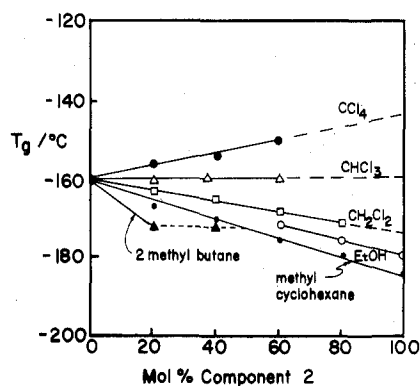


Figure 2. T_g -composition relations for ethylbenzene-based solutions of halomethanes and other second components showing extrapolations for halomethane T_g 's, and evidence for low temperature phase separation with 2-methylbutane.

to permit a complete separation. The growth of the second phase droplets only proceeds to microscopic (light wavelength) dimensions before vitrification arrests the structure. The two-phase character of solutions containing more than 20% 2-methylbutane is attested to by the constancy of measured T_g (T_g for the ethylbenzene-rich phase) for compositions containing more than 20% 2-methylbutane (Figure 2). T_g for the second phase would be too low to detect (68.2 K according to Sugisaki et al.¹⁶).

The results for systems involving cyclohexanol shown in Figure 1c are of particular interest. Pure cyclohexanol itself does not supercool significantly on quenching. However, the high temperature crystalline form of cyclohexanol is a plastic crystal which is readily supercooled and which at lower temperatures undergoes a relaxational transition which has all the thermal characteristics of the liquid-glass transition although it occurs within the crystalline state.^{17,18} It is of interest to determine whether or not the "glass" transition temperature determined for this crystalline material lies above or below that of liquid cyclohexanol as estimated by linear extrapolation of binary liquid solution data. Data published by Seki and co-workers^{17b,c} since this study commenced has shown that in cases such as 2,3-dimethylbutane and ethanol, where both normal glass and glassy crystal states can be obtained, the two glass temperatures lie within a degree or two of each other.

Other results are summarized in Table I, in which all pure liquids included in this study are listed, together with (1) the value of T_g determined in this work (either directly or by extrapolation), (2) additional liquid constants and their ratios (to be discussed below), and (3) summary information on the composition range of glass-forming solutions of the liquid in solutions with a designated glass-forming liquid (e.g., ethylbenzene 100-60%), and any noteworthy glass transition characteristics. Where possible, results are compared with data of others workers, e.g., T_g for CCl_4 and toluene obtained by Lesikar^{7,8} and for ethylbenzene and methylcyclohexane reported by Carpenter, Davies, and Matheson.¹⁹ In a number of cases, data obtained by these and other authors, and not repeated by us, are included in the table to extend the possible correlations.

Discussion

The data in Table I uphold well the general guideline for glass-forming ability in pure liquids, $T_B/T_M > 2.0$, given by Turnbull and Cohen.²⁰ Not only do those substances satisfying $T_B/T_M > 2.0$ all form glasses, but the range of glass-forming solutions in binary systems with one non-glass former increases as T_B/T_g for the non-glass former

approaches 2.0. The halomethane series provides a good example.

Both Turnbull and Cohen²¹ and Bondi in his book on organic liquids²² sought to identify a reduced glass temperature which would be a universal constant for molecular liquids. Bondi has concluded that neither the Cohen-Turnbull $T_g^* = kT_g/h$ (where h is the vaporization energy per molecule) nor his own $T_g^* = 5cRT_g/E^0$ (where $3c$ is the number of external degrees of freedom per molecule and E^0 is the molar vaporization energy at a fixed reduced volume) are satisfactory, and our own experience leads us to conclude that the glass transition temperature, when suitably defined to account for history dependence, should be regarded as an independent and unique characteristic of each liquid.

The data in Table I show that the ratio T_B/T_g varies greatly among liquids, tending to show low values for strongly hydrogen bonded liquids. In view of Trouton's rule for entropy changes on vaporization, and of the Gibbs-Dimarzio concept that T_g reflects the underlying thermodynamic fixed point T_0 (or T_b) at which the entropy associated with liquidlike degrees of freedom vanishes,²³ the temperature interval $T_B - T_g$ (more correctly, $T_B - T_0$) can be regarded as the temperature interval over which a particular degree of excitation (entropy generation) of the liquidlike degrees of freedom occurs. The ratio T_B/T_g represents this interval after scaling for T_g differences and should provide qualitative indications of how rapidly a given liquid is excited through its liquid range. Some inverse correlation of $T_B/T_g \approx 0.8T_b/T_0$ with the heat capacity change at T_g might be expected in this case, since

$$S_c(T) = \int_{T_0}^T \frac{\Delta C_p(T)}{T} dT \quad (2)$$

which gives

$$S_c(T_b) = \Delta C_p \ln (T_B/T_0) \quad (3)$$

if ΔC_p is assumed constant, or

$$S_c(T_B) = \Delta C_p(T_0)(T_b - T_0)/T_b T_0 \quad (4)$$

if ΔC_p is approximated as $\Delta C_p = \text{constant}/T$, which is a more accurate one parameter representation of the observed ΔC_p behavior.

Unfortunately there are inadequate data available for substances of different T_b/T_g but similar molecular type (hence validly comparable ΔC_p values) to test the above expectation quantitatively. However, it was observed in the present studies that the change in differential emf at T_g , which must reflect approximately the quantity $\Delta C_p/\text{unit volume}$, was unusually small for the hydrocarbons 2-methylbutane and methylcyclohexane, both of which have exceptionally large T_B/T_g ratios. In the substituted 4 carbon molecule series, furthermore, a systematic increase in Δemf with decreasing T_b/T_g was observed at constant heating rate. Ethylene glycol- H_2O solutions, on the other hand, were notable in this study for the large Δemf at T_g . Both components have small T_b/T_g values.

Large Δemf 's seem to be characteristic of hydrogen bonded systems. Glycerol, which has the same concentration of OH groups as ethylene glycol, has frequently been used in the laboratory for testing for instrumental detectability of glass transitions because of its pronounced Δemf .

In addition to these general observations, we will consider specifically the following: (i) some observations on the influence of chemical constitution on the value of T_g , (ii) comparison of crystal and liquid glass transitions for cyclohexanol, (iii) the composition dependence of T_g ,

and (iv) some apparent discrepancies between T_g 's for nonvitrifying liquids obtained by extrapolation of binary solution data and those obtained by direct observations on vapor-deposited vitreous phases of the pure substance.

Chemical Constitution and T_g . Among small molecule saturated hydrocarbons, the primary factor determining the T_g value is clearly molecular size. There is an approximately constant increment of 10 °C in T_g per added "bead" (i.e., mobile unit) for small molecules, leveling off at large molecular weights in the manner explained by the theory of Gibbs and Dimarzio.²³

If instead of adding methylene groups to a basic hydrocarbon we add polarizable atoms, e.g., chloride or bromide, then pronounced increases in T_g are produced. Substituting a bromo group for the side methyl group in 2-methylbutane raises T_g by 28 °C. A similar substitution made on a phenyl base yields a similar increase (compare bromobenzene with toluene, $\Delta T_g = 23$ °C). The importance of the van der Waals interactions associated with such polarizable atoms is even more clearly seen in the halomethane series where the addition of each chloride increases T_g by ~15 °C, and two added chlorides prove as effective in raising the T_g of methane as seven added methyl groups. Independent evidence for the importance of van der Waals interactions has been given by Lesikar.¹⁰

The van der Waals interactions are evidently more important to T_g than the static dipole-dipole interaction since methylene dichloride has the largest dipole moment but not the largest T_g in the halomethane series. The substantially increased mass of SnCl_4 over that of CCl_4 has not caused much change in T_g although the extrapolation is not very reliable in this case.

Somewhat smaller increases in T_g accompany introduction of double bonds. Between 2-methylbutane and 2-methylbutene there is a 4 °C increase, while between methylcyclohexane and 4-methylcyclohexene the difference is 7 °C. It is not clear from our data whether this is to be attributed to decreased flexibility of the hydrocarbon molecule, as has been suggested²³ or to the increased electron density of the double bond and the associated increase in intermolecular attractions. By adding two additional double bonds and a resonance condition to methylcyclohexene, we obtain the aromatic molecule toluene, and a concomitant increase in T_g of 21 °C. This is more than twice the first double bond increment, the difference being attributable to the increase in interaction between the π cloud electrons of adjacent molecules.

The effect of side chain lengths on the T_g of aromatic molecules is such as to produce a minimum in T_g at ethylbenzene, presumably because the tendency to higher T_g with increasing molecular weight is initially offset by the effect of withdrawal of electron density from the π cloud of the phenyl group.

The major effects of H bonding are obvious in the large T_g increases associated with the introduction of alcohol groups and amine groups, e.g., compare methanol with 2-methylbutane, cyclohexanol with methylcyclohexane, or benzyl alcohol and aniline with toluene (Figure 2). Hydrogen bonding effects are particularly marked when the OH group is associated with an electron-withdrawing aromatic ring (benzyl alcohol, phenol, and aniline).

Aniline is remarkable for the fact that it melts at a temperature only 40% above its (extrapolated) glass temperature and yet cannot be vitrified in the pure state. Recognized glass formers rarely have $T_m < 1.5T_g$. That failure to vitrify in the case of aniline is predicted by the $T_b/T_m < 2$ rule is an indication of the general reliability of this index. In the cases of aniline and phenol T_g reaches

an unprecedented fraction, 0.4, of the boiling point, suggesting that the heat capacities of these liquids may be worth investigating. It should be noted that phenol, which is isoelectronic with aniline and toluene, would not mix with toluene and the data for the estimate of T_g by extrapolation for this substance had to be obtained from solutions with the hydrogen-bonding solvent ethanol.

Glass vs. Glassy Crystal. The case of cyclohexanol deserves additional comment. The extrapolations to pure cyclohexanol from several binary solutions shown in Figure 2 do not yield consistent results. The most ideally behaving solution, methylcyclohexane + cyclohexanol, yields a value of 169 °C, some 7 °C above the range -161 to -164 °C indicated by the other binaries. However, all of these values are well above the temperature 150 °C at which the plastic crystal formed when cyclohexanol freezes undergoes its glasslike transition to an orientationally disordered "glassy crystal".¹⁶ In other instances of configurational arrest of both liquid and plastic crystalline phases of the same substance (a number of which have been studied in detail by Seki, Suga, and co-workers), the two glassy phases have essentially the same T_g . We did not investigate the nature of the crystal formed when the cyclohexanol-rich glasses recrystallized.

Composition Dependence of T_g and Nonideal Mixing. Most of the systems we have studied here, and many described by Lesikar⁷⁻¹⁰ and others,²⁴ have shown simple linear variations of T_g with composition (expressed in mole fractions), implying some simple form of mixing rules for T_g . Intuitively, one expects T_g to scale with the total system interaction energy, which will vary linearly with composition if the components mix ideally. Excess heats of mixing among organic liquids are generally rather small, and the approximate linearity of the plots of Figures 1 and 2 can be understood broadly in these terms.

A more formal approach can be taken by treating the glass transition as a kinetically retarded Ehrenfest second-order transition, and deriving a composition dependence for T_g complementary to the now well-known Ehrenfest-like relations for the pressure dependence²⁵⁻²⁷ (of which only the first is found fairly accurate in practice²⁷ where if $\Delta S = 0$, $S_{\text{ex}} = \text{constant}$, or $\Delta H = 0$, $H_{\text{ex}} = \text{constant}$, then

$$dT_g/dP = V_g T_g \frac{\Delta\alpha}{\Delta C_p} \quad (5)$$

and if $\Delta V = 0$, $V_{\text{ex}} = \text{constant}$

$$dT_g/dP = \Delta K_T / \Delta\alpha \quad (6)$$

dT_g/dN_i relations were derived some time ago by Moynihan and Angell²⁸ and are quoted in ref 12. We give here an alternative derivation of the composition dependences because it will help illustrate some of the difficulties encountered in applying thermodynamics to glassy state phenomenology.

Consider a thermodynamic cycle in which the enthalpy changes in response to changes in temperature and mole fraction of component 2, one half of the cycle being in the supercooled liquid and one half in the glass. If we assume the excess enthalpy per mole is constant at T_g , then in the equilibrium cycle, $\sum \Delta H = 0$, the only changes in enthalpy are the following, corresponding to stages I-IV in Figure 3:

$$\begin{aligned} \text{I} \quad \Delta H_{\text{I}} &= (\partial H / \partial T)_{X,1} \Delta T_g = C_{p,1} \Delta T_g \\ \text{II} \quad \Delta H_{\text{II}} &= (\partial H / \partial X)_{T,1} \Delta X \\ \text{III} \quad \Delta H_{\text{III}} &= -(\partial H / \partial T)_{X,g} \Delta T_g = -C_{p,g} \Delta T_g \\ \text{IV} \quad \Delta H_{\text{IV}} &= -(\partial H / \partial X)_{T,g} \Delta X \end{aligned}$$

TABLE I: Transition Temperatures for Molecular Liquids¹

substance	formula	T_B/K	T_m/K	T_g/K	T_B/T_m	T_B/T_g	T_m/T_g	solvent, approx glass-forming (gf) range, other comments
One Center Molecules								
carbon tetrachloride	CCl_4	349.8	250.2	129* 130.6 ^a	1.40	2.72	1.95	ethyl benzene ($PhCH_2CH_3$) to 60%
chloroform	$CHCl_3$	334	209.5	114* 105.9 ^b	1.60	2.93	1.84	$Ph-CH_2CH_3$ to 60%
methylene chloride	CH_2Cl_2	313.1	176.3	99* 103.1 ^b	1.78	3.16	1.78	$PhCH_2CH_3$ to 80%
methyl chloride	CH_3Cl							
acetonitrile	CH_3CN	335	232	93*	1.53	3.82	2.49	unreliable extrapn
methanol	CH_3OH	337.6	175.2	103 102.7 ^c	1.93	3.28	1.79	
stannic chloride	$SnCl_4$	387.1	240	130*	1.61	2.98	1.85	$PhCH_2CH_3$ to 50%, unreliable extrapn
water	H_2O	373	273	136* 136 ⁱ 139 ^f	1.37			ethylene glycol to 80%; large Δemf all solutions vapor deposit
Paraffins								
2-methylbutane	$CH_3CH(CH_2)CH_2CH_3$	306.0	113.3	69* 68.2 ^f	2.70	4.43	1.64	gf pure, small Δemf at T_g
2,2-dimethylpropane	$CH_3C(CH_3)_2CH_3$	282.6	256.5	?	1.10			
2-methylpentane	$CH_3CH(CH_3)(CH_2)_2CH_3$	333.4	119.5	79.5 ^g	2.79	4.19	1.50	gf pure
3-methylhexane	$CH_3CH_2CH(CH_3)(CH_2)_2CH_3$	365	153.6	88 ^g	2.38	4.15	1.75	gf pure
Modified 4 Carbon Chain Molecules								
2-methylbutane	$CH_3CH(CH_2)CH_2CH_3$	306.0	113.3	69*	2.70	4.43	1.64	gf pure, small Δemf at T_g
2-methyl-2-butene	$CH_3C=C(CH_2)CH_3$	311.4	149	73*	2.09	4.27	2.04	gf pure
2-bromobutane	$CH_3CHCH(Br)CH_3$	364.3	161.1	97	2.26	3.76	1.66	med Δemf , ΔC_p at T_g
chlorobenzene	C_6H_5Cl	405.0	228	128* 126.3 ^e	1.78	3.16	1.78	$PhCH_2CH_3$ to 60%
bromobenzene	C_6H_5Br	428	242.4	138* 135.2* ^e	1.76	3.1	1.76	$PhCH_2CH_3$ to 60%
nitrobenzene	$C_6H_5NO_2$	374.3	244.6	161* ^e	1.53	2.32	1.52	
aniline	$C_6H_5NH_2$	457.4	266.8	192* 188.9* ^e	1.71	2.38	1.39	toluene to 80%
phenol	C_6H_5OH	455	314	198* 206* ^e	1.45	2.30	1.59	ethanol to 60%
benzaldehyde	C_6H_5CHO	452.5	247.0	146.5 149.0 ^b	1.83	3.09	1.68	gf pure
benzyl alcohol	$C_6H_5CH_2OH$	478.2	257.7	171 171.9 ^e	1.85	2.79	1.51	gf pure, large Δemf
anisole	$C_6H_5OCH_3$	428	235.7	122*	1.82	3.51	1.93	ether to 30% unreliable extrapn
Alcohols and Poly Alcohols								
methanol	CH_3OH	337.6	175.2	103 102.6 ^c 110 ^h	1.93	3.28	1.79	large Δemf at T_g
ethanol	CH_3CH_2OH	351.5	155.7	96 97.2 ^c 100 ^h	2.26	3.78	1.67	T_g is for glassy crystal (see ref 15, 17)
1-propanol	$CH_3CH_2CH_2OH$	370.1	146.6	99.9 ^c 98 ^d 109 ^h	2.52	3.72	1.48	
1-butanol	$CH_3(CH_2)_3OH$	390.3	183.6	111.5 ^a 118 ^h	2.13	3.51	1.66	
trifluoroethanol				144.2 ^e 157				

TABLE I: (Continued)

substance	formula	T_B/K	T_m/K	T_g/K	T_B/T_m	T_B/T_g	T_m/T_g	solvent, approx glass-forming range, other comments
ethylene glycol	HOCH ₂ CH ₂ OH	470.2	255.6	154.2 ^e 155 ^c 185	1.84	2.99	1.63	not easily gf in pure state, large Δ emfs
glycerol	C ₃ H ₅ (OH) ₃	563	291.2	190.9 ^e 189.5 ⁱ	1.94	2.98	1.54	large Δ emfs
Cyclohexane Derivatives								
methylcyclohexane	C ₆ H ₁₂ CH ₃	373.3	146.6	87 85 ^a	2.55	4.29	1.68	small Δ emf
ethylcyclohexane	C ₆ H ₁₂ CH ₂ CH ₃	404.9	141.3	98 ^d	2.87	4.13	1.44	
isopropylcyclohexane	C ₆ H ₁₂ (CHCH ₃) ₂	427.6	183.3	108 ^d	2.33	3.96	1.70	
<i>n</i> -butylcyclohexane	C ₆ H ₁₂ (CH ₂) ₃ CH ₃	454.0	198.4	119 ^d	2.29	3.82	1.67	
4-methylcyclohexene		375.7	157.6	94	2.38	4.00	1.68	
cyclohexanol (a) liquid	C ₆ H ₁₂ OH	434.5	297	161	1.46	2.67	1.82	
(b) plastic crystal	C ₆ H ₁₂ OH		(T_{tr} 265)	150			(T_{tr}/T_g) 1.77	
Benzene Derivatives								
benzene	Ph	353.099	278.51	131*	1.27	2.70	2.13	PhCH ₂ CH ₃ to 40%, unreliable extrapn
toluene	PhCH ₃	383	178	115 117.2 ^a 113 ^d 113	2.15	3.33	1.55	
ethylbenzene	PhCH ₂ CH ₃	409.15	179.1	111 ^d 115.7 ^e 122 ^d	2.28	3.62	1.58	
<i>n</i> -propylbenzene	PhCH ₂ CH ₂ CH ₂	432.3	173.6	125.5 ^e 127.5	2.49	3.54	1.42	
<i>n</i> -butylbenzene	PhCH ₂ CH ₂ CH ₂ CH ₃	456.3	191.8	125 ^{d e} 129.6 ^e	2.38	3.58	1.50	
<i>tert</i> -butylbenzene	PhC(CH ₃) ₃	442.1	214.9	140 1.42 ^d	2.06	3.16	1.54	
<i>n</i> -pentylbenzene	Ph(CH ₂) ₄ CH ₃	478.5	198.1	128 ^d 135.7 ^e	2.42	3.53	1.46	
<i>n</i> -hexylbenzene	Ph(CH ₂) ₅ CH ₃	538		137 ^d 140.4 ^e		3.83		
Other Common Solvents								
acetaldehyde	CH ₃ CHO	294	149.5	82*	1.97	3.59	1.82	unreliable extrapn
acetonitrile	CH ₃ CN	355	232	~93*	1.53	3.82	2.49	unreliable extrapn
ether	C ₂ H ₅ OC ₂ H ₅	307.6	156.7	87 92.5 ^a	1.96	3.56	1.80	
acetone	CH ₃ C(=O)CH ₃	329.5	178	93 100 ^a	1.85	3.54	1.91	
dimethylformamide	(CH ₃) ₂ NCHO	426	212	129	2.01	3.30	1.64	
dimethylacetamide	(CH ₃) ₂ NCOCH ₃	440		146.1 ^a		3.02		
dimethyl sulfoxide (Me ₂ SO)	CH ₃ SOCH ₃	462.1	291.6	150 ^{i,j}	1.58	3.08	1.90	
dimethylsulfone (Me ₂ SO ₂)	CH ₃ SO ₂ CH ₃	511	383	190 ⁱ	1.33	2.69	2.02	
pyridine	C ₅ H ₅ N	388.7	231.3	116 ^k 128* ^b	1.68	3.04	1.80	

^a Reference 7. ^b Reference 8. ^c Reference 9. ^d Reference 19. ^e A. V. Lesikar, private communication, and Ref 32. ^f H. Suga and S. Seki, *J. Non-Cryst. Solids*, **16**, 171 (1974). ^g B. Wunderlich, *J. Phys. Chem.*, **64**, 1052 (1960). ^h J. A. Faucher and J. V. Koleske, *Phys. Chem. Glasses*, **7**, 202 (1966). These measurements were made using a mechanical technique with a pendulum, $f \approx 1$ Hz, suspended from a porous strip containing the liquid. T_g was chosen as the temperature of maximum damping. ⁱ Reference 38. ^j E. J. Sare and C. A. Angell, *J. Solution Chem.*, **2**, 53 (1973). ^k H. J. de Nordwall and Staveley, *Trans. Faraday Soc.*, **52**, 1207 (1956) (devitrification of vapor deposit). ^l Asterisks indicate extrapolated values.

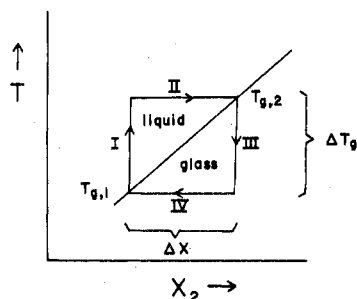


Figure 3.

Collecting terms, and defining $[(\partial H/\partial T)_{T,l} - (\partial H/\partial X)_{T,g}]$ as $\Delta(\partial H/\partial X)_T$, and $[C_{p,l} - C_{p,g}]$ as ΔC_p we obtain

$$\Delta(\partial H/\partial X)_T \Delta X + \Delta C_p \Delta T_g = 0$$

or in the limit of small ΔX

$$dT_g/dX = -\Delta(\partial H/\partial X)_T/\Delta C_p \quad (7)$$

An equivalent relation is derived in a problem in second-order thermodynamics by Landau and Lifschitz.²⁹

If $\Delta V = 0$, meaning $V_{ex} = \text{constant}$, is assumed as the appropriate criterion for glass transitions, then one derives from a similar cycle

$$dT_g/dX = \frac{-\Delta(\partial V/\partial X)_T}{V\Delta\alpha} \quad (8)$$

Finally, if $\Delta S = 0$, meaning $S_{ex} = \text{constant}$, is assumed as the criterion for glass transitions, then an entropy cycle (including self-cancelling ideal mixing entropy terms in stages I and III and the evidence that ΔS_{irr} at the glass transition is negligible¹⁶) yields the result

$$\frac{dT_g}{dX} = \frac{-T_g \Delta(\partial S/\partial X)_T}{\Delta C_p} \quad (9)$$

It is notable that, whereas the assumptions $S_{ex} = \text{constant}$ and $H_{ex} = \text{constant}$ lead to the same expression, eq 5, for dT_g/dP of a glass,²⁷ they do not lead to equivalent relations for the composition dependence. In particular the predictions for regular solutions ($\Delta S_{mix} = 0$, $\Delta H_{mix} >$ or < 0) are different. Goldstein's analysis of dT_g/dP findings²⁷ and others since^{30,31} have in most cases shown consistency with $H_{ex} = \text{constant}$ or $S_{ex} = \text{constant}$ criteria, but not with the $V_{ex} = \text{constant}$ criterion.

Before considering these issues further, however, it is necessary to confront the fact that, unlike the more familiar case of pressure dependence studies, the above cycle cannot be performed, even superficially, in the laboratory; i.e., whereas the pressure acting on a substance in the glassy state can be changed, the chemical "pressure" determined by composition cannot. This is because a composition change can in principle only occur by producing changes in an initial molecular configuration, and these must in practice be accomplished by a microscopic diffusion process, which latter is incompatible with the meaning of "glass" as a state in which configuration changes, via diffusion processes, are frozen out on the time scale of observations. This problem does not arise in the case of second-order transitions between phases in which no loss of mobile equilibrium is involved. The issue of composition changes in "ideal glasses" which are conceptually in equilibrium but infinitely immobile²³ is too close to metaphysical to be considered here.

The only sort of mixing conceptually compatible with the glassy state is "ideal mixing", i.e., a process in which labels are changed but positions remain inviolate, and $(\partial S/\partial X)_g = \partial/\partial X (\Delta S_{mix}[\text{ideal}])$. (If we allow component

volumes to differ then some volume change could occur during ideal mixing, and the phenomenon would be analogous to application of pressure to a glass, i.e., volume change without structure change.)

Unfortunately, therefore, the composition variable cannot be used to compare enthalpy, entropy, and volume theory predictions for the glass transition. To discuss T_g vs. X one is reduced to making some assumption about mixing entropies in liquid and glass states, such as supposing both to be ideal. In the latter case, which is the essential assumption introduced in the recent treatments of Gordon et al.³² and of Couchman and Karacz,³³ predictions can be made on the basis of pure compound properties. It amounts to fixing both $\Delta(\partial H/\partial X)_T$ and ΔC_p by the component ΔC_p and T_g values. Note that $\Delta(\partial H/\partial X)_T$ is in general a finite quantity for ideal solutions. Unless ΔC_p values for each component are the same, nonlinear T_g vs. X relations are predicted for the ideal case.^{32,33} For a number of experimental systems the nonlinear plots have been observed^{10,34} and semiquantitatively accounted for,^{32,34} though there are evidently counterexamples.³⁵ On the basis of the latter observations, Lesikar³⁵ has suggested $S_{ex} = \text{constant}$ may not be a satisfactory glass transition criterion, though thermodynamic mixing data are inadequate to permit proper consideration of the consequences of nonideal mixing.

If indeed $S_{ex} = \text{constant}$ at T_g in solutions, then a simple proportionality relation between $\Delta(\partial H/\partial X)_T$ and ΔC_p (eq 7), or $-T_g \Delta(\partial S/\partial X)_T$ and ΔC_p (eq 9), must exist in order to account for the linear variation in T_g observed so frequently despite very dissimilar components, large dT_g/dX , and unknown ΔC_p vs. X (see Figure 1). Possibly, nonideal mixing contributions tend to compensate the curvature expected to arise from the presence of different ΔC_p values. In general, nonideal mixing effects will act, through $\Delta(\partial H/\partial X)_T$, to increase or decrease dT_g/dX depending on whether the deviations are negative or positive, respectively. At the limit of positive deviations, dT_g/dX should vanish as $\Delta(\partial H/\partial X)_T \rightarrow 0$ and then the single T_g of the homogeneous glass will be replaced by two distinguishable glass transitions if separation into two distinct phases occurs. An observable flattening out of the T_g composition dependence has, in a number of past instances,^{13,36} been interpreted as an indication of imminent phase separation although, until now, a thermodynamic rationalization had not been provided. In the present work the vanishing of dT_g/dX has been seen in the case of ethylbenzene + 2-methylbutane solutions (Figure 2). As noted earlier, these were observed finally to become opalescent due presumably to microscopic phase separation.

At the other extreme, negative deviations from ideal mixing associated with molecular complex formation can cause greater than normal changes in T_g with X , which may then be reversed after the complex stoichiometry has been passed. Some striking examples of T_g maxima have recently been published by Lesikar,⁸ while some weak minima were found earlier by Easteal et al.¹² A deliberate investigation of correlations between dT_g/dX and the thermochemistry of mixing⁸ is clearly needed to clarify some of these questions.

Vapor-Deposited Vs. Liquid-Cooled Glasses. Returning to the values of T_g for halomethanes which yield a rather consistent correlation with van der Waals interaction energies we note rather striking discrepancies between the T_g values obtained from the extrapolations shown in Figure 2 and the results of recent DTA studies by Seki et al.³⁷ on amorphous forms of these substances produced by slow

deposition of the molecules from the vapor. Vapor deposition is commonly regarded as the equivalent of an extremely fast quench and, for a number of liquids such as ethanol and methanol, the glass temperature for the deposit has not differed detectably from that of the fast-quenched liquid. The supposition that the two glassy forms would be of similar natures would seem more reasonable for quasi-spherical molecules such as CCl_4 and CHCl_3 than for other cases.

It is therefore a surprise to find that the T_g estimated from Figure 2 and ref 6 for CCl_4 is almost twice as large as the temperature of the glasslike transition observed by Seki et al. for the vapor deposit.³⁷ A somewhat smaller discrepancy exists for CHCl_3 .

These findings must throw some doubt on the relevance of the glass temperature of vapor-deposited amorphous water,³⁸ to the values expected for a successfully super-cooled liquid water. Paradoxically, in this case binary solution extrapolations, which should be least reliable for the case of water, yield a good agreement with the T_g for the vapor-deposited glass^{13,39,40} (see Table I).

Less serious discrepancies between T_g 's for vapor-deposited glasses and those estimated for liquid-formed glasses by extrapolation of binary solution data and other methods have been reported in the literature and it seems that this matter should now be given a thorough examination.

Concluding Remarks

It is surprising, in view of the insight into the factors determining the magnitude of intermolecular interaction which can be gained from them, that T_g variations in mixtures have not been more extensively explored. Fortunately this position is now changing^{7-12,34} and it is expected that such surveys will be valuable in identifying systems deserving of more detailed thermodynamic and spectroscopic probing.

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