chlorinated paraffins were somewhat less than those observed for their parent hydrocarbons, primarily because their lower limits were noticeably higher. In comparison, trichloroethylene has a wider range of flammable compositions in air, oxygen, or NO_2^*. The minimum oxidant concentrations for flame propagation were greater in NO_2^* and nitrogen than in oxygen and nitrogen; they tended to increase with the number of substituted chlorine atoms in the particular hydrocarbon-base material.

LITERATURE CITED

(1) Baratov, A.N., Kucher, V.M., *J. Appl. Chem. U.S.S.R.* **38**, 1048 (1965).
(2) Coward, H.F., Jones, G.W., U.S. Bur. Mines, Bull. **503** (1952).
(3) Furno, A.L., Imhof, A.C., Kuchta, J.M., J. CHEM. ENG. DATA **13**, 421 (1968).
(4) "Handbook of Chemistry and Physics," 44th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1963.
(5) Hill, H.W., *Chem. Eng. Progr.* **58**, 46 (1962).
(6) Kaesche-Krischer, B., *Chem. Ing. Tech.* **35**, 856 (1963).
(7) Kaesche-Krischer, B., *Combust. Flame* **6**, 182 (1962).
(8) National Fire Protection Association, NFPA **325M** (1965).
(9) Perlee, H.E., Martindill, G.H., Zabetakis, M.G., U.S. Bur. Mines, Rept. Invest. No. **6748**, 12 (1966).
(10) Perlee, H.E., Scott, G.S., Martindill, G.H., *Ibid.*, No. **6766**, 8 (1966).
(11) Smith, L., *Acta Chem. Scand.* **7**, 65 (1953).
(12) Svehla, R.A., Brokaw, R.S., NASA Tech. Note **D-3327** (March 1966).
(13) Zabetakis, M.G., U.S. Bur. Mines, Bull. **627**, 121 (1965).
(14) Zabetakis, M.G., Scott, G.S., Jones, G.W., *Ind. Eng. Chem.* **43**, 2120 (1951).

RECEIVED for review January 25, 1968. Accepted April 4, 1968. Work done by the Bureau of Mines, U. S. Department of the Interior, under George C. Marshall Space Flight Center Government Order H-76708.

Re-evaluation of the Dissociation Energy of CaF

J. W. HASTIE and J. L. MARGRAVE
Department of Chemistry, Rice University, Houston, Tex. 77001

A disparity in the value for the dissociation energy of CaF is removed by an assessment of mass spectrometric thermodynamic observations of 14 vapor phase reactions involving CaF. D°_{298}(CaF) = 127.5 ± 2.5 kcal. mole^{-1} is indicated as the most reliable value. The data lead to the following values, D°_{298} (SiF) = 135 ± 3, $\Delta H^\circ_{298,\ \mathrm{atoms}}$ (SiF_2) = 288 ± 3 and D°_{298} (GeF) = 120 ± 3 kcal. mole^{-1} which are between 2 and 5 kcal. mole^{-1} larger than previous measurements.

THE FREQUENT USE of CaF_2 as a fluorinating agent in exchange equilibria—e.g., $CaF_2 + Ge \rightleftarrows GeF + CaF$ (*3, 4*)—for obtaining bond dissociation energies [D°(GeF) in this case] requires the establishment of accurate dissociation energies for CaF_2 and CaF. Several values for D°_{298}(CaF) are given in the literature. Both Blue *et al.* (*1*) and Hildenbrand and Murad (*5*) support a value of 125 ± 2 kcal. mole^{-1}, whereas Ryabova and Gurvich (*13*) claim 135 ± 7. Recent re-evaluation (*6*) of the primary standard, D°_{298}(AlF), for the original work of Blue *et al.* (*1*), increases the lower value of D°_{298} CaF to 127.5 ± 1.4 kcal. mole^{-1}. This disparity of about 8 kcal. mole^{-1} between the data of Blue *et al.* and Ryabova and Gurvich also exists for the dissociation energies of SrF and BaF.

A review of reactions involving CaF supports the original data of Blue *et al.* (*1*). Table I lists a number of reactions and their enthalpies which either directly or indirectly involve CaF. These were obtained by the well established Knudsen effusion–mass spectrometric technique.

From Reactions 1 and 2 the original D°_{298}(CaF) value was obtained. The well-established (*6, 7*) value of D°_{298}(AlF) = 160.2 ± 1.2 kcal. mole^{-1}, the heat of formation of CaF_2(s), and free-energy functions for each species were used (*2, 7*) to calculate D°_{298}(CaF) = 127.5 ± 1.4 kcal. mole^{-1} (Reaction 1) and D°_{298}(CaF) = 127.3 ± 2.8 (Reaction 2). These third-law data probably have an extra uncertainty of not more than 1 kcal. mole^{-1}, owing to the approximations, such as estimation of cross sections and multiplier efficiencies for each species. Hence, on the basis of these

Table I. Reactions Relating to Formation of CaF

	Reaction	ΔH°_{298} (Reaction)[a], Kcal. Mole^{-1}	Ref.
(1)	$Ca + AlF = Al + CaF$	34.6 ± 2.7[b]	(*1*)
		32.7 ± 0.2	(*1*)
(2)	$Ca + CaF_2(s) = 2CaF$	120.7 ± 0.8	(*1*)
(3)	$Ca + BF_3 = BF + CaF_2$	12.2 ± 2.5	(*5*)
		15.6 ± 2.5[c]	
(4)	$2Ca + BF_3 = BF + 2CaF$	29.8 ± 2.0	(*5*)
		ΔH°_f(BeF)	
(5)	$Be + BeF_2 = 2BeF$	40.0 ± 1.5	(*6*)
(6)	$Be + CaF = BeF + Ca$	40.0 ± 3	(*6*)
(7)	$Be + AlF = BeF + Al$	40.0 ± 3	(*6*)
		ΔH°_{298}	
(8)	$2Ca + SiF_2 = Si + 2CaF$	34.7 ± 0.9	(*4*)
(9)	$Ca + SiF_2 = CaF_2 + Si$	20.1 ± 1.5	(*15*)
(10)	$Ge + SiF_2 = GeF + SiF$	31.8 ± 0.5	(*15*)
(11)	$Ge + CaF = Ca + GeF$	7.7 ± 0.3	(*15*)
(12)	$Ca + SiF_2 = CaF + SiF$	24.0 ± 0.5	(*15*)
(13)	$2SiF = SiF_2 + Si$	20.3 ± 2[d]	(*4*)
(14)	$ScF_3 + 3Ca = 3CaF + Sc$	63.0 ± 2	(*16*)

[a] All gas phase reactions unless otherwise indicated. [b] Second-law determination. All other data use third law. [c] Value obtained by use in third law calculation of more recently determined spectroscopic constants for CaF_2 (*11, 14*). [d] Recalculated from Ehlert's original equilibrium data, using recently established (*9*), more accurate SiF_2, free-energy functions.

two reactions a selected value of $D^\circ_{298}(CaF) = 127.5 \pm 2.5$ kcal. mole^{-1} appears to be appropriate.

The thermodynamic consistency of this value can be tested by considering the following reactions. For example, Reactions 3 and 4 may be combined to give Reaction 2 and indicate a value of $D^\circ_{298}(CaF) = 126 \pm 3$ kcal. mole^{-1}, in good agreement with the result of Reactions 1 and 2. Reactions 5, 6, and 7 lead to identical enthalpies of formation for BeF, and one can infer that the value of $D^\circ_{298}(CaF)$ equal to 127.5 kcal. mole^{-1} is at least as reliable as, and self-consistent with, the $\Delta H^\circ_{298,\ \mathrm{atoms}}(BeF_2)$ and $D^\circ_{298}(AlF)$ values.

From the $D^\circ_{298}(CaF)$ value of 127.5 kcal. mole^{-1} and the enthalpy of Reaction 8 one obtains $\Delta H^\circ_{298,\ \mathrm{atoms}}(SiF_2) = 288.7 \pm 6$ kcal. mole^{-1}, whereas Reaction 9, which is independent of $D^\circ_{298}(CaF)$, implies $\Delta H^\circ_{298,\ \mathrm{atoms}}(SiF_2) = 288 \pm 2$ kcal. mole^{-1}. Thus, these reactions are also consistent with a value of $D^\circ_{298}(CaF) = 127.5$ kcal. mole^{-1}.

By taking the value of $\Delta H_{298,\ \mathrm{atoms}}$ SiF_2 equal to 288 ± 2, as indicated by Reactions 8 and 9, Reactions 10 to 12 yield the following self-consistent values: $D^\circ_{298}(CaF) = 127.5 \pm 2.5$, $D^\circ_{298}(SiF) = 136 \pm 4$ (Reactions 10 and 12) or 134 ± 2 (Reaction 13), $D^\circ_{298}(GeF) = 119.8 \pm 3$ (Reaction 11), or 126 ± 5 (Reaction 10), all in kilocalories per mole. Hence the CaF dissociation energy is further verified. From Reaction 14 and the known enthalpies of formation, $[\Delta H^\circ_{f,298}(ScF_3) = -383.9$ kcal. mole$^{-1}]$ (*11*) and vaporization (*8, 12*), one calculates $D^\circ_{298}(CaF) = 122 \pm 8$ kcal. mole^{-1}.

Thus the reactions listed in Table I, obtained by a number of different workers, support the value for $D^\circ_{298}(CaF)$ of 127 ± 2.5 kcal. mole^{-1} rather than the alternative value of 135 ± 7 kcal. mole^{-1}. One can similarly show that values of $D^\circ_{298}(SrF)$ and $D^\circ_{298}(BaF)$ lower than those obtained by the spectroscopic method lead to more consistent thermodynamic data. Krasnov and Karaseva (*10*) have also re-evaluated the dissociation energies of the Group IIA subhalides and suggest $D^\circ_{298}(CaF) = 125$ kcal. mole^{-1} as the most reliable value. The higher values were all obtained by spectroscopic observation of reactions in flames where (*1*) the establishment of equilibrium appears less likely than for Knudsen effusion methods, (*2*) reliable absolute temperature measurements are more difficult, and (*3*) self-absorption, abnormal excitation processes, and quantitative accounting for all elements may create large uncertainties in the interpretation of experimental results.

LITERATURE CITED

(1) Blue, G.D., Green, J.W., Bautista, R.G., Margrave, J.L., *J. Phys. Chem.* **67**, 877 (1963).
(2) Brewer, L., Somayajulu, G.R., Brackett, E., Lawrence Radiation Labs., Rept. **UCRL-9840** (September 1961); *Chem. Revs.* **63**, 111 (1963).
(3) Ehlert, T.C., Ph.D. thesis, University of Wisconsin, Madison, Wis., 1963.
(4) Ehlert, T.C., Margrave, J.L., *J. Chem. Phys.* **41**, 1066 (1964).
(5) Hildenbrand, D.L., Murad, E., *Ibid.*, **43**, 1400 (1965).
(6) *Ibid.*, **44**, 1524 (1966).
(7) JANAF Thermochemical Tables, D.R. Stull, ed., Dow Chemical Co., Midland, Mich., 1964; U. S. Government Doc. **PB-168-370**.
(8) Kent, R.A., Zmbov, K., McDonald, J.D., Besenbruch, G., Kana'an, A.S., Margrave, J.L., *J. Inorg. Nucl. Chem.* **28**, 1419 (1966).
(9) Khanna, V., Hauge, R., Curl, R., Margrave, J.L., *J. Chem. Phys.* **47**, 5031 (1967).
(10) Krasnov, K.S., Karaseva, N.V., *Opt. Spectr.* **19**, 14 (1965).
(11) National Bureau of Standards Rept. **9389**, 29 (July 1, 1966).
(12) Rudzitis, E., Argonne National Laboratory, private communication, (1967).
(13) Ryabova, V.G., Gurvich, L.V., *Teplofiz Vysokikh Temperatur, Akad. Nauk SSSR* **2** (5), 834 (1964).
(14) Snelson, A., *J. Phys. Chem.* **70**, 3208 (1966).
(15) Zmbov, K.F., Hastie, J.W., Hauge, R., Margrave, J.L., "Thermodynamics of Vaporization of GeF_2, SnF_2 and PbF_2 and Bond Dissociation Energies of Group IVA Fluorides," Proceedings of Third International Symposium on High Temperature Technology (Asilomar, 1967), to be published.
(16) Zmbov, K.F., Margrave, J.L., *J. Chem. Phys.* **47**, 3122 (1967).

RECEIVED for review January 26, 1968. Accepted April 24, 1968. Work supported by the Robert A. Welch Foundation.

Activity Coefficients and Thermodynamics of Hydrobromic Acid in Methanol-Water Mixtures and Anhydrous Methanol From Electromotive Force Studies

SHARON L. MELTON and EDWARD S. AMIS
Department of Chemistry, University of Arkansas, Fayetteville, Ark. 72701

HARNED, Keston, and Donelson (*13*) determined the standard electromotive force of the cell, Pt; H_2 (1 atm.), HBr (m), AgBr, Ag, and the activity coefficients and certain thermodynamic functions of HBr in aqueous solutions over considerable temperature and concentration ranges. Other investigators (*12, 18, 21, 23*) have also reported standard potential of the silver-silver bromide electrode at various temperatures in water. There is as much as 0.37-mv. difference in the reported values. Hetzer, Robinson, and Bates (*16*) redetermined the standard electromotive force of the same cell in an effort to resolve a discrepancy appearing in the literature. Their results are in satisfactory agreement with the work of Harned, Keston, and Donelson, but did not confirm the later values of Harned and Donelson (*12*) and of Owen and Foering (*21*) which were in agreement. The activity coefficients that Hetzer *et al.* derived from three separate studies agreed well, suggesting that the differences in the standard potential might be attributed to differences in electrodes prepared in different ways. Keston (*18*), Harned *et al.* (*13*), and Hetzer *et al.* (*16*) used the thermal type of the silver–silver bromide electrode. Feakins and Watson (*7*) and Kanning and Campbell (*17*), using this type of electrode, measured the electromotive forces of cell 1 in 10 and 43.12 weight % methanol and pure methanol, respectively, at 25° C.

In this study electromotive forces of the reversible cell

$$H_2\ (1\ \mathrm{atm.})\ |\ HBr\ (m),\ X\%\ CH_3OH,\ Y\%\ H_2O\ |\ AgBr\text{-}Ag \qquad (1)$$