found which were caused by spontaneous fission were separately photographed and their positions recorded. After neutron irradiation the sample was re-etched for the same length of time, the total number of tracks was counted, and the locations of each of the original 79 tracks were photographed once again. Figure 1 shows one area after etching, before and after neutron irradiation. By point counts on the two groups of 79 photographs the ratio of the final glass area to that exposed during the spontaneous track count was found to be 0.416 ± 0.018.

Using this number along with the track counts, we obtained an age of 2.03 ± 0.30 million years. About 0.04 million years of the indicated standard deviation arose from the fact that the etching time used removed a slightly thinner layer of material than that crossed by a fission fragment. The need for this correction is discussed elsewhere (*7*).

If we now combine our two results, the final age is 2.03 ± 0.28 million years.

The possible sources of wrong ages in the K-Ar and fission-track methods are different. For example, the presence of "inherited" argon in the anorthoclase, which would lead to too high an age value by the K-Ar method, would not affect a fission-track age. On the other hand, fission tracks may be destroyed by heating—an effect which would lead to too low an apparent age. The fact that the two ages agree within the precision of the experimental procedures is therefore strong support for the validity of an age of nearly 2 million years. It would seem to be clear that if the age of the Upper Villafranchian is of the order of 1.75 to 2 million years then we must revise our ideas about the age of the beginning of the Pleistocene. The difference between the mammalian faunae of the Lower and Upper Villafranchian is such that we may reasonably expect that the former may have started no less than 3 million years ago.

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Lewis Acidity of Polar Organic Solvents from Thermodynamic Measurements

Abstract. *A quantitative measure of the Lewis acidity of common organic solvents is given by the equilibrium constant for complex formation between the solvent and a π-donor such as an aromatic hydrocarbon. Lewis acidities are reported for 12 solvents from new distribution and vapor-pressure measurements.*

A Lewis acid is a substance which has a tendency to attract electrons, and one direct measure of Lewis acidity is given by the electron affinity. Measurement of electron affinities of polyatomic molecules is at present essentially impossible and therefore, to characterize the strength of Lewis acids, indirect measurements must be employed.

In view of the potential importance of Lewis acidity in a variety of chemical and biological phenomena we have calculated Lewis acidities of several common polar organic solvents as obtained from our thermodynamic measurements. The use of thermodynamic data to give information on the formation of a complex between Lewis acid and Lewis base has been reviewed by Andrews (*1*) and by Briegleb (*2*), and our studies are in principle very similar to the technique used by Brown and Brady (*3*) to characterize the relative basicities of aromatic hydrocarbons.

We characterize the Lewis acidity of a polar solvent by comparing its volatility in a saturated hydrocarbon with that in an unsaturated hydrocarbon which is our reference Lewis base. We restrict ourselves to solutions which are very dilute in Lewis acid. If a 1:1 complex is formed in solution, the equilibrium constant for complex formation is

$$K_x \equiv x_C / x_1 x_2 \qquad (1)$$

where x_C is the mole fraction of complex in solution and x_1 and x_2 are, respectively, the true (equilibrium) mole fractions of acid and base. We propose to use this equilibrium constant as our measure of Lewis acidity. If $x_1 \ll 1$, then $x_2 \approx 1$, and

$$K_x = \frac{x_C}{x_1{}^o - x_C}, \qquad (2)$$

where $x_1{}^o$ is the apparent mole fraction or the true mole fraction in the absence of complex formation. Let P_1 be the partial pressure of the polar species in the saturated hydrocarbon. If the complex is nonvolatile, then P_1', the partial pressure of the polar species in the unsaturated hydrocarbon, is less than P_1 by an amount of $H_1 x_C$, that is,

$$P_1' = x_1{}^o H_1' = P_1 - H_1 x_C = H_1(x_1{}^o - x_C) \quad (3)$$

$$(H_1'/H_1) = 1 - (x_C/x_1{}^o) \qquad (4)$$

where H_1 is Henry's constant for the polar solvent in the saturated hydrocarbon and H_1' is Henry's constant in the unsaturated hydrocarbon. Combining Eqs. 2 and 4,

$$K_x = \frac{H_1}{H_1'} - 1 \qquad (5)$$

or, since the ratio of Henry's constants is identical to the ratio of the activity

Table 1. Lewis acidity constants for polar organic solvents at 25°C from *n*-hexane–*p*-xylene distribution coefficients.

Polar species	K_x (dimensionless)
Dimethyl carbonate	2.3 ± 0.7
Methoxyacetone	2.3 ± 1.4
2,3-Butanedione	2.5 ± 0.7
Acetone	2.6 ± 0.3
2,4-Pentanedione	3.3 ± 1.0
Nitrobenzene	4.2 ± 1.5
Propionitrile	4.5 ± 1.0
Nitroethane	5.1 ± 1.0
Methoxyacetonitrile	6.8 ± 1.0
Acetonitrile	8.0 ± 3.0
Triethyl phosphate	8.6 ± 2.4
Nitromethane	9.0 ± 1.0

Table 2. Lewis acidity constants at 45°C from vapor pressure measurements of polar organic solvents in toluene and methylcyclohexane solutions.

Polar solvent	K_x
2,3-Butanedione	1.2 ± 0.3
Dimethylcarbonate	1.7 ± .2
Acetone	2.3 ± .2
Methoxyacetone	2.5 ± .2
Nitroethane	5.5 ± .4

coefficients (γ) of the polar solute at infinite dilution in the two hydrocarbons,

$$K_x = \frac{\gamma_1^\infty}{\gamma_1^{\infty\prime}} - 1 \qquad (6)$$

One method for determining the ratio $\gamma_1{}^\infty/\gamma_1{}^{\infty\prime}$ is through the measurement of distribution coefficients. Since saturated and unsaturated hydrocarbons are normally miscible, it is necessary to use a third solvent immiscible with the hydrocarbons, such as water, and to measure the distribution of the polar material between water and each hydrocarbon independently. After extrapolating these distribution coefficients (S) to infinite dilution of the polar species the effect of the water phase may be eliminated, and the desired ratio of activity coefficients in hydrocarbons may be obtained. That is, if

$$S_1{}^\infty = \frac{\gamma_1{}^\infty \text{ in saturated hydrocarbon}}{\gamma_1{}^\infty \text{ in water}} \qquad (7)$$

and

$$S_1{}^{\infty\prime} = \frac{\gamma_1{}^{\infty\prime} \text{ in unsaturated hydrocarbon}}{\gamma_1{}^\infty \text{ in water}}, \qquad (8)$$

then

$$\frac{S_1{}^\infty}{S_1{}^{\infty\prime}} = \frac{\gamma_1{}^\infty \text{ in saturated hydrocarbon}}{\gamma_1{}^{\infty\prime} \text{ in unsaturated hydrocarbon}}, \qquad (9)$$

which is the desired ratio. Lewis acidity constants for twelve polar solvents have been obtained in this way from the ratios of their activity coefficients in *n*-hexane and *p*-xylene (*4*) (Table 1).

Activity coefficients of polar solvents in hydrocarbon solutions have also been obtained from isothermal total vapor pressure measurements at 45°C by the data-reduction method of Barker (*5*). From the activity coefficients at infinite dilution, five Lewis acidity constants were calculated from Eq. 6; the results are given in Table 2. In this case comparison is made between the activity coefficients of the polar organic solvent in toluene and in methylcyclohexane.

The interesting feature of our measurements is that the volatility of a polar organic solvent is always lower when dissolved in an unsaturated hydrocarbon than when dissolved under the same conditions in a saturated hydrocarbon of approximately equal size. Although this has been known for many years, it has not been emphasized that this fact may be ascribed quantitatively to the acidic nature of the polar solvent.

The hypothesis that polar organic solvents form complexes with unsaturated hydrocarbons is also supported by our calorimetric data. We find that the heat of mixing of a polar solvent with an unsaturated hydrocarbon is always more exothermic than the heat of mixing with a saturated hydrocarbon of similar size. For example, at 45°C the heat of mixing of an equimolar mixture of acetone and cyclohexane is 410 cal/mole whereas that for an equimolar mixture of acetone and benzene is only 38 cal/mole (*6*); the lower heat for the benzene solution is due to the exothermic formation of a complex between the aromatic and the polar solvent. Further, since lower temperatures favor complex stability, we would expect that the heat of mixing for solutions of aromatics and polar solvents should decrease with falling temperature. We find that this is indeed the case. In Table 3 we report some calorimetric measurements which show the effect of temperature on the heat of mixing for three solutions of polar solvents and toluene (*7*).

The data of Schäfer (*8*) on mixtures of acetone with straight-chain normal paraffins also show increased exothermicity with decreasing temperature from 20° to −30°C. However, these heats of mixing are an order of magnitude larger than those reported in our work and, as Schäfer indicates, the positive temperature coefficients of the heats of mixing in his experiments are a result of the acetone-paraffin mixtures being near their critical solution temperatures. Schäfer confirms by Raman spectra that as the temperature is lowered acetone-*n*-paraffin systems become more and more incompletely mixed, which causes decreased endothermicity.

Table 3. Effect of temperature (T) on heats of mixing (h^M) in solutions which form complexes.

Mol fraction toluene	h^M (cal/mol) 45°C	h^M (cal/mol) 25°C	$\Delta h^M/\Delta T$ (cal/mol, °C)
	Acetone-toluene		
0.42	58.8	52.2	0.33
	Acetonitrile-toluene		
0.46	121.3	111.9*	0.38
	Nitroethane-toluene		
0.41	86.1	69.9	0.81

* At 20.5°C

For mixtures of nitroethane, acetonitrile, and acetone with aromatics, such as toluene, the critical solution temperatures are much lower. Near room temperature the dispersion of the toluene molecules in solution should be nearly random. It appears probable that complex formation is the cause of reduced endothermicity in mixtures of polar solvents and aromatic hydrocarbons.

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Precambrian Graphitic Compressions of Possible Biologic Origin from Canada

Abstract. *Further occurrences of elliptical graphitic bodies of possible biologic origin have been recovered from Proterozoic black shales of the Labrador Trough, Quebec. The bodies are plausibly organic because of constancy of form, manner of fossilization, and similarities to Michigan forms associated with extractable organic compounds.*

During the summer of 1964, graphitic compressions of possible biologic origin were collected from Proterozoic rocks of the Labrador Trough, Quebec, Canada (*1*). The strata from which the collections were made are