

On the Temperature Dependence of Cooperative Relaxation Properties in Glass-Forming Liquids—Comment on a Paper by Adam and Gibbs

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the resulting cross section is too small to account for the observed result.

Large disorientation cross sections (in the range 10^{-17} – 10^{-20} cm²) have been observed for ammonia, dimethyl ether, and benzene. In a gas containing the latter molecule, a large, negative pressure shift of the ($F=2$, $M_F=0$) \rightarrow ($F=1$, $M_F=0$) hyperfine transition frequency of the ⁸⁷Rb ground state has been observed and attributed to a partial and transient electron transfer from rubidium to the benzene molecule during the collision.⁵ If such an electron transfer occurs also for the two polar molecules, then the large disorientation cross sections might result from interactions of the electron during association with the buffer-gas molecule rather than from intermolecular spin-rotation coupling.

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On the Temperature Dependence of Cooperative Relaxation Properties in Glass-Forming Liquids—Comment on a Paper by Adam and Gibbs

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AN equation has been derived by Adam and Gibbs¹ for the temperature dependence of the transition probability determining relaxation or flow of the form $W(T) = A \exp(-C/TS_e)$, A being a temperature-insensitive frequency factor, C dimensionally an energy, and S_e the excess configurational entropy of the liquid, a quantity whose changes with T or P are experimentally measurable² and whose magnitude is asserted, in a thermodynamic theory of the glass transition,³ to vanish at a temperature T_2 , lying somewhat below the experimental T_g . They have further shown that this relation leads to an equation similar in form to the WLF equation⁴ and experimentally indistinguishable from it, and that the calorimetrically determined S_e agrees with the value derived from the temperature dependence of relaxation processes. The ratio T_g/T_2 appears to have a nearly universal value of 1.30.

It is the purpose of this comment to point out three further types of experiments for which the Adam-Gibbs equation gives either quantitative or qualitative agreement, which the free-volume theory notably fails to do: these are pressure dependence, volume relaxation below T_g , and plasticity.

O'Reilly⁵ has shown that the pressure coefficient of T_g is approximately equal to $TV\Delta\alpha/\Delta C_P$, but only

about half as great as $\Delta\beta/\Delta\alpha$ (see Ref. 2 or 5 for definitions). Additional evidence that this is an almost general situation was reviewed by the author.² In the author's earlier paper² it was shown that the experimental situation $dT_g/dP = TV\Delta\alpha/\Delta C_P < \Delta\beta/\Delta\alpha$ implies that free volume cannot determine relaxation times, but either configurational entropy or enthalpy could. It seemed then that the approximate universality of ΔC_P as contrasted with the variability of $\Delta C_P/T_g$ implied the WLF equation could not be deduced from an entropy criterion, but could from an enthalpy one. It appears however that, if relaxation times are a function of the product TS_e , the WLF equation can be derived; it is further true that a nearly correct pressure dependence can be deduced: on the assumption of a negligible activation volume (see, however, below) and a constant ΔC_P down to T_2 the following results:

$$dT_g/dP = T_2 V \Delta\alpha / \Delta C_P.$$

The difference between this and O'Reilly's equation applied near T_g is about 30%; it is not clear that the experimental data are precise enough to make the distinction, or for that matter whether quantitative agreement of a greater degree than this should indeed be demanded of the theory.

The Adam-Gibbs formula contains both an explicit dependence on temperature and an implicit one through S_e , the latter reflecting the changing structure of the liquid. It has been pointed out that experimental studies of volume flow in the glass transition region, where the structure can be temporarily frozen in while temperature is changed, permit a separation of a direct from an implicit effect of temperature⁶; a role for both is found; the relative importance of each depends on the particular substance; structure dominates in polyvinyl acetate,⁷ but the two being of about equal importance in borosilicate glass⁸ and zinc chloride.⁸ The ratio of the structural to the direct effect can be shown from the Adam-Gibbs equation to be $\Delta C_P/S_e$, whose universal value is about 3. This agrees well with the measurements on polyvinyl acetate both in shear⁹ and volume.⁷ There are no experimental data on ΔC_P or S_e in either borosilicate glass or zinc chloride. In any event the qualitative correctness of the Adam-Gibbs equation is to be noted, in contrast to the need in free-volume theories to introduce quite *ad hoc* a temperature dependence of free volume below T_g .

The Adam-Gibbs equation can be viewed as a reversion to the idea of viscosity as a thermally activated process,¹⁰ but with the rapidly changing activation energy near T_g explained by the changing structure. Their derivation proceeds through the calculation of the free energy of an activated state, which therefore contains a volume of activation V^* as well as an energy of activation: $W(T)$ is thus more generally written as

$$\frac{A}{\exp[-(C+DP)/TS_e]},$$

with $D = S_0 V^*/R$. The introduction of this term allows for a direct as well as an implicit effect for pressure just as for temperature, again in qualitative agreement with observation.⁶ It remains to be seen whether quantitative agreement can be found among the various experiments, both thermodynamic and kinetic, discussed here.

A third area of qualitative agreement is provided by the apparently greater plausibility of the interpretation of plasticity in glassy polymers in terms of a stress-biased thermally activated process^{11,12} over a free-volume explanation.

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Comment on the Far-Ultraviolet Photolysis of Nitric Oxide

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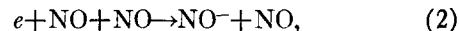
IN a recent paper,¹ Leiga and Taylor report the results of the photolysis of nitric oxide at three wavelengths in the vacuum ultraviolet. They demonstrate that for nitric oxide pressures in the range of 10 to 700 Torr, the quantum yield of nitrogen is approximately 0.4 for irradiation in the 1600-Å spectral region, and approximately 0.5 at 1470 and 1236 Å. Since the primary process at 1236 Å is photoionization of nitric oxide, they conclude from the relative insensitivity of the quantum yield to wavelength that the recombination of NO^+ with an electron leads to an excited nitric oxide molecule similar to ones formed by absorption of

light at 1600 and 1470 Å. These excited molecules may be quenched, radiate, or as a result of a collision, decompose in N and O atoms. Leiga and Taylor suggest that the direct dissociative recombination reaction



does not occur. The purpose of this comment is to show that under the conditions employed by Leiga and Taylor, Reaction (1) cannot be expected to be important, and consequently no conclusions as to whether or not it does ever occur should be drawn from this work. There is an alternate mechanism for photolysis in the photoionization region that is consistent with the observations of Leiga and Taylor, and which incorporates what is known about the behavior of electrons in nitric oxide.

Investigations^{2,3} of the photoionization of nitric oxide with probes and microwave cavity resonance have demonstrated that the dominant electron-loss process is the attachment reaction



when the pressure of nitric oxide is greater than a few torr, and the ion concentration is no greater than 10^{10} ion/cc. From the reported lamp intensity,¹ the absorption coefficient of nitric oxide,⁴ and approximate values for the ion-electron^{2,3} or ion-ion⁵ recombination coefficients for this system it is possible to estimate that the ion concentration in the experiments of Leiga and Taylor did not exceed approximately 5×10^9 ion/cc at a nitric oxide pressure of 10 Torr. This figure is consistent with our own⁵ direct measurements of ion concentration in such photochemical systems. Even if the ion-electron dissociative recombination coefficient is as large^{2,3} as 10^{-6} cc/ion·sec, and if the three-body electron-attachment coefficient³ is 4×10^{-31} cc³/ion²·sec, then electron attachment should be approximately 10 times as fast as ion-electron recombination at a nitric oxide pressure of 10 Torr. For greater nitric oxide pressures the ion concentration may approach 10^{10} cc⁻¹, because the light is absorbed in a shorter distance from the lamp window. At pressures below 100 Torr, however, electron attachment can be expected to be the dominant electron-loss mechanism. For pressures much above 100 Torr, the fact that most of the light is absorbed in the first millimeter from the window may complicate interpretation of the experiments.

The existence of positive and negative gaseous ions offers an obvious mechanism for populating some of the lower excited electronic states of the nitric oxide molecule. At total pressures of 10 Torr and above, ions neutralize each other⁶ by both two- and three-body processes that can lead to electronically excited states of the neutral fragments:

