Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THERMODYNAMICS OF VAPORIZATION OF ALKALI FLUORIDES

JING CHAO*
Thermal Research Laboratory, The Dow Chemical Co., Midland, Mich. (U. S. A.)

(Received July 12th, 1969)

ABSTRACT

Mass spectrometric, torsion effusion, and molecular-beam studies have shown that the vapors in equilibrium with condensed phases of alkali-fluorides, LiF, NaF, KF, and CsF, are usually complex, being mixtures of monomeric, dimeric, and in some cases, trimeric molecules. The total pressures of these mixtures at high temperatures have been measured directly by static method and torsion-effusion method without knowing their vapor compositions. However, for measurements over solid phases where the vapor pressures are lower than 1×10^{-4} atm, Knudsen-effusion and transpiration methods were employed.

The purpose of this paper is to present a method which can be used for the evaluation of the partial pressures of the monomeric and polymeric alkali fluoride species from the total vapor pressure data by use of thermodynamic calculations. The calculations of vapor pressures from experimental observations by use of torsion-effusion, Knudsen-effusion, Langmuir free evaporation, transpiration, molecular-beam velocity-selector, and mass spectroscopic methods are briefly reviewed. The basic thermal data employed for the derivation of thermodynamic properties of crystal and gaseous alkali fluorides are shown. The method of derivation is discussed.

Based on the partial pressures and thermodynamic properties of alkali fluorides obtained, the enthalpy changes for the follow reactions: $MF(c) = MF(g)$, $MF(c, g) = M^+(g)+F^-(g)$, $MF(c, g) = M(g)+F(g)$, $M_2F_2(g) = 2MF(g)$, and $Li_3F_3(g) = 3LiF(g)$, are evaluated, where M = Li, Na, K, and Cs. The vapor compositions of alkali fluorides over the condensed phases in the temperature range 700–2000°K are calculated and plotted.

INTRODUCTION

Vapor pressure and heat of vaporization of chemical substances are two important thermal data used in the study of chemical equilibria and design of reactors and distillation equipment in the chemical industry. In order to evaluate the vapor

---

*Present address: Thermodynamics Research Center, Department of Chemistry, Texas A & M University, College Station, Texas 77843, U. S. A.

pressures obtained from experimental measurements, it is necessary to know the composition and the kinds of species present in the vapor phase under the experimental conditions. On vaporization, many chemical substances form polymeric gaseous species in addition to the production of monomers, for example, acetic acid, alkali halides, stannous fluorides, *etc*. In such cases, the method of derivation of the partial pressures for each vapor species from the determined total pressures in not simple and unique.

The purpose of this report is to present a method which can be used to obtain the partial pressures of the component species in a gaseous mixture from total pressure measurements by thermodynamic calculations. As illustration, the partial pressures of the monomeric and polymeric species of the $LiF-Li_2F_2-Li_3F_3$, $NaF-Na_2F_2$, $KF-K_2F_2$, and $CsF-Cs_2F_2$ systems, in equilibrium with the condensed phases, are calculated. Due to the low vapor pressures of inorganic alkali fluorides, Knudsen-effusion, torsion-effusion, transpiration, and molecular-beam velocity-selector methods are usually employed for the determinations. Based on the evaluated partial pressures and the Gibbs energy functions of reactants and products, the enthalpy changes for the following reactions are calculated: $M_2F_2(g) = 2MF(g)$, $MF(c, l) = MF(g)$, $MF(c, g) = M^+(g)+F^-(g)$, and $MF(c, g) = M(g)+F(g)$. The equilibrium vapor compositions of the four alkali fluorides over condensed phases at temperatures 700–2000 K are evaluated and plotted.

EXPERIMENTAL AND RESULTS

Experimental evidence for the presence of polymers

The presence of polymeric species in the vapor phases of alkali fluorides, LiF, NaF, KF and CsF, in equilibrium with the condensed phases, has been a timely interesting problem for over ten years. Eisenstadt *et al.*[6] observed such polymers and determined their abundances in the vapor phase, using a molecular-beam velocity-selector method[15]. Table I indicates the reported results. The presence of polymers was later confirmed by Schoonmaker and Porter[14] who studied these systems by a mass spectrometric method, as listed in Table II, and also by many other investigators[4,5,8,10,12], using effusion and transpiration methods. The principles involved in obtaining the true total pressures from the experimentally determined apparent pressures are different for each method. They are briefly reviewed as follows.

Vapor pressure measurements

The total pressures of the alkali fluoride vapor mixtures at high temperatures can be measured by static methods[1–3] and the torsion-effusion method without knowing their vapor compositions. However, for low vapor pressure measurements, say $P < 1\times10^{-4}$ atm, Knudsen-effusion and transpiration methods are often employed which need information about the vapor compositions from other sources, *e.g.* mass spectroscopy, *etc.*

The torsion-effusion method was developed in 1931 by Mayer and Volmer[53].

TABLE I

ABUNDANCES OF POLYMERS IN MF VAPORS

MF	*T* (°*K*) *at* $P = 1 \times 10^{-2}$ *torr*	*Dimer/monomer*	*Trimer/monomer*
LiF	1127	0.471	0.066
NaF	1170	0.165	
KF	1009	0.098	
RbF	951	0.086	
CsF	863	0.066	

TABLE II

EVIDENCE OF POLYMERS IN MF VAPORS BY MASS SPECTROMETRY

MF	*T* (°*K*)	$I_{M_2F^+}/I_{M^+}$	$I_{M_3F_2^+}/I_{M^+}$
LiF	954	3.30	0.31
NaF	1017	0.80	0.015
KF	1031	0.93	0.013
RbF	888	0.59	0.0055
CsF	764	0.29	0.0022

A typical apparatus has been described by Searcy and Freeman[51]. In this method. the torque F resulting from the effusion of vapor from a cell, through holes of area a_1 and a_2 at distances q_1 and q_2 from the axis of suspension of the cell, is determined from the angle ϕ through which the torque twists the fine wire of torsion constant D by which the cell is suspended. The torque is related to ϕ and to the pressure P_T in the cell by $F = D\phi = (q_1 a_1 + q_2 a_2) f P_T/2$ or $P_T = 2D\phi/f(q_1 a_1 + q_2 a_2)$. The factor f is the ratio of the force resulting from the effusion of vapor through a hole in finite length to the force expected if the hole had an infinitesimal length. The torsion constant D is calculated from the period of oscillation t of the suspension system alone and the period t_w with a weight of known moment of inertia I added, $D = 4\pi^2 I/(t_w^2 - t^2)$.

The Knudsen-effusion method[22] has become one of the classical methods for measuring low vapor pressures at high temperatures. The experimental work is started by the determination of weight loss rates of the sample in a Knudsen cell. This can be done by several methods for example with the aid of a recording thermobalance operating in vacuum. The lower pressure limit of application is about 1×10^{-4} torr. Langmuir[23] used the free evaporation method to measure directly the rate of evaporation from specimens in wire form, heated electrically. The amount evaporated is measured. In both methods the vapor pressure P (atm) is calculated from the formula

$$P = \frac{m}{t \cdot A} \sqrt{\frac{2\pi RT}{M}} = 0.02256 \frac{m}{t \cdot A} \sqrt{\frac{T}{M}}$$

where m(g) is the mass of vapor of molecular weight M which evaporates from an area A(cm^2) in time t (sec). For a gaseous mixture, the value of M is the average molecular weight. The method of Langmuir enables measurements to be made of pressures as low as 1×10^{-7} torr. For the validity of Knudsen's method, it is necessary to assume that no collisions between molecules take place while they pass through the orifice, and the thickness of the orifice is negligibly small. Otherwise, a Clausing correction factor (K) should be applied to the above formula[24,30,34]. This factor is the probability that a molecule having entered one end of a hole of finite length, will escape from the opposite end.

In the transpiration method, a measured volume of inert gas is saturated by passing it through or over the sample substance at a definite temperature. The quantitity of sample vaporized is obtained from the loss in weight of the sample or by removal of the vapor from the gas stream in a weighed absorbing tube. The partial pressures of the components of a system are calculated according to the relation

$$P_i = \frac{m_i}{M + \Sigma m_i} P_a$$

where P_i = partial pressure of the ith component, P_a = total pressure of the system, m_i = moles of ith component in condenser, and M = moles of carrier gas collected[25,26].

Using the molecular-beam velocity-selector method, Miller and Kusch[13,15] have shown that an analysis of the distribution of velocities among molecules effusing from an isothermal enclosure with an ideal aperture can yield values for the relative concentrations of the various polymeric species of a chemical substance present in the vapor space. When several polymeric species are present in the beam, the total distribution is the sum of the separate distributions. If a three-component system is assumed, the concentrations of the molecules within the oven are C_1, $C_2 = C_1 a_2 \sqrt{2}$, and $C_3 = C_1 a_3 \sqrt{3}$. The equilibrium constant for the reaction dimer ⇄ 2 monomer is $K_c = C_1^2/C_2 = C_1/a_2\sqrt{2}$, and that for the reaction trimer ⇄ dimer + monomer is $K_c' = C_2 C_1/C_3 = C_1 a_2 \sqrt{2}/a_3\sqrt{3}$, where a_2 and a_3 are the ratios of the flux of dimers and trimers to the flux of monomers effusing from the oven. The total pressure of the gas in the oven is $P = \sum_n P_n = kTC_1(1 + \Sigma a_n \sqrt{n})$, where P_n are the partial pressures of the constituent species. The vapor pressures of each component may be found separately as $P_1 = P/f$, $P_2 = Pa_2\sqrt{2}/f$, and $P_3 = Pa_3\sqrt{3}/f$, where $f = 1 + a_2\sqrt{2} + a_3\sqrt{3}$.

Schoonmaker and Porter[14] have used a mass spectrometer to analyze vapors in equilibrium with alkali fluoride condensed phases, effusing from a Knudsen cell. Thermochemical data can be calculated from the results of a systematic study of ions produced, appearance potentials, and the temperature dependence of ion current intensities (I). The partial pressures of a monomer and dimer are proportional to $TI_{M^+}/[\sigma(MF)S(M^+)]$ and $TI_{M_2F^+}/[\sigma(M_2F_2)S(M_2F^+)]$, respectively, where σ = the relative partial dissociative ionization cross section and S = the relative electron multiplier efficiency term.

By use of the above calculation methods, the total vapor pressures of the four alkali fluorides are evaluated. The sources of the vapor pressure data used for evaluation are listed in Table III.

TABLE III

VAPOR PRESSURE DATA ON ALKALI FLUORIDES[a]

Experimental method	*LiF*	*NaF*	*KF*	*CsF*
Boiling point	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3
Torsion-effusion	4, 5	4, 9	4	4
Knudsen-effusion	—	10, 11	10	21
Transpiration	8	12	16	—
Molecular-beam velocity-selector	6, 7	6, 13	6	6

[a]Values are reference numbers.

TABLE IV

HEAT CAPACITY AND ENTHALPY DATA[a]

MF(c)	*Low temperature heat capacity*	*High temperature enthalpy*
LiF	33 (19–272°K), 34 (10–111°K)	35 (293–1169°K), 36 (672–1411°K)
NaF	37 (0.05–15°K), 38 (54–296°K)	39 (406–1282°K)
KF	40 (16–323°K)	40 (298–530°K), 41 (291–1187°K)
CsF	Unavailable	42 (298–976°K)

[a]Values are reference numbers, those in parentheses are temperature range of data points.

Calculation of thermodynamic functions

In order to evaluate the vapor pressure data, the thermodynamic functions (*i.e.* heat capacities, entropies, Gibbs energy functions, *etc.*) and heats of vaporization and sublimation of MF(l) and MF(c) to form MF(g) and M_2F_2(g) must be known or estimated. The basic thermal data needed for the calculation of the thermodynamic functions of chemical substances in the crystal and liquid states are heat capacities (Cp^0), entropy (S°_{298}), and temperatures and heats of transition (ΔH_t^c) and melting (ΔH_m^c). The high temperature heat capacities and S^c_{298} can be derived from enthalpy measurements and low temperature heat capacities, respectively, by use of the relationship:

$$Cp^0 = \left(\frac{\partial H^0}{\partial T}\right)_p \text{ and } S^{\circ}_{298} = \int_0^{T^*} \frac{Cp^*}{T} dT + \int_{T^*}^{T_t} \frac{Cp^0}{T} dT + \frac{\Delta H_t^0}{T} + \int_{T_t}^{298} \frac{Cp^0}{T} dT$$

where T^* = the lowest temperature of measurement, Cp^* = estimated heat capacities and T_t = transition temperature (if any). The low and high temperature heat capacities are joined smoothly at 298 °K. Incorporating the two formulas:

$$H_T^\circ - H_{298}^\circ = \int_{298}^{T} Cp^0 dT \text{ and } S_T = \int_0^T \frac{Cp^0}{T} dT$$

with the relationship

$$G^\circ = H^\circ - TS^\circ$$

the Gibbs energy function can be derived as

$$-\frac{G^\circ - H_{298}^\circ}{T} = \int_0^T \frac{Cp^0}{T} dT - \frac{1}{T} \int_{298}^{T} Cp^0 dT = \text{GEF}$$

The low temperature Cp^0 and high temperature enthalpy data used to derive the thermodynamic functions for the alkali fluorides are shown in Table IV. Tables V and VI list the melting data adopted for calculation and the Gibbs functions derived for MF(c, l), respectively.

TABLE V

PHASE TRANSITION DATA[a]

Property	*LiF*	*NaF*	*KF*	*CsF*
T_m (°K)	1121.3 (35)	1269 (43)	1131 (44)	976 (46)
ΔH_m° (kcal/mole)	6.474 (35, 36)	7.97	6.50 (45)	5.19 (47)
ΔS_m° (e.u.)	5.774	6.281	5.747	5.318
$\Delta H_{s,298}^\circ$ (to monomer) (kcal/mole)	66.0	68.1	57.8	47.4
$\Delta H_{s,298}^\circ$ (to dimer) (kcal/mole)	69.6	72.7	65.6	52.4
$\Delta H_{s,298}^\circ$ (to trimer) (kcal/mole)	79.7	—	—	—
T_b (°K)	1990	2060	1790	1504
ΔH_v° (to mixture) (kcal/mole of liq.)	35.08	42.1	33.9	27.6
$\Delta H_{v,298}^\circ$ (to monomer) (kcal/mole)	61.63	61.1	54.4	44.8
$\Delta H_{v,298}^\circ$ (to dimer) (kcal/mole)	60.83	58.8	58.8	47.2
$\Delta H_{v,298}^\circ$ (to trimer) (kcal/mole)	66.62	—	—	—

[a] Values in parentheses are reference numbers.

The thermodynamic functions for the monomeric and polymeric alkali fluoride molecules, in the ideal gaseous state, at atmospheric pressure, are calculated by the statistical method described by Mayer and Mayer[58]. Tables VII and IX give the molecular constants for alkali fluoride monomers and polymers employed for calculation. The Gibbs energy functions obtained are presented in Tables VIII and X.

TABLE VI

GIBBS ENERGY FUNCTIONS

T (°K)	$-\frac{G^\circ - H^\circ_{298}}{T}$ (gibbs/mole)[a]			
	LiF(c, l)	*NaF(c, l)*	*KF(c, l)*	*CsF(c, l)*
298	8.523	12.240	15.905	21.100
400	8.932	12.689	16.371	21.593
600	10.668	14.544	18.285	23.611
800	12.576	16.537	20.340	25.781
1000	14.392	18.405	22.265	27.945
1200	16.460	20.127	24.373	30.723
1400	18.800	22.315	26.816	33.131
1600	20.830	24.521	28.957	35.255
1800	22.623	26.463	30.861	37.153
2000	24.227	28.194	32.576	38.868

[a] One gibbs = 1 defined cal/°K, see ref. 60 for more information.

TABLE VII

MOLECULAR CONSTANTS FOR ALKALI FLUORIDE MONOMERS

	LiF (*ref. 49, 50*)	*NaF* (*ref. 31*)	*KF* (*ref. 31*)	*CsF* (*refs. 32, 27*)
B_e(cm^{-1})	1.3588	0.4369	0.2799	0.1844
x_e(cm^{-1})	0.02030	0.000456	0.00234	0.00111
ω_e(cm^{-1})	914.33	536.1	426.04	353
$\omega_e x_e$(cm^{-1})	8.00	3.83	2.43	1.23
r_e(Å)	1.563	1.926	2.1716	2.345

TABLE VIII

GIBBS ENERGY FUNCTIONS

T (°K)	$-\frac{G^\circ - H^\circ_{298}}{T}$ (gibbs/mole)			
	LiF(g)	*NaF(g)*	*KF(g)*	*CsF(g)*
298	47.840	51.983	54.135	58.102
400	48.139	52.308	54.469	58.441
600	49.373	53.638	55.825	59.812
800	50.700	55.048	57.256	61.254
1000	51.932	56.344	58.569	62.573
1200	53.049	57.510	59.747	63.755
1400	54.061	58.560	60.606	64.816
1600	54.980	59.511	61.764	65.776
1800	55.821	60.379	62.637	66.649
2000	56.596	61.175	63.438	67.450

TABLE IX

ADOPTED MOLECULAR CONSTANTS FOR POLYMERIC ALKALI FLUROIDES ((M_nF_n))[a]

	Li_2F_2	Na_2F_2	K_2F_2	Cs_2F_2	Li_3F_3
Molecular structure[b]	P. Rh.	P. Rh.	P. Rh.	P. Rh.	P. R.
Point group	D_{2h}^c	D_{2h}	D_{2h}	D_{2h}	D_{3h}
Symmetry number	4	4	4	4	6
Bond distance (Å)					
M–F	1.68[d]	2.02[c]	2.20	2.35	1.68
F–F	2.67[d]	2.98[c]	3.11	3.18	2.91
Bond angles (°)					
M–F–M	74.8[d]	85	90	95	120
F–M–F	105.2[d]	95	90	85	120
$I_AI_BI_C(g^3\cdot cm^6)$	3.677×10^{-115}	5.614×10^{-114}	2.240×10^{-113}	3.126×10^{-112}	1.212×10^{-113}
Vibrational frequencies (cm^{-1})[e]					
ν_1	570	420	273	200	280
ν_2	570	400	150	110	430
ν_3	490	350	235	210	640
ν_4	301.5	200	150	120	480
ν_5	571.5	425	255	220	530
ν_6	658.0	500	258	230	755
ν_7	—	—	—	—	245
ν_8	—	—	—	—	140

[a] All values are estimated unless otherwise referenced.

[b] P. Rh. = planar rhombic; P. R. = planar ring. A matrix stabilized linear structure of Li_2F_2 was suggested by Redington[54], and Abramowitz *et al.*[55].

[c] Molecular structure was determined by Buchler *et al.*[28], and Akishin and Rambidi[29].

[d] Determined by Akishin and Rambidi[29].

[e] The vibrational frequencies for Li_2F_2 and Li_3F_3 are obtained from Snelson[56], of which the ν_4, ν_5, ν_6 and ν_1, ν_5, ν_6, ν_7 for Li_2F_2 and Li_3F_3, respectively are observed. The frequencies for K_2F_2 are taken from Berkowitz[57], which are calculated based on ionic model.

TABLE X

GIBBS ENERGY FUNCTIONS

T(°K)	$-\frac{G^\circ - H^\circ_{298}}{T}$ *(gibbs/mole)*				
	$Li_2F_2(g)$	$Na_2F_2(g)$	$K_2F_2(g)$	$Cs_2F_2(g)$	$Li_3F_3(g)$
298	61.788	68.655	76.444	84.179	75.997
400	62.404	69.336	77.188	84.933	76.995
600	65.022	72.161	80.201	87.979	81.214
800	67.880	75.183	83.369	91.171	85.806
1000	70.551	77.975	86.266	94.084	90.094
1200	72.979	80.492	88.860	96.691	93.989
1400	75.179	82.760	91.187	99.027	97.515
1600	77.179	84.814	93.287	101.135	100.721
1800	79.009	86.686	95.196	103.050	103.653
2000	80.691	88.405	96.945	104.803	106.348

The uncertainties in the values of Gibbs energy functions for MF(c, l) are estimated as ±0.2 gibbs/mole where M = Li, Na and K. Due to lack of low temperature Cp data for CsF(c), the value of S°_{298}(CsF, c) is estimated by comparison with other alkali fluorides. The uncertainties in the derived Gibbs energy functions are expected to be ±1.5 kcal/mole. The molecular constants used for the calculation of Gibbs energy functions for MF(g) are consistent and best values. The value ±0.1 kcal/mole is assigned as the uncertainties for these derived Gibbs energy functions. For the polymeric species, the molecular constants are mostly not well established. Therefore the missing data are estimated. The uncertainties of the derived Gibbs energy functions may be as high as ±2 kcal/mole.

Evaluation of vapor pressure data

Based on the total vapor pressures and the Gibbs energy functions (GEF) obtained for the MF–M_2F_2 systems, where M = Li, Na, K and Cs, the partial pressures for MF(g) and M_2F_2(g) are derived by use of the method below. According to the third law, for the reactions: (1) MF(c, l) = MF(g), and (2) 2MF(c, l) = M_2F_2(g), we have

$$\frac{(\Delta H^\circ_{s,298})_1}{T} = -R\ln P_{\mathrm{MF}} + (\mathrm{GEF})_{\mathrm{MF(g)}} - (\mathrm{GEF})_{\mathrm{MF(c)}}$$

$$\frac{(\Delta H^\circ_{s,298})_2}{T} = -R\ln P_{\mathrm{M_2F_2}} + (\mathrm{GEF})_{\mathrm{M_2F_2(g)}} - 2(\mathrm{GEF})_{\mathrm{MF(c)}}$$

$$\frac{(\Delta H^\circ_{v,298})_1}{T} = -R\ln P_{\mathrm{MF}} + (\mathrm{GEF})_{\mathrm{MF(g)}} - (\mathrm{GEF})_{\mathrm{MF(l)}}$$

$$\frac{(\Delta H^\circ_{v,298})_2}{T} = -R\ln P_{\mathrm{M_2F_2}} + (\mathrm{GEF})_{\mathrm{M_2F_2(g)}} - 2(\mathrm{GEF})_{\mathrm{MF(l)}}$$

where the values of P_{MF} and $P_{\mathrm{M_2F_2}}$ are calculated by choosing appropriate values for $\Delta H^\circ_{s,298}$ for Reactions 1 and 2, such that the sum of the calculated partial pressures of MF(g) and $\mathrm{M_2F_2(g)}$ is in reasonable agreement with the total pressures determined experimentally. Basically, there is only one variable involved. The other three may be derived from the following relationships:

$$(1)\ (\Delta H^\circ_{s,T_m})_1 = (\Delta H^\circ_{v,T_m})_1 + \Delta H^\circ_m$$

$$(2)\ (\Delta H^\circ_{s,T_m})_2 = (\Delta H^\circ_{v,T_m})_2 + 2\Delta H^\circ_m$$

$$(3)\ (\Delta H_{d,298}) = 2(\Delta H^\circ_{s,298})_1 - (\Delta H^\circ_{s,298})_2 = 2(\Delta H^\circ_{v,298})_1 - (\Delta H^\circ_{v,298})_2$$

The values of ΔH°_m are available from the calculated thermodynamic functions mentioned previously. The $\Delta H^\circ_{d,298}$ values are obtained from the third law analyses of the dimer dissociation equilibrium data.

The method of trial and error is used in choosing the proper values of $\Delta H^\circ_{s,298}$ and $\Delta H^\circ_{v,298}$ for evaluation. It should be noted that the total pressures adopted for comparison are obtained from a critical evaluation of the reported vapor pressure data. The more recent and reliable data are given more weight.

For the $\mathrm{LiF{-}Li_2F_2{-}Li_3F_3}$ system, the vapor pressures of LiF(g) and $\mathrm{Li_2F_2(g)}$ are obtained by subtraction of the partial pressures of $\mathrm{Li_3F_3(g)}$ from the measured total pressures. The partial pressures of $\mathrm{Li_3F_3(g)}$ are calculated by use of the value $\Delta H^\circ_{s,298} = 79.73$ kcal/mole for the reaction (3), $\mathrm{3LiF(c) = Li_3F_3(g)}$, and the relationship

$$\frac{(\Delta H^\circ_{s,298})_3}{T} = -R\ln P_{\mathrm{Li_3F_3}} + (\mathrm{GEF})_{\mathrm{Li_3F_3(g)}} - 3(\mathrm{GEF})_{\mathrm{LiF(c)}}$$

The adopted $\Delta H^\circ_{s,298}$ value is derived as 73.9 kcal/mole at 1000°K which is consistent with the values $\Delta H^\circ_{s,1000} = 73.9 \pm 3$ and 74.9 ± 1 kcal/mole reported by Buchler and Stauffer[19] and Akishin *et al.*[17], respectively.

Table V gives the values of $\Delta H^\circ_{s,298}$ and $\Delta H^\circ_{v,298}$ for LiF, NaF, KF and CsF crystals and liquids to form monomeric and polymeric gaseous species. Based on these enthalpy values and the derived Gibbs energy functions, the partial pressures of monomers and dimers of the alkali fluorides are evaluated from the measured total pressures. From the partial pressures of monomers and polymers in the vapor phase, the corresponding vapor compositions are calculated. Table XI lists the vapor compositions of $\mathrm{LiF{-}Li_2F_2{-}Li_3F_3}$, and $\mathrm{NaF{-}Na_2F_2}$ systems over the condensed phases in the temperature range 900–2000°K. Those for $\mathrm{KF{-}K_2F_2}$ and $\mathrm{CsF{-}Cs_2F_2}$ systems at temperatures 700–1800°K are shown in Table XII. The compositions of monomers and dimers in the MF vapors are plotted in Figs. 1 and 2, respectively.

In Table V, the boiling point T_b is calculated as the temperature at which the total pressure of the vapor mixture equals one atmosphere. The heat required to vaporize 1 mole of liquid alkali fluoride to form the vapor mixture at T_b is ΔH°_v.

TABLE XI

VAPOR COMPOSITIONS OF LITHIUM AND SODIUM FLUORIDE OVER THE CONDENSED PHASES (%)

T(°K)	*Lithium fluoride*[a]			*Sodium fluoride*[b]	
	Monomer	*Dimer*	*Trimer*	*Monomer*	*Dimer*
900	43.2	54.2	2.6	—	—
1000	39.9	55.6	4.6	66.6	33.4
1100	37.4	55.8	6.8	63.9	36.1
1200	40.6	52.1	7.3	62.0	38.0
1300	45.0	47.9	7.1	61.7	38.3
1400	49.2	44.0	6.8	66.1	33.9
1500	53.3	40.3	6.4	70.0	30.0
1600	57.0	37.1	5.9	73.4	26.6
1700	60.4	34.1	5.5	76.5	23.5
1800	63.6	31.3	5.1	79.1	20.9
1900	66.6	28.8	4.6	81.4	18.6
2000	69.2	26.6	4.2	83.3	16.7

[a] T_m = 1121.3 °K. [b] T_m = 1269 °K.

TABLE XII

VAPOR COMPOSITIONS OF POTASSIUM AND CESIUM FLUORIDES OVER THE CONDENSED PHASES (%)

T(°K)	*Potassium fluoride*[a]		*Cesium fluoride*[b]	
	Monomer	*Dimer*	*Monomer*	*Dimer*
700	—	—	94.1	5.9
800	—	—	90.5	9.5
900	82.4	17.6	86.8	13.2
1000	76.7	23.3	84.2	15.8
1100	71.6	28.4	84.7	15.3
1200	70.8	29.2	85.5	14.5
1300	72.0	28.0	86.4	13.6
1400	73.3	26.7	87.3	12.7
1500	74.7	25.3	88.3	11.7
1600	76.2	23.8	89.2	10.8
1700	77.6	22.4	—	—
1800	79.0	21.0	—	—

[a] T_m = 1131 °K. [b] T_m = 976 °K.

Derived thermodynamic data

The heat of dissociation of Li_2F_2(g) calculated from the partial pressures derived from the adopted total pressures is comparable to the reported values obtained by different experimental methods, as shown in Table XIII. Using the partial pressures evaluated for NaF–Na_2F_2, KF–K_2F_2, and CsF–Cs_2F_2 systems, the enthalpies and entropies of dissociation of the dimeric alkali fluorides are calculated by the second

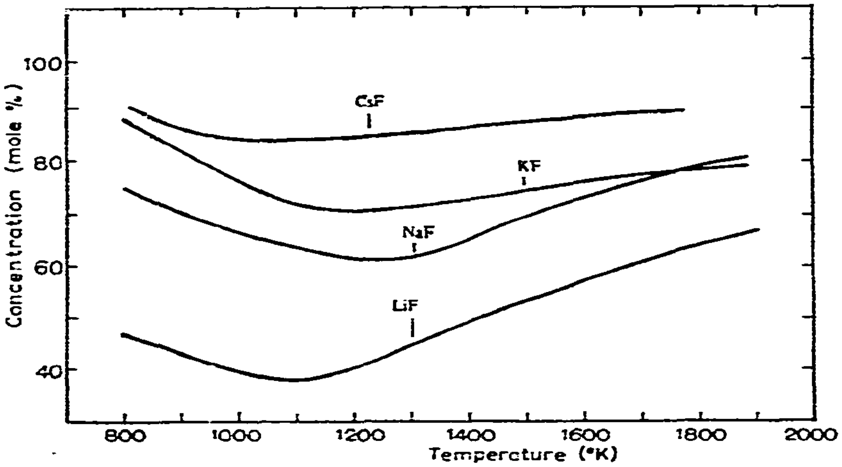

Fig. 1. Concentration of monomers in MF vapors.

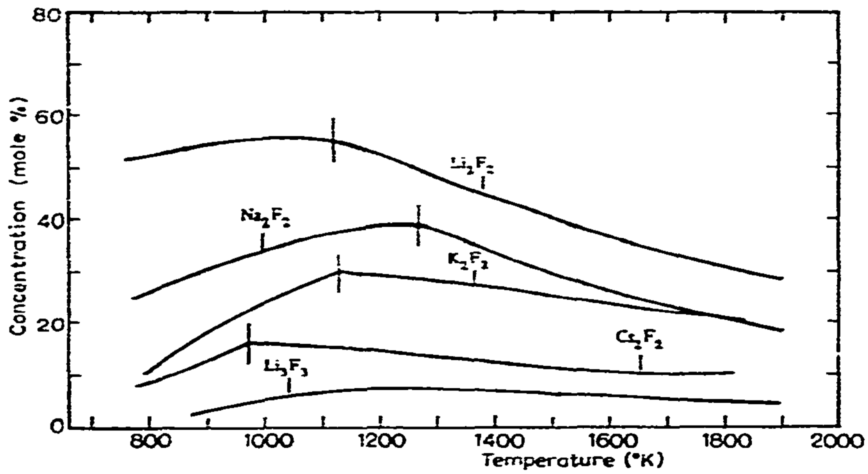

Fig. 2. Concentration of dimers in MF vapors.

TABLE XIII

COMPARISON OF HEAT OF DISSOCIATION

$Li_2F_2(g) = 2LiF(g)$.

$\Delta H^\circ_{d,1000}$ (*kcal/mole*)	*References*	*Experimental method*
65.0	11	Mass spectrometry with a Mo Knudsen cell
62.4	[a]	
61.6±2	18	Mass spectrometry with a double-oven apparatus
61.3±3	19	Mass spectrometry with two piece Ni Knudsen cell
61.2	6	Molecular-beam velocity-selector
60.4±3	5	Torsion effusion
59.5±3	17	Mass spectrometry with a double effusion chamber

[a] The value adopted here.

TABLE XIV

COMPARISON OF ENTHALPY AND ENTROPY OF DISSOCIATION[a]
$M_2F_2(g) = 2MF(g)$

Reaction	*$\Delta H^\circ_{d,298}$ (kcal/mole)*		*$\Delta S^\circ_{d,298}$ (e.u.)*		
	Third law	*Second law*	*Third law*	*Second law*	*Literature value*
$Na_2F_2 = 2NaF$	64.1 (11)	—	—	—	32.5 (48)
	63.5 (6)[b]	58.1±2.9	35.3	30.6	28.5 (6)
	62.0 (20)	—	—	—	—
$K_2F_2 = 2KF$	50.0 (6)[b]	51.0±1.6	31.9	32.8	30.4 (6)
$Cs_2F_2 = 2CsF$	42.3 (6)[b]	40.5±1.8	32.2	30.0	27.8 (6)

[a] All values are evaluated by using the derived functions except $\Delta S^\circ_{d,298}$ values in the last column which are taken from the original papers. [b] The adopted value.

and third law methods. The results are presented in Table XIV. The agreement between the second and third law $\Delta H^\circ_{d,298}$ values indicates the proper choice of the heats of sublimation and reasonable estimates for the missing molecular constants for the dimers upon which the Gibbs energy functions are based. The entropy changes ($\Delta S^\circ_{d,298}$) for the dimer dissociation reaction are compared with those reported in the literature in Table XIV. The discrepancies between them are expected, due to the use of different thermodynamic function for the species involved for evaluation. Table IX shows the adopted molecular constants employed for the calculation of the thermodynamic properties of $(MF)_n$ species. Some of these values are estimated by comparison with other similar compounds. Therefore the uncertainties in $\Delta S^\circ_{d,298}$ may be ± 2e.u.

Incorporating the values of $\Delta H^\circ_{f,298}(MF, c)$ with those of $\Delta H^\circ_{s,298}$, given in Tables XV and V, the heats of formation for gaseous MF, M_2F_2 and Li_3F_3 are evaluated. Table XV lists $\Delta H^\circ_{f,0}$, $\Delta H^\circ_{f,298}$ and S°_{298} for MF(g). The heats of formation at 0° and 298°K for dimeric alkali fluorides and Li_3F_3 are presented in Table XVI.

Based on the $\Delta H^\circ_{f,0}$ values for M(g), as given in Table XVII, the $(MF)_2 \rightarrow 2MF$ and M–F bond energies (D_0) and atomization energies ($D_{a,0}$) of M_2F_2 and Li_3F_3 molecules are evaluated, where M = Li, Na, K and Cs. Employing the $\Delta H^\circ_{f,0}$ values for MF(c), MF(g), $M^+(g)$, $F^-(g)$, M(g) and F(g), the enthalpy changes of the following reactions:

$$MF(c) = MF(g) \quad (1)$$

$$MF(c) = M^+(g)+F^-(g) \quad (2)$$

$$MF(g) = M^+(g)+F^-(g) \quad (3)$$

$$MF(c) = M(g)+F(g) \quad (4)$$

$$MF(g) = M(g)+F(g) \quad (5)$$

are derived and presented in Table XVIII. The values of $\Delta H^\circ_{f,0}$ for $M^+(g)$ and $F^-(g)$

are given in Table XVII. Due to lack of low temperature heat capacity data for CsF(c), the heats of reactions involving CsF(c) are calculated at 298°K.

All the heat of formation data used for calculation are taken from ref. 59.

TABLE XV

HEATS OF FORMATION AND ENTROPIES OF ALKALI FLUORIDES (c, g)

MF	*MF(c)*			*MF(g)*		
	$\Delta H^\circ_{f,0}$ (*kcal/mole*)	$\Delta H^\circ_{f,298}$ (*kcal/mole*)	S°_{298} (*e.u.*)	$\Delta H^\circ_{f,0}$ (*kcal/mole*)	$\Delta H^\circ_{f,298}$ (*kcal/mole*)	S°_{298} (*e.u.*)
LiF	−146.84	−147.45	8.523	−81.40	−81.45	47.85
NaF	−136.95	−137.52	12.240	−69.03	−69.42	51.98
KF	−135.54	−135.90	15.905	−77.61	−78.10	54.13
CsF	—	−132.57	21.1[a]	−84.61	−85.20	58.10

[a] Estimated value.

TABLE XVI

HEATS OF FORMATION AND BOND ENERGIES OF GASEOUS ALKALI FLUORIDE POLYMERS

M_nF_n	ΔH°_f (*kcal/mole*)		D_0 (*kcal/mole*)		D_a (*kcal/mole*)
	0°K	*298°K*	$(MF)_2 \rightarrow 2MF$	*M–F*	*0°K*
Li_2F_2	−224.20	−225.33	61.40	137.79	336.98
Na_2F_2	−200.75	−202.30	62.69	113.21	289.11
K_2F_2	−205.08	−206.20	49.86	117.49	284.84
Cs_2F_2	−211.55	−212.74	42.33	121.65	285.63
Li_3F_3	−361.02	−362.62	116.82[a]	137.79	530.19

[a] The enthalpy change for the reaction $Li_3F_3(g) = 3LiF(g)$.

TABLE XVII

HEATS OF FORMATION OF GASEOUS IONS AND ATOMS

M	$\Delta H^\circ_{f,0}$ (*kcal/mole*)		$\Delta H^\circ_{f,298}$ (*kcal/mole*)	
	M^+	*M*	M^+	*M*
Li	162.38	38.03	164.24	38.41
Na	144.33	25.82	145.76	25.76
K	121.63	21.52	122.90	21.31
Cs	108.50	18.68	108.10	18.32
F	−61.1[b]	18.36	−62.2[b]	18.86

[a] All ΔH°_f values taken from *JANAF Thermochemical Tables*[59].

[b] The given values refer to F^- instead of F^+.

TABLE XVIII

DERIVED HEATS OF REACTIONS

Reactions	$\Delta H^{\circ}_{r,0}$ *(kcal/mole)*			$\Delta H^{\circ}_{r,298}$ *(kcal/mole)*
	LiF	*NaF*	*KF*	*CsF*
$MF(c) = MF(g)$	65.44	67.92	57.94	47.37
$MF(c) = M^{+}(g)+F^{-}(g)$	248.12	220.18	196.07	178.47
$MF(g) = M^{+}(g)+F^{-}(g)$	182.68	152.26	138.14	131.10
$MF(c) = M(g)+F(g)$	203.23	181.13	175.42	169.75
$MF(g) = M(g)+F(g)$	137.79	113.21	117.49	122.38

DISCUSSION

On evaluation of the vapor pressure data, the following two conditions are satisfied: (1) the sum of the calculated partial pressures of the monomeric and polymeric species is consistent with the measured total pressures: (2) the derived second and third law values of heats of sublimation, vaporization, and dissociation of dimer into monomer are in reasonable agreement. Therefore the calculated heats of formation for the gaseous monomeric and polymeric alkali fluorides are probably the best values available at the present time.

Fig. 1 indicates that the curves of the concentrations of monomers in the vapors over the condensed phases have minima which correspond to maxima in Fig. 2 for the corresponding dimers. It is interesting to notice that the maximum concentration of dimer is always at the melting temperature of the alkali fluoride. The explanation of this phenomenon needs to be explored.

As mentioned previously, some of the molecular constants for the alkali fluoride dimers are unavailable and estimated. Some more experimental work seems necessary in these areas.

REFERENCES

1 H. V. Wartenberg and H. Schulz, *Z. Electrochem.*, 27 (1921) 568.
2 O. Ruff, G. Schmidt and S. Mugdan, *Z. Anorg. Allgem. Chem.*, 123 (1922) 83.
3 S. Cantor and F. Blankenship, private communication.
4 A. C. P. Pugh and R. F. Barrow, *Trans. Faraday Soc.*, 54 (1958) 671.
5 D. L. Hildenbrand, W. F. Hall, F. Ju and N. D. Potter, *J. Chem. Phys.*, 40 (1964) 2882.
6 M. Eisenstadt, G. M. Rothberg and P. Kusch, *J. Chem. Phys.*, 29 (1958) 797.
7 G. M. Rothberg, M. Eisenstadt and P. Kusch, *J. Chem. Phys.*, 30 (1959) 517.
8 K. A. Sense and R. W. Stone, *J. Phys. Chem.*, 62 (1958) 1411.
9 P. Entner and A. Neckel, *Monatsh. Chem.*, 98 (1967) 1083.
10 K. Niwa, *J. Fac. Sci. Hokkaido Imp. Univ. Ser. III*, 2 (1938) 201.
11 R. F. Porter and R. C. Schoonmaker, *J. Chem. Phys.*, 29 (1958) 1070.
12 K. A. Sense, C. A. Alexander, R. E. Bowman, R. W. Stone and R. B. Filbert, Jr., *J. Phys. Chem.*, 61 (1957) 384.
13 R. C. Miller and P. Kusch, *J. Chem. Phys.*, 25 (1956) 860.
14 R. C. Schoonmaker and R. F. Porter, *J. Chem. Phys.*, 30 (1959) 283.
15 R. C. Miller and P. Kusch, *J. Chem. Phys.*, 27 (1957) 981.
16 I. I. Naryshkin, *Zh. Fiz. Khim.*, 13 (1939) 528.

17 P. A. Akishin, L. N. Gorokhov and L. N. Sidorov, *Russ. J. Chem. (English Transl.)*, 33 (1959) 648.

18 J. Berkowitz, H. A. Tasman and W. A. Chupka, *J. Chem. Phys.*, 36 (1962) 2170.

19 A. Buchler and J. L. Stauffer, *Thermodynamics*, Vol. I, International Atomic Energy Agency, Vienna, 1966.

20 L. N. Sidorov, P. A. Akishin, V. I. Belousov and V. V. Shol'ts, *Russ. J. Phys. Chem. (English Transl.)*, 38 (1964) 641.

21 M. D. Scheer and J. Fine, *J. Chem. Phys.*, 36 (1962) 1647.

22 M. Knudsen, *Ann. Physik*, 28 (1909) 75, 999; 29 (1909) 179.

23 I. Langmuir, *Phys. Rev.*, 11 (1913) 329.

24 P. Clausing, *Ann. Physik*, 12 (1932) 961.

25 K. A. Sense, M. J. Snyder and J. W. Clegg, *J. Phys. Chem.*, 58 (1954) 223.

26 K. A. Sense, M. J. Snyder and R. B. Filbert, Jr., *J. Phys. Chem.*, 58 (1954) 995.

27 V. I. Baikov and K. P. Vasilevskii, *Opt. Spect. (USSR) (English Transl.)*, 22 (1967) 198.

28 A. Buchler, J. L. Stauffer and W. Klemperer, *J. Amer. Chem. Soc.*, 86 (1964) 4544.

29 P. A. Akishin and N. G. Rambidi, *Z. Physik. Chem. (Leipzig)*, 213 (1960) 111.

30 K. Motzfeldt, *J. Phys. Chem.*, 59 (1955) 139.

31 S. E. Veazey and W. Gordy, *Phys. Rev.*, 138 (1965) A1303.

32 A. Honig, M. Mandel, M. L. Stitch and C. H. Townes, *Phys. Rev.*, 96 (1954) 629.

33 K. Clusius, J. Goldman and A. Perlick, *Z. Naturforsch.*, 49 (1949) 424.

34 K. Clusius and W. Eichenauer, *Z. Naturforsch.*, 29 (1956) 715.

35 T. B. Douglas and J. L. Dever, *J. Amer. Chem. Soc.*, 76 (1954) 4826.

36 N. K. Voskresenskaya, V. A. Sokolov, E. I. Banashek and N. E. Schmidt, *Akad. Nauk SSSR, Izvest. Sect. Fiz. Khim. Anal.*, 27 (1956) 233.

37 J. P. Harrison, G. Lombardo and P. P. Peressini, *J. Phys. Chem. Solids*, 29 (1968) 557.

38 E. G. King, *J. Am. Chem. Soc.*, 79 (1957) 2056.

39 C. J. O'Brien and K. K. Kelley, *J. Amer. Chem. Soc.*, 79 (1957) 5616.

40 E. F. Westrum, Jr. and K. S. Pitzer, *J. Amer. Chem. Soc.*, 71 (1949) 1940.

41 V. S. Lyashenko, *Met. SSSR*, 10 (1935) 85.

42 A. S. Dworkin, private communication, Oak Ridge National Laboratory, Dec. 1, 1964.

43 K. A. Sense, C. A. Alexander, R. E. Bowman, R. W. Stone and R. B. Filbert, Jr., *J. Phys. Chem.*, 61 (1957) 384.

44 J. W. Johnson and M. A. Bredig, *J. Phys. Chem.*, 62 (1958) 604.

45 K. K. Kelley, *U.S. Bur. Mines Bull.*, 393 (1936).

46 M. A. Bredig, H. R. Bronstein and W. T. Smith, Jr., *J. Amer. Chem. Soc.*, 77 (1955) 1454.

47 A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.*, 64 (1960) 269.

48 S. H. Bauer, R. M. Diner and R. F. Porter, *J. Chem. Phys.*, 29 (1958) 991.

49 G. L. Vidale, *J. Phys. Chem.*, 64 (1960) 314.

50 L. Wharton, W. Klemperer, L. P. Godd, R. Strauch, J. J. Gallapher and V. E. Derr, *J. Chem. Phys.*, 38 (1963) 1203.

51 A. W. Searcy and R. D. Freeman, *J. Amer. Chem. Soc.*, 76 (1954) 5229.

52 H. Mayer, *Z. Physik*, 67 (1931) 240.

53 M. Volmer, *Z. Physik. Chem.*, Bodenstein-Festband, (1931) 863.

54 R. L. Redington, *J. Chem. Phys.*, 44 (1966) 1238.

55 S. Abramowitz, N. Acquista and I. W. Levin, *U. S. Nat. Bur. Stand. Rept.*, 9601, July 1 (1967).

56 A. Snelson, IITRI-U6001-13, May 14, 1963–August 12, 1966, Illinois Institute of Technology Research Institute, Chicago, Ill.

57 J. Berkowitz, *J. Chem. Phys.*, 32 (1960) 1519.

58 J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, John Wiley and Sons, New York, N.Y., 1940.

59 D. R. Stull and co-workers, *JANAF Thermochemical Tables*, Thermal Research Laboratory, The Dow Chemical Co., Midland, Mich.; available as PB168370, 1965, and addenda, from Clearinghouse for Scientific and Technical Information, U.S. Department of Commerce, Springfield, Va. 22151.

60 W. F. Giauque, E. W. Hornung, J. E. Kunzler and T. R. Rubin, *J. Amer. Chem. Soc.*, 82 (1960) 62.