similar experiments at different temperatures suggest that stability of the high density lipoprotein against ether extraction is strongly temperature dependent.

Acknowledgments.—The authors wish to acknowledge helpful discussions with Drs. John W. Gofman and N. K. Freeman.

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COMMUNICATIONS TO THE EDITOR

HEAT OF FORMATION OF NITROGEN TRIFLUORIDE AND THE N-F BOND ENERGY

Sir:

The heats of reaction (1) and (2) have been determined using calorimetric procedures customary in our laboratory, and reasonably concordant values for the heat of formation of NF_3 have been

$$NF_3(g) + {}^3/_2\,H_2(g) = {}^1/_2N_2(g) + 3\,HF(aq, a = 1) \quad (1)$$

$$NF_3(g) + 4NH_3(g) = 3NH_4F(c) + N_2(g) \quad (2)$$

derived from the measurements.

For reaction (1) measured quantities of NF_3 and excess hydrogen over water were ignited in a bomb. No residual NF_3 was found in the products. ΔH^0_{25} for reaction (1) was determined by four experiments for which averages are shown in Table I as calculated on the basis of (a) NF_3 dosage and (b) HF titration. Uncertainties listed are standard deviations of the means.

Reaction (2), carried out by igniting a measured quantity of NF_3 mixed with excess ammonia, with no water, resulted in the formation of a crystalline deposit of NH_4F on the bomb walls. Eight experiments were performed. In Table I are shown values for ΔH^0_{25} calculated from (c) volume of NF_3, (d) weight of NF_3, (e) weight of NH_4F, (f) moles NH_3 determined by analysis of the NH_4F, and the mean of these weighted inversely as the squares of the standard deviations.

TABLE I

RESULTS OF CALORIMETRIC MEASUREMENTS

	Reaction	Basis of calculation	ΔH^0_{25} kj./mole	$\Delta Hf^0_{25}(NF_3)$ kcal./mole
(a)	(1)	NF_3	-845.6 ± 1.7	
(b)	(1)	HF	-871.9 ± 0.6	
	(1)	Mean	-859.0 ± 13.4	
			(= -205.3 ± 3.2 kcal./mole)	-30.7 ± 3.4
(c)	(2)	NF_3 volume	-1084.1 ± 7.1	
(d)	(2)	NF_3 weight	-1081.1 ± 3.3	
(e)	(2)	NH_4F weight	-1087.0 ± 2.5	
(f)	(2)	NH_3 titration	-1098.7 ± 8.4	
	(2)	Mean	-1085.7 ± 4.2	
			(= -259.5 ± 1.0 kcal./mole)	-29.4 ± 2.1
	(1 and 2)	Mean		-29.7 ± 1.8

The heat of formation of NF_3 is calculated from the measurements on reaction (1) using ΔH^0[HF(aq., $a = 1$)] = -78.66 kcal./mole.[1] It is calculated from the measurements on reaction (2) using $\Delta H_f[NH_3(g)] = -11.04$ kcal./mole[1] and $\Delta H_f[NH_4F(c)] = -111.0$ kcal./mole.[2] In the latter calculation, the principal uncertainty is in the heat of formation of NH_4F, which we estimate to be ±0.6 kcal./mole. The weighted average of the results gives $\Delta H_{f25}[NF_3] = -29.7 \pm 1.8$ kcal./mole, and indicates that NF_3 is slightly more stable than was found by Ruff and Wallauer.[3,1]

With E(F–F) = 37.7 ± 1 kcal./mole[4] and E(N≡N) = 225.92 ± 0.1 kcal./mole,[5,1] the mean N–F bond energy E(N–F) in the NF_3 molecule is 66.4 ± 0.8 kcal./mole. Following Reese and Dibeler[6] the dissociation energies of the individual bonds are estimated to be at 25°: $D(NF_2\text{–}F) = 74.0$; D(NF–F) = 62.6 D(N–F) = 62.6 kcal./mole.

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[1] National Bureau of Standards Circular 500, 1952.

[2] T. L. Higgins, "Dissertation Abstracts," **17**, 1231 (1957).

[3] O. Ruff and H. Wallauer, *Z. anorg. allgem. Chem.*, **196**, 421 (1931).

[4] W. H. Evans, T. R. Munson and D. D. Wagman, *J. Research, Nat. Bur. Standards*, **55**, 147 (1955).

[5] L. Brewer and A. W. Searcy, *Ann. Rev. Phys. Chem.*, **7**, 221 (1956).

[6] R. M. Reese and V. H. Dibeler, *J. Chem. Phys.*, **24**, 1175 (1956).

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RECEIVED MAY 27, 1959

A MODEL FOR CELLULAR CATION DISCRIMINATION

Sir:

The preferential uptake of potassium (or rubidium) ions from solutions containing 20–30 times more sodium than potassium by cells is a fundamental fact of biology. However, no cationic discrimination system has been isolated from cells nor does any known chelating agent or ion exchange resin exhibit this degree of preference for potassium over sodium.[1] This note describes results with orthoclase, a silicate feldspar ($KAlSi_3O_8$) which shows properties of cationic selection, similar to that exhibited by living cells.

In the orthoclase lattice there is insufficient free space surrounding the potassium to accommodate a single water molecule in the structure.[2] When orthoclase particles[3] (20–80 mesh) are incubated with Rb^{86} or Na^{22} (added as the chloride) these cations are taken up from solution (esti-

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[1] *Cf.* I. M. Glynn, *Progress in Biophysics*, **8**, 241 (1957).

[2] C. E. Marshall, "Colloid Chemistry of the Silicate Minerals," Academic Press, New York, N. Y., 1949, pp. 23–25.

[3] Silicate minerals, obtained from Wards Natural Science Establishment, N. Y., included orthoclase *var.* Adularia (Brimfield, Mass.), microcline (Ontario), and leucite (Rome); samples were crushed, sieved, and washed with water, ethanol, and ether.

mated by disappearance of radioactivity from medium) presumably as the resultant of an exchange reaction with potassium at certain sites of the external surface. Typical results obtained after 16–24 hours of rotary shaking at 22–25° (at which time Rb uptake is near maximal) are shown in Table I. In the absence of a competing ion orthoclase prefers Rb to Na by a factor of about 4:1. However, Rb uptake is not significantly diminished by the presence of 10 times more Na (or Li) than Rb; similar Rb uptake values are obtained with Na:Rb mixtures at 30:1, but K in equimolar amounts inhibits Rb uptake. Na^{22} uptake cannot be detected in the presence of Rb.

TABLE I

2 g. orthoclase (20–80 mesh) incubated for 24 hr. with 2 ml. medium.

Medium	Concen., uM./ml.	Rb^{86} uptake uM. per 2 g.	Na^{22} uptake uM. per 2 g.
$Rb^{86}Cl$	2	2.06	
$Na^{22}Cl$	2		0.44
$Rb^{86}Cl$	2		
+ NaCl	20	2.00	
$Na^{22}Cl$	2		
+ RbCl	20		<0.1

Another feldspar, Microcline ($KAlSi_3O_8$), 20–80 mesh, exhibits ion selectivity properties similar to orthoclase, but Rb uptake is only about one-fifth that obtained with orthoclase; leucite (20–80 mesh) a feldspathoid, whose structure may be slightly more open than the feldspars,[3] does *not* exhibit a preference for Rb as against Na.

The selective cation uptake by orthoclase emphasizes the importance of steric relationships for "fitting" cations into sites at the surface of this crystal lattice. Highly hydrated cations (Li and Na) may have difficulty in approaching and replacing potassium at these sites relative to K and Rb, which have fewer molecules of associated water.

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RECEIVED MAY 22, 1959

SOLVENT CHARACTERISTICS OF TETRAMETHYLENE SULFONE

Sir:

Since sulfones should have moderately large dielectric constants and very small autoprotolysis constants, we have commenced a study of their characteristics as solvents for acid–base reactions. Tetramethylene sulfone (sulfolane)[1] was chosen because its melting point, reported to be 28.86°,[2] permits cryoscopy as a control upon other measurements. Some solvent characteristics, determined preliminary to a study of the acid–base aspects, are of unusual interest, particularly the very large cryoscopic constant (Table I). Sulfolane should find application in molecular weight determinations.

TABLE I

PHYSICAL PROPERTIES OF SULFOLANE

Dielectric constant (30°)	44
Density (30°)	1.2615 g./cc.
Viscosity (30°)	0.0987 poise
Heat of fusion (cryoscopic, 26°)	2.73 ± 0.03 cal./g.
Molal f.p. depression	66.2 ± 0.6 deg./mole

Plots of freezing point *vs.* concentration exhibit a sharp inflection at 15° indicative of a new solid phase. Below 15°, slopes correspond to a heat of fusion of 10.6 cal./g. Calorimetric measurements are consistent with these values.[3]

Ideal monomer depressions were taken as those given by acetanilide and benzothiophene sulfone. Acetic acid behaves as a monomer and water as a dimer over the concentration range 0.01 to 0.1 molal. Methanol shows some association. Tetraethylammonium iodide is extensively dissociated.

Using a cell with bright platinum electrodes, conductivities of five salts were determined in the concentration range 3×10^{-4} to 5×10^{-3} *M*. The specific conductance of the solvent was less than 2×10^{-8} ohm^{-1} cm.$^{-1}$ and always less than 1% of the conductivities of the solutions. As shown in Fig. 1, plots of Λ *vs.* $\sqrt{c}$ were linear. Tetraphenylarsonium chloride and phenyltrimeth-

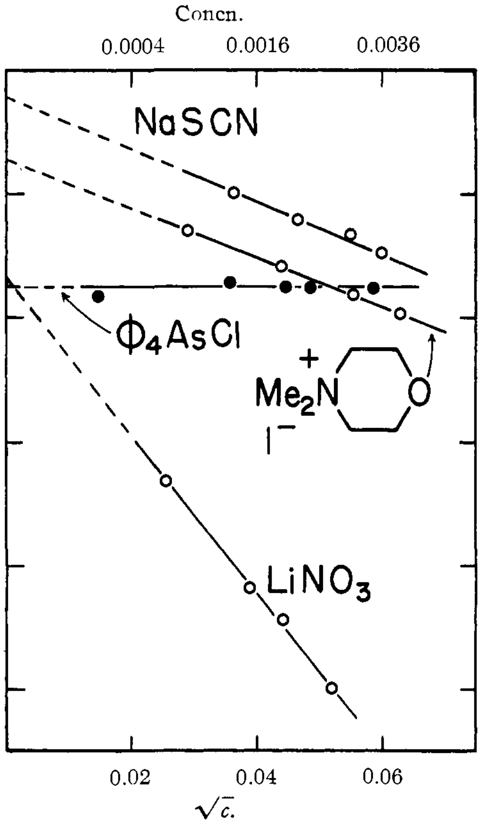

Fig. 1.—Equivalent conductances of several salts in sulfolane, at 30°.

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[1] We are indebted to the Shell Development Company for our sample of sulfolane. It could be purified adequately by vacuum distillation from powdered sodium hydroxide.

[2] A. R. Birch and J. MacAllen, *J. Chem. Soc.*, 2556 (1951).

[3] We are indebted to Mr. R. M. Hammaker and Professor M. Dole for a heat capacity study from −20 to 35° on the adiabatic calorimeter described by A. E. Worthington, P. C. Marx and M. Dole, *Rev. Sci. Instr.*, **26**, 698 (1955).