

of the subjects completed at least part of a third set, two completed a fourth set, and one subject completed a fifth set. Thus, in phase I the fewest trials completed by any subject was 1000, and the most was 2500. These discrepancies were caused by differences in starting dates due to individual differences in length of pretraining. The termination date was the same for all, and was due to factors unrelated to the experiment.

The results of phase I showed that initially subjects matched objects at about chance level but improved rapidly. By the end of the first set of 500 trials, four of the subjects were performing at better than 90 percent accuracy, with the remaining subject at better than 80 percent. When the discriminanda were recombined for the second set (beginning with trial 501), the accuracy of two subjects initially decreased slightly, while the other three performed at least as well as before. But from the middle of the second set, this high level (90 percent or better) was maintained by all subjects even when recombinations were introduced, for example, trials 1001 to 1020, and 1501 to 1520.

During the course of the experiment, subjects' response method also evolved: whereas at the beginning of phase I subjects usually felt both objects before choosing, with further training they responded immediately if the matching object was touched first.

Clearly, in phase I subjects were operationally matching to sample across sensory modalities. But the question remained, was their successful performance based on the perception of the similarity between the visible object and its mate (the concept of equivalence of stimuli), or were they performing a rapidly learned conditional response across modalities.

Phase II was designed to answer this critical question. Subjects were presented once with each of 40 unique combinations, composed of discriminanda not used previously, not repeated here, and with which subjects had had no experience. Ten of the unique trials were presented each day for a period of 4 days.

If the high level of accuracy in phase I was due to specific training with a limited number of objects, then performance on phase II would be chance. But if subjects had grasped the essential nature of the problem, "If A, then another A," their matching scores on

the 40 unique trials with novel discriminanda should be significantly better than chance.

The results of phase II clearly support the latter alternative, since the three subjects performed with a degree of accuracy significantly above chance (33, 31, 29 correct choices out of 40; $\chi^2 = 18.55$, d.f. = 2, $P < .01$). Thus, we submit that this experiment demonstrates the presence in apes of a meta-modal concept of stimulus equivalence which is based on a mediation process independent of verbal language.

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References and Notes

1. G. Ettliger, in *Brain Mechanisms Underlying Speech and Language*, F. L. Darley and C. H. Millikan, Eds. (Grune & Stratton, New York, 1967), pp. 53-60; N. Geschwind, *Brain* **88**, 237-294 (1965); J. Lancaster, in *Primates, Studies in Adaptation and Variability*, P. C. Jay, Ed. (Holt, Rinehart & Winston, 1968), pp. 439-457.
2. P. Blakeslee and R. Gunter, *Behaviour* **26**, 76-90 (1966); D. Burton and G. Ettliger, *Nature* **186**, 1071 (1960); G. Ettliger, *Behaviour* **16**, 56 (1960); L. Rothblat and W. Wilson, *J. Comp. Physiol. Psychol.* **66**, 549 (1968); J. Wegener, *ibid.* **59**, 450 (1965); W. Wilson, *Neuropsychologia* **3**, 363 (1965); W. Wilson and O. C. Shaffer, *Nature* **197**, 107 (1963).
3. Of the other two, one chimpanzee died in experimental surgery and one orang-utan was transferred to another facility.
4. Details of pretraining are available from us on request.
5. Supported by NIH grant FR-00165.

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Vitreous Water: Identification and Characterization

Yannas (1) has stated that he had found only one previous detailed article on the possible formation of vitreous water. In deference to the work which has been done on this subject in recent years, we feel it is necessary to correct the impression left by this statement.

There have in fact been quite a number of attempts (2-9) to prepare and characterize vitreous water, and the success to be accorded these depends to some extent on what one chooses to define as a vitreous substance. If we adopt the definition suggested recently by a National Research Council Materials Advisory Board Ad Hoc Committee (10) that a glass, or vitreous substance, is a solid giving a typical amorphous-phase x-ray pattern

and capable of exhibiting the glass transition (10), then the vapor-deposited amorphous ices studied by x-ray diffraction (2, 6, 7) or by electron diffraction (5) must be judged to have been inadequately characterized. If we accept that careful deposition from the vapor phase produces amorphous deposits that satisfy the first criterion, then by thermal studies, several of which have been performed (3, 4), one can in principle prove the existence of a vitreous form of water by detecting the change in heat capacity which occurs at the glass transition. However, until 1965, no such glass transition had been detected and hence no vitreous ice identified completely.

The first clear demonstration that an actual vitreous ice satisfying both criteria could be formed was presented by McMillan and Los (8), who carefully deposited water out of the vapor phase onto a copper surface held at liquid-nitrogen temperature. Differential thermal analysis in situ of the samples obtained revealed a characteristic glass transition at 139°K. Although the findings of McMillan and Los were later contested by Ghormley (9), who failed to find any transition in simple calorimetric studies of amorphous deposits, we are well satisfied, on the basis of our own experience in characterizing kinetically unstable aqueous glasses by differential thermal analysis, that McMillan and Los observed a true glass transition. There is no doubt that the glass transition temperature they reported is that expected from the extrapolation of plots of the glass transition temperature as a function of composition for binary molecular solutions such as H₂O-H₂O₂ (11), H₂O-N₂H₄ (12), and H₂O-dimethylsulfoxide (13), electrolyte solutions such as LiCl-H₂O (14) and Ca(NO₃)₂·H₂O (15), and numerous other electrolyte solutions (16, 17). The findings of McMillan and Los are also substantiated by what is no doubt the most sophisticated piece of research yet performed on vitreous water, the adiabatic calorimetry studies performed by Sugisaki *et al.* (18) on in situ vapor-deposited material. These workers measured the actual increase in heat capacity (C_p) of the glass as it passed from the vitreous to the supercooled liquid state and confirmed the glass transition temperature reported by McMillan and Los. They also noted that conditions of deposition were critical in determining whether the deposit

would be partly microcrystalline or not.

These successful preparations have all taken the vapor-phase route to the vitreous state. Although it seems that this route normally produces the same material [as judged by the T_g , and ΔC_p at the T_g , in the case of ethanol (4) and methanol (19)] as that produced by quenching the liquid, it is a striking feature of vitreous ice that the heat capacity of the supercooled water above the glass transition is only six-tenths that of water at 0°C (18) (the heat capacity of which increases with decreasing temperature at the lowest temperatures studied). Indeed it can be shown (17) that, were water to maintain its observed heat capacity during extended supercooling, it would have to pass through the glass transition at a temperature above about 160°K in order that conflict with the second and third laws of thermodynamics be avoided. Also, according to a fit of the existing viscosity data to the normally reliable Vogel-Tammann-Fulcher equation, the glass transition for water must fall above 150°K (20), and Miller (21), using the general rule $\eta = 10^{13}$ poise at the glass transition, suggests T_g would occur at 162°K. From these results, some structural distinction between the now-characterized vapor-deposited vitreous water and the material which might be anticipated from a successful supercooling of liquid water seems inescapable. Indeed Dowell and Rinfret (7) noted that the radial distribution function for their amorphous ice was distinctly different from that of liquid water. At this point the discussion of possible (metastable) equilibrium paths between such structures is probably unwarranted [for example, the behavior of water below its homogeneous nucleation temperature (22) would be involved].

On the other hand, the vitreous water which would appear to be the natural end product of the removal of the second component from the binary solutions referred to above [see also Yannas's plot for glycerol-water solutions (1)], coincides in glass transition temperature and presumably structure with that of the vapor-deposited glass. It has been claimed (14, 17) that this form of water separates near the glass transition temperature from certain binary solutions rich in water, under circumstances similar to the subliquidus phase separation characteristic of other glass-forming binary

solutions involving highly structured substances as one component, for example, $\text{BeF}_2 + \text{LiF}$ (23), $\text{SiO}_2 + \text{Na}_2\text{O}$, and $\text{B}_2\text{O}_3 +$ oxides of groups I a and II a (24). If this is the case, then vitreous water can indeed be prepared by both vapor-phase and liquid-phase routes, but the structural relation of the glass to ordinary bulk water remains obscure.

With respect to Yannas's suggestion that a search be conducted for a solute that in small amounts would suppress the crystallization of water and enable it to be vitrified, such a solute may have already been found. One of the surprising properties of water condensed from unsaturated water vapor in very small capillaries (~ 1 to $10 \mu\text{m}$ in diameter) and now becoming known variously as anomalous water (25), polywater (26), and structurally modified water (27), is that, depending on the relative quantities of the two forms of water present in the sample (28, 29), in (presumed) mixtures with ordinary water the "anomalous water" phase separates at various temperatures below 0°C. Ignoring for the moment the parallel between this behavior and that mentioned earlier for moderately concentrated aqueous solutions (for example, 3 mole percent AlCl_3 in water), we note that it is ordinary liquid water contaminated with "anomalous water" which separates out of the solution. Neither of these aqueous phases appears to crystallize at the temperatures of phase separation or below, down to -90°C (29). It is not clear whether the vitrification temperature for the water-rich phase has been established (the "anomalous water"-rich phase evidently vitrifies near -40°C). In view of the foregoing discussion, and the widespread interest, particularly in biological circles (13), in the circumvention of the crystallization process in dilute aqueous systems, this determination of T_g may be deemed a pressing experimental problem.

Note added in proof: Very recently density measurements for an amorphous ice, prepared in a manner which should have yielded the vitreous water discussed in the present paper, were reported (30). Although the density they cite, 2.32 g cm^{-3} , is at the limit of credibility, a larger density than that of cubic or hexagonal ice is in agreement with expectations from extrapolations of densities of low-temperature solu-

tions and from the explosions of glass capillaries, which accompany the crystallization of vitreous ice when confined in vitreous solution matrixes (31).

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References and Notes

1. I. Yannas, *Science* **160**, 298 (1968).
2. E. F. Burton and W. F. Oliver, *Proc. Roy. Soc. London Ser. A. Math. Phys. Sci.* **153**, 166 (1935).
3. L. Staronka, *Rocz. Chem.* **19**, 201 (1939); H. J. deNordwall and L. A. K. Staveley, *Trans. Faraday Soc.* **52**, 1061 (1956); J. A. Ghormley, *J. Chem. Phys.* **25**, 599 (1956).
4. J. A. Pryde and G. O. Jones, *Nature* **170**, 685 (1952).
5. M. Blackman and N. D. Linsgarten, *Proc. Roy. Soc. London Ser. A. Math. Phys. Sci.* **239**, 93 (1957); *Nature* **178**, 39 (1956).
6. F. V. Shallcross and G. B. Carpenter, *J. Chem. Phys.* **26**, 782 (1957); R. H. Beaumont, H. Chihara, J. A. Morrison, *ibid.* **34**, 1456 (1961).
7. L. G. Dowell and A. P. Rinfret, *Nature* **188**, 1144 (1960).
8. J. A. McMillan and S. C. Los, *ibid.* **206**, 806 (1965).
9. J. A. Ghormley, *J. Chem. Phys.* **48**, 503 (1968).
10. Materials Advisory Board, *Nat. Acad. Sci. Nat. Res. Council. Eng. Publ. MAB-243* (1968), p. 1. This source defines the glass transition as "that phenomenon in which a vitreous phase exhibits with changing temperature a more or less sudden change in the derivative thermodynamic properties, such as heat capacity and expansion coefficient, from crystal-like to liquid-like values. The temperature of the transition is called the glass (transition) temperature and denoted T_g ."
11. J. A. Ghormley, *J. Amer. Chem. Soc.* **79**, 1862 (1957).
12. J. A. McMillan and S. C. Los, *J. Chem. Phys.* **42**, 829 (1965).
13. D. H. Rasmussen and A. P. MacKenzie, *Nature* **220**, 1315 (1968).
14. C. A. Angell and E. J. Sare, *J. Chem. Phys.* **49**, 4713 (1968).
15. ———, R. D. Bressel, *J. Phys. Chem.* **71**, 2759 (1967).
16. G. Vuillard, *Ann. Chim. Paris* [13] **2**, 233 (1957).
17. C. A. Angell and E. J. Sare, *J. Chem. Phys.* **52**, 1058 (1970).
18. M. Sugisaki, H. Suga, S. Seki, *Bull. Chem. Soc. Jap.* **41**, 2591 (1968).
19. ———, *ibid.*, p. 2586.
20. F. Gutmann and L. M. Simmons, *J. Appl. Phys.* **23**, 977 (1952).
21. A. A. Miller, *Science* **163**, 1325 (1969).
22. N. K. Gilra, *Phys. Lett.* **28A**, 51 (1968).
23. W. Vogel and K. Gerth, *Glastech. Ber.* **31**, 15 (1958).
24. R. R. Shaw and D. R. Uhlman, *J. Amer. Ceram. Soc.* **51**, 377 (1968).
25. E. Willis, G. K. Rennie, C. Smart, B. A. Pethica, *Nature* **222**, 160 (1969).
26. E. R. Lippincott, R. R. Stromberg, W. H. Grant, G. L. Cessac, *Science* **164**, 1482 (1969).
27. B. V. Deryagin, V. I. Anisimova, I. G. Ershova, D. S. Lychnikov, Ya. I. Rabinovich, V. Kh. Simonova, N. V. Churaev, *Russ. J. Phys. Chem. Engl. Transl.* **41**, 1282 (1967).
28. B. V. Deryagin, N. V. Churaev, N. N. Fedyaikin, M. V. Talaev, I. G. Ershova, *Izv. Akad. Nauk SSSR* **10**, 2178 (1967); *Bull. Acad. Sci. USSR Div. Chem. Sci. Engl. Transl.* **10**, 2095 (1967).
29. B. V. Deryagin, I. G. Ershova, B. V. Zheleznyi, N. V. Churaev, *Dokl. Akad. Nauk SSSR* **172**, 1121 (1967); *Proc. Acad. Sci. USSR Phys. Chem. Sect. Engl. Transl.* **172**, 129 (1967).
30. A. H. Delsemme and A. Wenger, *Science* **167**, 44 (1970).
31. C. A. Angell and E. J. Sare, in preparation.

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