KFA

KERNFORSCHUNGSANLAGE JÜLICH GmbH

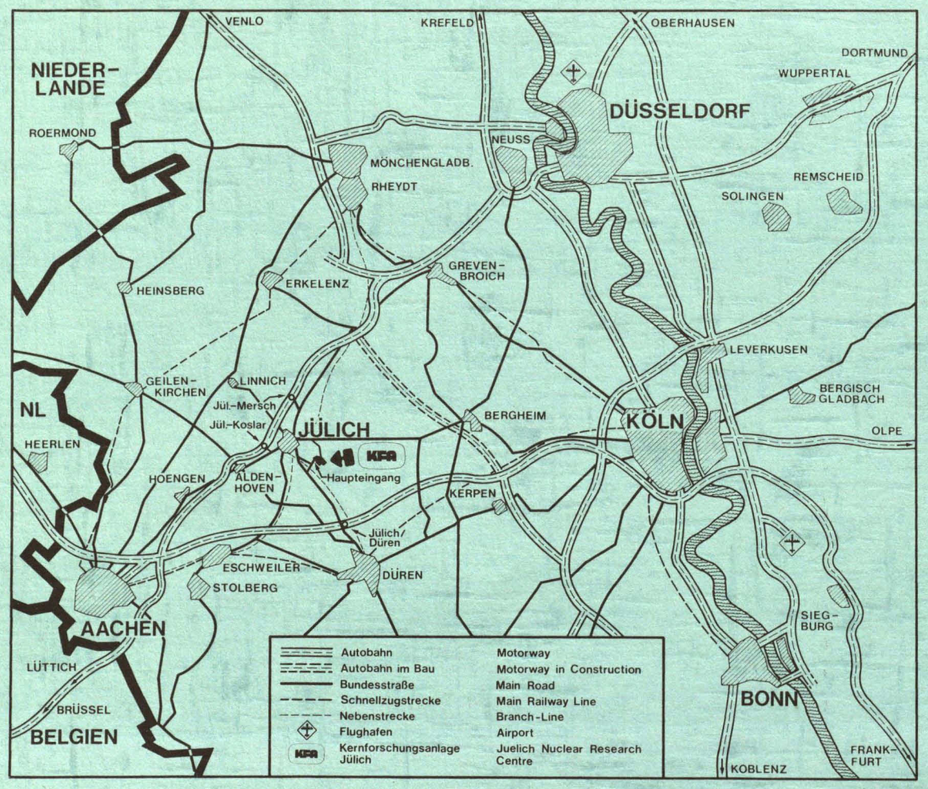
Institut für Chemie

The Thermodynamic Study of Alkali Metal Clusters, and Gaseous Molecules in the Lithium Hydride, Oxide and Cyanide Systems

von

C. H. Wu

Jül - 1878
November 1983
ISSN 0366-0885



Als Manuskript gedruckt

Berichte der Kernforschungsanlage Jülich – Nr. 1878

Institut für Chemie Jül – 1878

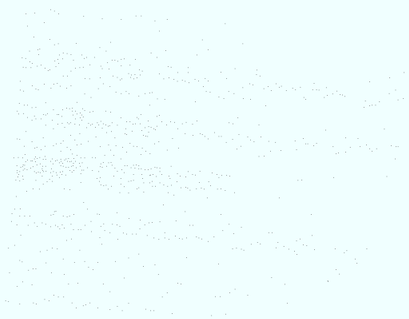
Zu beziehen durch: ZENTRALBIBLIOTHEK der Kernforschungsanlage Jülich GmbH
Postfach 1913 · D-5170 Jülich (Bundesrepublik Deutschland)
Telefon: 02461/610 · Telex: 833556-0 kf d

The Thermodynamic Study of Alkali Metal Clusters, and Gaseous Molecules in the Lithium Hydride, Oxide and Cyanide Systems

von

C. H. Wu

Diese Arbeit wurde von der Fakultät für Bergbau und Hüttenwesen der Rheinisch-Westfälischen Technischen Hochschule Aachen zur Erlangung der venia legendi als Habilitationsschrift genehmigt.



CONTENTS

INTRODUCTION

The study of the thermodynamic properties and the structure of gas molecules is becoming increasingly important, not only for theoretical interest which may help towards the understanding of the natural process of nucleation phenomena, point defects, chemisorption, the growth of small metal clusters and the problems related to heterogeneous catalysis, but also for the application of gas molecules [1, 2].

Early ab initio calculations on gas molecules were attempts to describe the species observed experimentally among the carbon gas molecules over graphite, and the lithium hydride molecules.

A recent lithium molecule study suggests that these gas molecules may represent some of the radiation damage products occuring in materials subjected to intense radiation. Metal clusters may also realistically represent systems involved in both homogeneous and heterogeneous catalysis. The photographic process, for example, is known to rely on the catalytic activity of photochemically produced silver clusters thought to contain four or more atoms.

Another interesting aspect of these molecules is the way in which various properties of increasingly large clusters approach those of the bulk crystal. This problem was considered by Stoll and Preuss in their study of lithium clusters[3]. Particularly the systems Li-H, Li-O, and the system of lithium clusters have been much studied theoretically.

A1 Lithium-Hydrogen System

The system of lithium-hydrogen molecules is one of the most important and interesting objects for theoretical investigation. Much theoretical work has been carried out on the lithium hydride molecule, which has lately become the work bench of the theoretical chemist[4]. Wilkinson[5] obtained for the LiH^+ molecule a binding energy of 1.3 ± 0.5 eV from thermodynamic cycle calculations. According to the results of theoretical calculations by Hurst, Plats and Matsen[6], LiH^+ should not be a stable ion. Browne's[7] ab initio calculation yielded a dissociation energy of $0.15\ eV < D_0^o(LiH^+) < 0.038\ eV$. The results of theoretical calculations by Fraga and Ransil[8] lie within these limits.

Due to these discrepancies in the calculated binding energy of the LiH^+ molecule, the estimates for the I.P(LiH) lie between 6.5 and 7.9 eV; this situation creates some hope that it might be possible to detect the LiH^+ ion by mass spectrometry under suitably chosen conditions, and study the properties of the LiH molecules.

Companion[9] has applied the diatomic-in-molecule theory to the Li_2H molecule and concluded that a linear symmetrical $^2\Sigma u^+$ state and an isosceles triangle $^2A_1$ state are stable; two corresponding atomization energies are predicted. Wu and Ellison[10] have used the same theory to analyse and discuss the stability of the ion Li_2H^+. Recently, England, Sabell and Wahl[11] have reported a theoretical study of Li_2H in the reaction $H + Li_2 \leftrightarrows Li_2H \leftrightarrows LiH + Li$. Sieghahn and Schaefer[12] predict from theoretical calculations a stable C_{2O} geometry with $^2A_1$ as lowest electronic state.

Companion[13] has also used the diatomic-in-molecule theory to study the stability of the LiH_2 molecule; and has reported that for linear HLiH there is a dissociation energy of 20.9 kcal/mol for the reaction: $HLiH(^2\Sigma u^+) = H(^2S) + LiH(^1\Sigma^+)$.

A second, more stable, LiH_2 is predicted as a C_{2v} isosceles triangular configuration with the hydrogen atoms at their equilibrium distance in a diatomic H_2 molecule, and the lithium atom 3.66 Bohr units from each. This author has given an atomization energy: $D_0^o(LiH_2)$ = 124.6 kcal/mol for the molecule LiH_2 with the C_{2v} isosceles triangular configuration. The heat of reaction for: $LiH_2(^2A_1) = H_2(^2\Sigma_g^+) + Li$ is predicted to be 13.5 kcal/mol.

When the atomization energy of LiH_2 predicted by Companion is combined with the atomization energy of Li_2H^+ (zero orbital overlap) predicted by Wu and Ellison[10] using the same theory, the ionization potential of LiH_2 is predicted to be $I.P(LiH_2)$ = 5.96 eV.

J.D. Switalsk, J.T. Huang, and M.E. Schwarz[14] have used the valence-only electronic structure theory to predict the reaction energy for: $LiH_2^+ \rightarrow Li^+ + H_2$ and given: ΔE = 3.8 kcal/mol.

Finally, Tyndall and Companion[15] have studied the stability of Li_2H_2 by application of diatomic-in-molecule theory and given the following heats of reaction:

$2LiH(^1\Sigma^+) \rightarrow Li_2H_2(^1B_{19})$ $\quad \Delta H_0^\circ = -28.4$ kcal/mol

and

$Li_2(^1\Sigma_g^+) + H_2(^1\Sigma_g^+) \rightarrow Li_2H_2(^1A_1)$ $\quad \Delta H_0^\circ = -26.7$ kcal/mol

In the investigation of P. Kollman, C. F. Bender and S. Rothenberg[16] by configuration interaction calculation, a heat of dimerization $\Delta H_0^\circ = -47.2$ kcal/mol for Li_2H_2 has been predicted.

From the results of the theoretical studies on the molecules in the lithium-hydrogen system, the molecules Li_2H, LiH_2, Li_2H_2, LiH^+, Li_2H^+ and $Li_2H_2^+$ could be stable. The existence of these stable molecules had not been demonstrated experimentaly prior to this investigation; this motivated us to investigate the existence of these molecules and their stabilities.

The other aspect is the increasing importance of the lithium-hydrogen system for the DT Fusion Reactor[17]. There are numerous principal fusion reactions. These involve the isotopes deuterium (D), tritium (T) and helium-3 (He^3):

$$D + D \begin{cases} \nearrow He^3 (0.82\ MeV) + n(2.45\ MeV) \\ \searrow T(1.10\ MeV) + H(3.02\ MeV) \end{cases} \qquad (1)$$

$$D + T \rightarrow He^4 (3.5\ MeV) + n(14.1\ MeV) \qquad (2)$$

$$D + He^3 \rightarrow He^4 (3.6\ MeV) + H(14.7\ MeV) \qquad (3)$$

Reaction (2) has the highest fusion reaction probability at the lowest temperature, so that this is the most promising reaction for the concept of a fusion reactor. Deuterium can be obtained from natural sources. The isotope tritium can be produced by neutron-lithium reactions:

$$Li^6 + n \rightarrow He^4 + T + 4.78\ MeV$$

$$Li^7 + n \rightarrow n + He^4 + T - 2.47\ MeV.$$

The successful use of lithium or lithium compounds as blanket materials to breed tritium in fusion reactors will depend on very detailed knowledge of their thermodynamic and physical chemical properties.

A2 Lithium-Oxygen System

The nature of the gaseous species over solid lithium oxides has been the subject of considerable speculation and experimentation.

Brewer[18] decided that there was no evidence for the existence of important lithium oxide gaseous molecules except possibly Li_2O and LiO.

Brewer and Margrave[19] have used the Knudsen effusion weight loss method to determine the total pressure of gaseous Li_2O. Berkowitz et al.[20] have used mass spectrometric Knudsen effusion techniques to confirm the existence of $Li_2O(g)$ and determined the atomization energy. In later works, White et al.[21] and Hildenbrand[22] have reported more precise information on the ionization potential and stability of the species Li_2O. White et al.[21] have used infrared matrix-isolation spectroscopy to study the vapor species over $Li_2O(s)$, and assigned two observed frequencies to the Li_2O_2 molecule without the O-O bond; and the remaining frequencies have been predicted by using the ionic model calculation. The matrix-isolation work of Andrew[23] on the Li_2O_2 molecule produced evidence for a molecule containing two equivalent lithium atoms and two equivalent oxygen atoms. The experimental vibrational frequencies for infrared modes are given. These values agree very well with the values given by Yates and Pitzer[24] using ab initio calculations.

Because of the different interpretations of the structure of Li_2O_2 by White et al.[21], and Andrew[23] and Yates and Pitzer[24], it is interesting to study the thermochemical properties of Li_2O_2 and to investigate whether other important gaseous lithium oxide molecules exist besides LiO and Li_2O.

It has been proposed by Powell et al.[25] that solid blanket materials have certain advantages in comparison with liquid metals or fused salts in a controlled thermonuclear reactor, and in particular, that lithium oxide has the highest lithium density (ρ_{Li} = 0.95 g/cm^3) among the lithium compounds. This property is essential for the efficient breeding of tritium in the blanket of a controlled thermonuclear reactor.

Detailed knowledge of the thermochemical properties is essential for the successful use of lithium oxide as a solid blanket material in fusion reactors.

The emphasis on the study of the lithium-oxygen system is relevant both from the theoretical and practical points of view.

Alkali Metal Systems

The study of polymer molecules of alkali metals is becoming increasingly important, not only for theoretical interest which may help towards the understanding of the natural process of nucleation phenomena, the growth of small metal clusters and the problems related to heterogeneous catalysis, but also for the application of alkali metal vapors[26].

By improvement on the method for semiempirical and ab initio calculation, it is possible to predict the existence of small clusters of alkali metal atoms. A.L. Companion[27] has investigated the structure and the stability of Li_3 and Li_4 clusters by diatomic-in-molecule theory, which was introduced by Ellison[28]. Subsequently, a number of theoretical works on Li_3 and Li_4 have been published[29, 30, 31].

In recent years some interesting alkali metal clusters have been detected experimentally. Li_2 and Li_3 molecules have been detected by means of high temperature Knudsen-effusion mass spectrometry in equilibrium vapors, and their thermodynamic properties have been determined[32].

The sodium clusters Na_2 through Na_{14} have been identified in supersonic nozzle beams of sodium, and their ionization potentials have been measured by photoionization[33].

The alkali metal systems are particularly widely used because of their unique properties[26] (see Table I).

Table I: Unique Properties of Alkali Vapors

1. Lowest ionization potentials
   (e.g. I.P(Na) = 5.139 eV I.P(Li) = 5.392 eV
   I.P(Li_2) = 4.86 eV I.P(Li_3) = 4.35 eV
   I.P(Li_4) = 4.69 eV I.P(NaLi) = 4.94 eV
   I.P(KLi) = 4.69 eV)
2. Strong visible-near IR absortion and emission
3. Theoretical simplicity (comparable with "visible hydrogen atoms and molecules")
4. Reversible equilibria over a wide temperature range
5. Tritium breeding (^6Li and ^7Li)

Some important energy related applications of alkali metals are shown in Table II.

Table II: Some Important Energy Related Applications of Alkali Metals Systems

1. Arc lamps (Na)
2. Flash lamps (Cs, K)
3. High resolution optically pumped lasers (Li_2, Na_2, K_2)
4. Infrared photography (K, Rb)
5. Thermoionic converters (Cs)
6. Magnetohydrodynamics (K, Cs)
7. Coolant (Li, Na, K)(including heat pipes)
8. Tritium breeder (^6Li, ^7Li)
9. Shield for first wall structure of inertial confinement fusion reactor (liquid lithium)
10. Neutral beam injection charge exchange cells (Na, Cs)
11. Solar pumped lasers
12. Discharge pumped high energy lasers or laser amplifiers
13. Optical devices
14. Thermoelectric solar energy converters
15. Solar boilers
16. Spin aligned atomic energy storage (Li)
17. Alternative negative ion for neutral beam injection (Li^-)
18. Diagnostic ion for inertial confinement (Li_2^+)
19. Alternative clean fusion reaction ($H + {}^6Li \rightarrow {}^3He + {}^4He + 4$ MeV) (no tritium or neutrons)
20. Measurement of tritium inventory in molten lithium (Li_2, LiT, Li_2T, Li_2T_2)

These applications are a strong argument for selecting alkali metals for particularly intensive basic research study.

B. METHOD OF THE THERMODYNAMIC STUDY

B1 High Temperature Mass Spectrometric Method

The mass spectrometric method is one of the most powerful universal and effective tools for the study of gas phase reactions and the reaction of the gas phase with condensed systems at high temperatures.

Chupka and Inghram[34], and Honig[35] studied the equilibrium between carbon vapor and graphite by mass spectrometry. They discovered that the species C_1, C_2 and C_3 have the same order of magnitude of concentration at a temperature of about 2500 K. This finding settled the long controversial questions of the behavior of the vaporization of graphite. Thereafter, investigations extended rapidly to other chemical elements, intermetallic and other chemical compounds, e.g. hydrides nitrides, etc. The existence of a large number of molecules has been proved for the first time by the mass spectrometric method. Also, some molecules, of which the existence had been predicted by theory, were identified in this way. This method became increasingly important as a sophisticated means of studying the thermodynamic properties and the kinetics of vaporization of a condensed phase.

The principles of the high temperature mass spectrometric method, experimental procedure and the evaluation of the thermodynamic data have been discussed previously[36, 37]. The high temperature mass spectrometric Knudsen effusion technique uses a Knudsen cell as a source of an effusate.

By analysis of the species in an effusate from a Knudsen cell by mass spectrometry, the thermodynamic properties are calculated.

Identification of the ions with the corresponding neutrals is usually achieved from their mass to charge ratio, shutterability, appearance potential, isotope abundance and the ionization efficiency curve. The measured ion current, I^+, for ions formed by electron impact reaction with a neutral molecule, is related to the partial pressure P_i of this neutral molecule in the gas phase at equilibrium by the relation

$$P_i = K \frac{I^+ T}{\sigma_i \gamma_i \Delta E \alpha_i} \qquad (1)$$

where K is the sensitivity constant of the apparatus, which can be obtained by the quantitative vaporization of a standard substance.

α_i is the isotopic abundance of the measured ions, σ_i is the ionization cross section, $\Delta E = E - A.P.$ (E = electron energy and A.P. = appearance potential), and γ_i is the multiplier gain.

The multipler gains, γ_i, are usually measured for the major species in the gas equilibria. If the multiplier gains are not available, the empirical relation $\gamma_M \approx M^{-1/2}$ could be used for heavier masses; and for polyatomic molecules the following relation can be used

$$\gamma = \gamma_M \quad 1 + \frac{\frac{(\Sigma m_i)^{1/2}}{(\Sigma m_i)^{1/2}} - 1}{3} \qquad (2)$$

The ionization cross section, σ, obtained by experiment is available for only a limited number of molecules. Mann[38] has compiled the calculated ionization cross sections of the chemical elements; this compilation has been widely used for the evaluation of absolute partial pressures. The ionization cross section of molecules is obtained from the sum of atomic values. From the experimental results, Pottie[39], Drowart and Goldfinger[36] recommend taking 0.75 times the sum of Mann's cross sections.

The partial pressure can be obtained directly by evaporation of standard substances according to the relation

$$P_i = I_i + T_i \left(\frac{P_s}{I_s + T_s}\right)\left(\frac{\sigma_s}{\sigma_i}\right)\left(\frac{\gamma_s}{\gamma_i}\right)\left(\frac{\Delta E_s}{\Delta E_i}\right) \qquad (3)$$

where s means standard.

The use of ratios in this manner permits the determination of the partial pressure without a direct determination of the sensitivity constant K.

C. EVALUATION OF THERMODYNAMIC PROPERTIES

C1 Properties of Molecules

The enthalpies of reaction of a homogeneous or heteregeneous chemical reaction can be calculated by the third law method or second law method using the measured equilibrium constant. The third law method will be evaluated by the following relation:

$$\Delta H_0^\circ = -RT\ln K - T[\Delta(G_T^\circ - H_0^\circ)/T] \qquad (4)$$

where ΔH_0° is the standard enthalpy of the chemical reaction, K is the equilibrium constant and

$$\frac{G_T^\circ - H_0^\circ}{T}$$

is the free energy function. The equilibrium constants are obtained from the measured partial pressures of the species involved in the chemical reaction; but for isomolecular exchange reactions, the equilibrium constants are calculated directly from the measured ion intensities of the species, since it is assumed that the ionization cross sections and multiplier gains for the species involved in the chemical reaction cancel each other.

The Gibbs energy functions $(G_T^\circ - H_0^\circ)/T$ are taken from literature compilations, or are obtained by using the molecular parameters, which are obtained by optical spectroscopic methods or by estimations according to statistical thermodynamical procedures.

The Gibbs energy functions are contributed to by translation, rotation, vibration, electronic and anharmonicity corrections. The following relations have been used for the evaluation of the molecules[40, 41].

I. Monatomic gas

a) Translation

$$-(G_0^\circ - H_0^\circ)/T = 6.863426 \log M + 11.439043 \log T - 7.282868 \quad (5)$$

b) Electronic

$$-(G_0^\circ - H_0^\circ)/T = 4.565717 \log \Sigma_{g_i} e^{-\frac{1.438790\ \varepsilon_i}{T}} \quad (6)$$

II. Diatomic molecules

a) Translation and rotation

$$-(G_T^\circ - H_0^\circ)/T = 6.863426 \log M + 11.439043 \log T - 4.575617 \log (B\sigma/T) + 0.953038\ (B/T) + 0.0457074\ (B/T)^2 - 8.005804 \quad (7)$$

b) Vibration

$$-(G_T^\circ - H_0^\circ)/T = -4.575617\ (1 - e^{-u}) \quad (8)$$

c) Electronic

Same as I(b) when the i th-state vibrational partition function Q_v^i, and the i th-state rotational partition function, Q_r^i, are equal to the respective ground state partition function $Q = Q_t\ Q_v\ Q_r \sum_i Q_e^i$, otherwise all the thermodynamic functions are derived from $Q = Q_t \sum_i Q_e^i\ Q_v^i\ Q_r^i$, where Q_t is the translational partition function and $Q_e^i = q_i \exp(\delta_i/KT)$

d) Anharmonicity corrections

$$-(G_T - H_0^\circ)/T = 1.987165 \left[\frac{8\gamma}{u} + \frac{\delta}{(e^u-1)} + \frac{2 \times u}{(e^u-1)^2}\right] \quad (9)$$

III. Linear polyatomic molecule

a) Translation and rotation same as for II a)

b) Vibration same as II b) for 3N-5 vibrational degrees of freedom

c) Electronic same as II c) where levels and quantum weight are known

d) Anharmonic correction neglected

IV. Nonlinear polyatomic molecule

a) Translation and rotation

$$-(G_T^\circ - H_0^\circ)/T = 6.863426 \log M + 18.302469 \log T - 4.575617 \log \sigma + 2.287809 \log I_x I_y I_z X\ 10^{117} - 10.297926 \quad (10)$$

b) Vibration same as II b) for 3N-6 vibrational degrees of freedom

c) Electronic same as II c) where levels and quantum weight are known

d) Anharmonic corrections neglected

If the experiment is carried out over a wide range of temperature, the enthalpies of reaction can be evaluated by the second law method, where

$$\Delta H_T^\circ = -R \frac{d \ln K}{d(\frac{1}{T})} \quad (11)$$

To obtain the corresponding value ΔH_0°, the enthalpy in the standard state at temperature T, H_T°, and the enthalpy in the standard state of O K of the species involved in the chemical reactions need to be known. These values are taken from the literature, or calculated by the following equations using an estimated molecular constant.

I. Monatomic gas

a) Translation

$$(H_T^\circ - H_0^\circ)/T = 4.967913 \tag{12}$$

b) Electronic

$$(H_T^\circ - H_0^\circ)/T = \frac{2.859114}{T} \frac{\sum \varepsilon_i g_i^{\,e^{-\frac{1.438790\,\varepsilon_i}{T}}}}{\sum g_i^{\,e^{-\frac{1.438790\,\varepsilon_i}{T}}}} \tag{13}$$

II. Diatomic molecule

a) Translation and rotation

$$(H_T^\circ - H_0^\circ)/T = 6.955079 - 0.953038\ (B/T) - 0.091418\ (B/T)^2 \tag{14}$$

b) Vibration

$$(H_T^\circ - H_0^\circ)/T = 1.987165\ ue^{-u}/(1-e^{-u}) \tag{15}$$

c) Electronic

Same as I b)

d) Anharmonicity correction

$$(H_T^\circ - H_0^\circ)/T = 1.987165\left[\frac{8r}{u} + \frac{u(e^u - 2x)}{(e^u - 1)^2} + \frac{4Xu^2e^u}{(e^u-1)^3}\right] \tag{16}$$

III. Linear polyatomic molecule

Same statement as for Gibbs energy function

IV. Non-linear polyatomic molecule

a) Translation and rotation

$$(H_T^\circ - H_0^\circ)/T = 7.948662 \qquad (17)$$

b) Vibration same as II b) for 3N-6 vibrational degrees of freedom

c) Electronic same as II c) where levels and quantum weight are known

d) Anharmonic correction neglected and the corresponding value ΔH_0° is given by

$$\Delta H_0^\circ = \Delta H_T^\circ + \Sigma(H_T^\circ + H_0^\circ)_{\text{reactants}} - \Sigma(H_T^\circ - H_0^\circ)_{\text{prod.}} \qquad (18)$$

The analysis of data by the third law method is generally considered superior to the second law method. It is definitely superior if the Gibbs energy functions are reliable, because each data point is independent of the others. It is to be recommended, that for all the evaluations of thermodynamic properties, a combination of the third law and the second law methods is appropriate. The mutual consistence between Gibbs energy functions and equilibrium data can be proved by the second law method.

It is shown in equation (11) that the second law method requires only the knowledge of relative values of equilibrium constants. Absolute values of entropies and Gibbs energy functions need not be known; this advantage has been stressed frequently.

The measured values for the reaction enthalpies represent in many cases the desired thermodynamic property, such as dissociation energy, heat of atomization or heat of sublimation. In other cases such thermodynamic quantities can be calculated from these reaction enthalpies and additional literature data.

Ionization Potential of Gas Molecules

The ionization potential of molecules is by definition the energy difference between the ground vibrational level of the lowest electronic state of the molecule and the ground vibrational level of the molecular ion.

The experimental determination of ionization potential has been discussed in detail elsewhere[42]. There are several methods of determining the ionization potential:

a) linear extrapolation

b) initial break method

c) extrapolated voltage differences method

d) semi-logarithmic plot method

e) the critical slope method

f) energy compensation technique.

The ionization potentials of the molecules which were studied in this work have been determined by means of the extrapolated voltage differences method, so this method is discussed in more detail as follows.

The extrapolated voltage differences method was proposed by J. W. Warren[43], and has been used for the determination of the ionization potential of a number of new molecules[44]. It is recognized as one of the most reliable and satisfactory methods. The ionization efficiency curves of the various ions from the effusate and of the ion from the calibrant gas are determined. The ion current scale of either the sample ion or the calibrant ion is arbitrarily adjusted to make the linear portions of the ionization efficiency curves parallel.

The voltage differences, ΔE, at various values of ion intensity, I, are determined from the curves. Finally, a new plot of ΔE versus ion intensity is prepared, and the curve is linearly extrapolated to I = 0. The value of ΔE at I = 0 is taken as the difference between the ionization potentials of the molecules in the effusate and the calibrant gas. Once the ionization potentials of molecules are known, the binding energy or dissociation energy of the ion is obtained by the thermocycle calculation[45].

D. APPARATUS

The apparatus, consisting of an effusion molecular beam source and a quadrupole mass spectrometer (Quad. 250 B, EAI, palo Alto, CA) for studying the species produced in the Knudsen cell is shown schematically in Fig. 1.

The Knudsen cells were heated by a rf generator (6 kW, 0.5 MHz) which was maintained at a constant power output by means of an alternating current stabilizer. A cell temperature stability of ± 1.5 K was achieved. Cell temperatures were measured with a PtRh/Pt thermocouple and with an optical pyrometer; these instruments were calibrated in situ at the triple points of Li (thermocouple only), Ag and Au.

To assure the attainment of equilibrium inside the cell, the quantity of sample used and the crucible size were such as to provide a sample surface area at least 100 times that of the orifice area.

The cells were degassed by heating under vacuum before loading of the sample. The distance between the cell orifice and the electron beam of the ion source was about 3 cm.

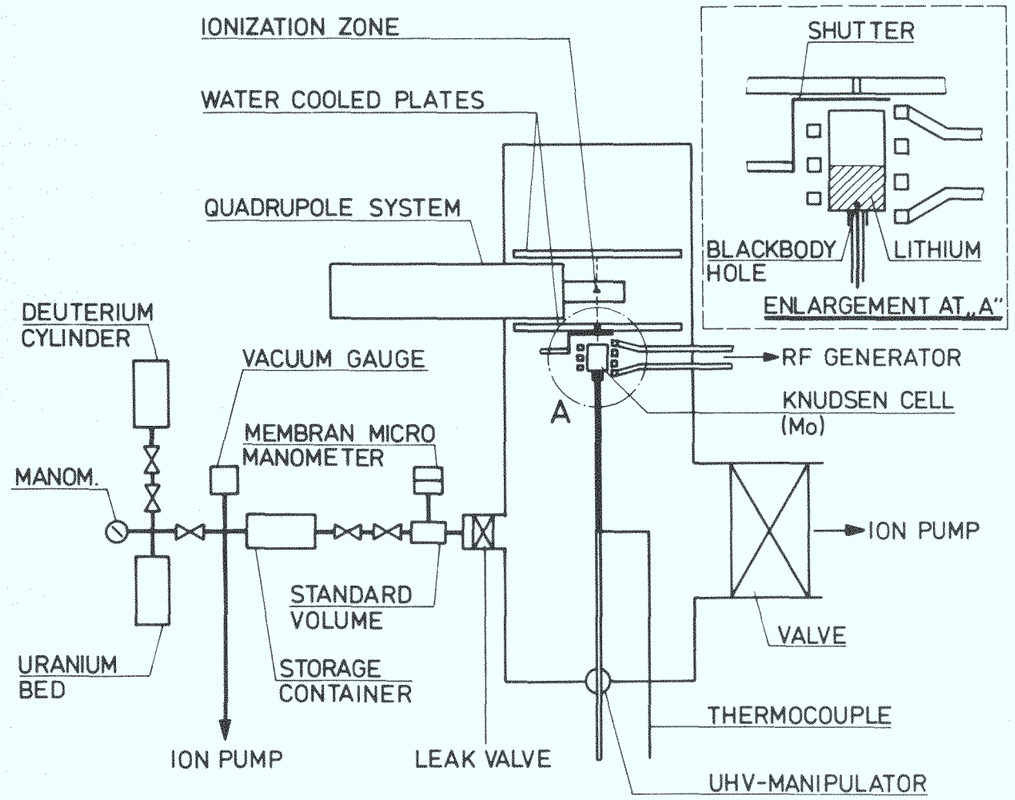


Fig. 1 Schematic diagram of the experimental arrangement.

The molecular, electron, and ion beams were mutually perpendicular, and the geometrical arrangement was such that the molecular beam passed through the ion source without sticking to the walls and was subsequently quenched on a water cooled copper plate placed immediately behind the ion source.

A shutter was installed between the Knudsen cell and the ion source of the mass spectrometer in order to discriminate between the atoms and molecules effusing from the Knudsen cell and the residual gas. Ion getter pumps maintained the pressure at less than 10^{-8} Torr in the beam source region during the measurements.

This quadrupole mass spectrometric system has a high sensitivity, and an ion current of ~ 3.5×10^{-16} A can be detected. This detection limit corresponds to an effusion rate of ~ 2.1×10^{8} particle x sec^{-1}. Furthermore, the dynamic range of the system is 10^{7}. This means that intensity ratios of 1 : 10^{7} for neighboring masses can be well distinguished.

The ionization potentials of Li, Ag, Au, H_2O, N_2, and Ar were used to calibrate the electron energy of the mass spectrometer.

For the evaluation of the ionization potentials of the newly identified molecules in this work, the extrapolated voltage difference method was applied using an ionization potential of 5.392 eV for lithium as standard .

E. EXPERIMENTAL AND RESULTS OF THIS STUDY

E1 The System Lithium-Hydrogen

First generation fusion power reactors are expected to operate by means of the deuterium-tritium fusion reaction, because of the high cross section of the D-T reaction. Tritium can be bred by nuclear reaction of neutrons with lithium (see introduction).

Both economic and safety considerations require rather low maximum allowable tritium concentrations in the lithium blanket; and it is generally agreed that safety considerations set the more stringent constraint. In particular, if liquid lithium is to be used as both the breeding material and reactor coolant, the steady state concentration of tritium must be maintained at a low level to prevent significant permeation of tritium through the blanket structure material and heat exchanger. It is belived that this requirement will limit the permissible tritium concentration in the blanket to 1 ~ 10 ppm. An efficient method for extraction and recovery of tritium from very low concentrations of tritium in liquid lithium is essential for fuel recycling in the fusion reactor.

A number of authors have reported on the thermodynamic properties of the system "Li-H". Most of these works are concerned with the measurement of the equilibrium pressure of hydrogen by a static method, and determined the enthalpy of reaction of LiH accordingly. It is noteworthy that in all this work the composition of the gaseous species was not observed. From the recent experimental results[46, 47], it is seen that the molecule LiH should play an important role in the removal of hydrogen from the metallic lithium blankets of fusion reactors. Also, the other polyatomic lithium-hydrogen molecules could exist; and these will provide important information on tritium breeding, removal and recycling. In addition, it is apparent that there is much scatter in the data, and an insufficient study of the dilute solution region. This motivated us to undertake the study on the Li-H system.

E1.1 Experimental

The apparatus used for this work has been described in detail in chapter A (introduction). Fig. 2 shows the phase diagram of the lithium-lithium hydride system.

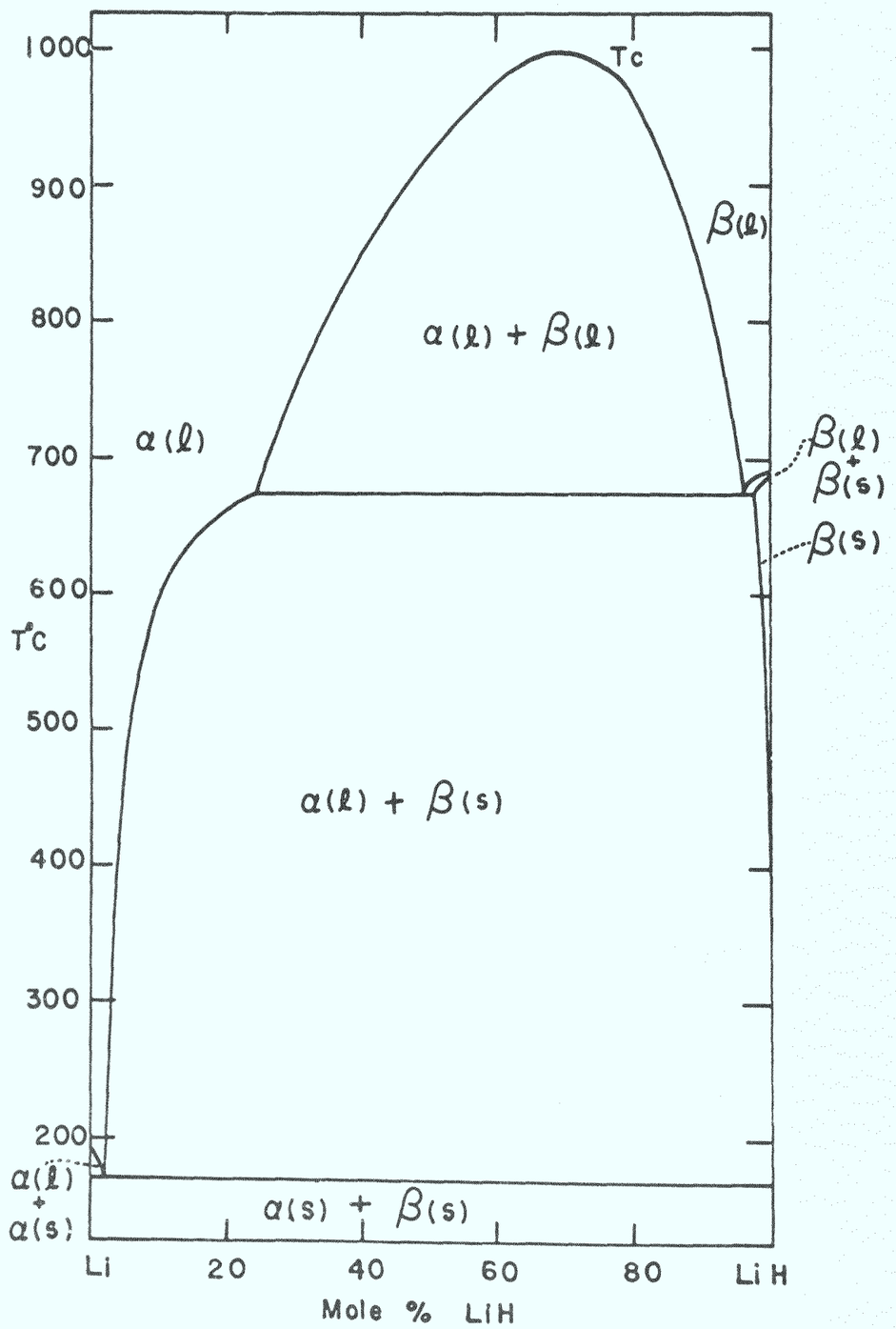


Fig. 2 Phase diagram of the lithium-hydrogen system.

In the left part of the phase diagram, the "α" phase is a solution of hydrogen in lithium, where the partial pressure of hydrogen is dependant on the atom fraction of hydrogen in lithium. The experiments have been carried out in the region of the "α" phase.

Solutions of hydrogen in lithium have been prepared by reaction of pure lithium contained in a Kundsen cell with a known amount of hydrogen. The hydrogen used in these measurements was purified by formation and decomposition of uranium hydride.

In early work[48] we have measured the partial pressures of LiH(g), $Li_2H(g)$, $LiH_2(g)$ and $Li_2H_2(g)$ as functions of temperature and concentration of hydrogen in the lithium. From the results of this study, it is found that in a temperature range of 800 K to 1000 K, and at a concentration of about 1000 ppm hydrogen in liquid lithium, the partial pressures of LiH(g), $LiH_2(g)$, $Li_2H(g)$ and $Li_2H_2(g)$ are of the same order of magnitude. For example, at 950 K and 1000 ppm, the partial pressures are

$$P_{Li_2H_2} \sim 6.2 \times 10^{-8} \text{ atm}$$
$$P_{LiH_2} \sim 1.9 \times 10^{-7} \text{ atm}$$
$$P_{Li_2H} \sim 1.5 \times 10^{-8} \text{ atm}$$
$$P_{LiH} \sim 4.0 \times 10^{-8} \text{ atm.}$$

The experiments were carried out under these conditions.

E1.2 Results and Discussion

E1.2.1 Thermodynamics of the Molecule $Li_2H(g)$

The following gas equilibria have been measured for the evaluation of thermodynamic data of Li_2H:

$$Li_2H(g) + Li(g) = LiH(g) + Li_2(g) \qquad (19)$$

$$Li_2H(g) + Li_2(g) = LiH(g) + Li_3(g) \qquad (20)$$

The measurements of the gaseous isomolecular exchange equilibria (19) and (20) were carried out at temperatures between 840 K and 950 K.

The equilibrium constants for the reactions were calculated from the measured ion currents:

$$K_{19} = \frac{I(LiH^+)\,I(Li_2{}^+)}{I(Li_2H^+)\,I(Li^+)} \qquad (21)$$

and

$$K_{20} = \frac{I(LiH^+)\,I(Li_3{}^+)}{I(Li_2H^+)\,I(Li_2{}^+)} \qquad (22)$$

The heat content and the Gibbs energy function for Li(g), Li_2(g) and LiH(g) were taken from the JANAF tables, and those for Li_3(g), Li_2H(g) were calculated by the statistical mechanical method with estimated molecular parameters. The results of the third law enthalpies are shown in Tables III and IV.

The measured equilibrium constants for reactions (19) and (20) as a function of temperature are shown in Fig. 3. The reaction enthalpies for reactions (19) and (20), calculated by using the second law treatment, are $\Delta H^{\circ}_{890} = 10.1 \pm 4.8$ kcal/mol and $\Delta H^{\circ}_{890} = 18.5 \pm 3.0$ kcal/mol respectively.

Using the calculated heat content of Li_2H(g), $H^{\circ}_{890} - H^{\circ}_{0} = 10.8$ kcal/mol (linear symmetrical), $H^{\circ}_{890} - H^{\circ}_{0} = 11.4$ kcal/mol (isosceles triangle), and the calculated heat content of Li_3(g) (see chapter E2), the corresponding ΔH°_{0} values were obtained as 11.6 ± 4.8 (linear symmetrical) and 12.1 ± 4.8 kcal/mol (isosceles triangle), respectively for reaction (19), and 18.3 ± 3.0 kcal/mol (linear symmetrical) and 18.6 ± 3.0 kcal/mol (isosceles triangle) respectively, for reaction (20).

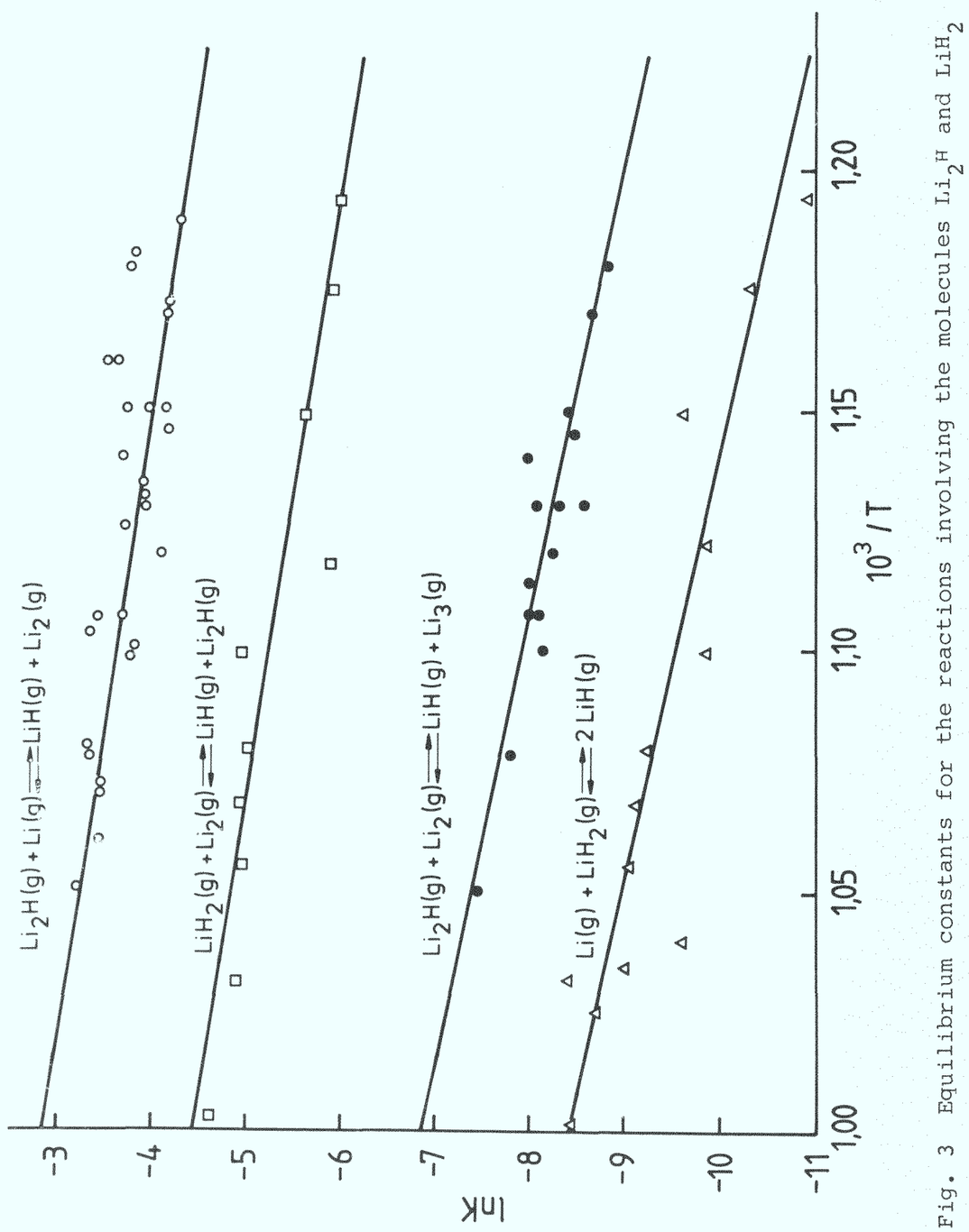


Fig. 3 Equilibrium constants for the reactions involving the molecules Li_2H and LiH_2 as a function of temperature.

Table III: Third Law Enthalpies for Reaction:

$$Li_2H(g) + Li(g) \rightleftarrows LiH(g) + Li_2(g)$$

		Linear Symmetrical		Isosceles Triangle	
T	-R ln K	$-\Delta[(G_T^\circ - H_0^\circ)/T]$ (cal $mol^{-1}K^{-1}$)	ΔH_0° kcal/mol	$-\Delta[(G_T^\circ - H_0^\circ)/T]$ (cal $mol^{-1}K^{-1}$)	ΔH_0° kcal/mol
838	9.28	4.51	11.56	-3.93	4.40
840	8.61	4.50	11.01	-3.94	3.90
853	8.34	4.50	11.00	-3.94	3.80
857	7.16	4.52	10.00	-3.93	2.80
866	7.87	4.53	10.73	-3.93	3.40
872	8.46	4.54	11.33	-3.93	3.95
876	7.34	4.54	10.40	-3.94	3.00
883	7.88	4.53	11.00	-3.95	3.48
890	8.24	4.54	11.37	-3.95	3.80
903	6.83	4.55	10.27	-3.95	2.50
908	7.68	4.55	11.10	-3.95	3.39
910	7.65	4.66	11.20	-3.95	3.37
927	6.67	4.57	10.40	-3.95	2.50
933	6.87	4.57	10.67	-3.96	2.73
941	6.87	4.57	10.76	-3.97	2.73
950	6.35	4.58	10.40	-3.97	2.30
			Av. 10.83 ± 0.45		Av. 3.25 ± 0.62

Table IV: Third Law Enthalpies for Reaction:

$$Li_2H(g) + Li_2(g) \rightleftharpoons LiH(g) + Li_3(g)$$

		Linear Symmetrical		Isosceles Triangle	
T	-R ln K	$-\Delta[(G_T^\circ - H_0^\circ)/T]$ (cal $mol^{-1}K^{-1}$)	ΔH_0° kcal/mol	$-\Delta[G_T^\circ - H_0^\circ)/T]$ (cal $mol^{-1}K^{-1}$)	ΔH_0° kcal/mol
845	17.58	7.24	20.97	-1.16	13.87
853	17.25	7.25	20.90	-1.15	13.73
868	16.79	7.27	20.88	-1.13	13.59
873	16.81	7.27	21.02	-1.12	13.70
876	15.73	7.29	20.17	-1.11	12.81
883	17.18	7.29	21.61	-1.11	14.18
883	16.67	7.29	21.16	-1.11	13.74
885	16.02	7.30	20.64	-1.10	13.20
888	16.47	7.30	21.11	-1.10	13.65
897	15.97	7.31	20.88	-1.09	13.34
903	16.01	7.31	21.06	-1.19	13.38
903	16.09	7.31	21.13	-1.19	13.45
908	16.47	7.31	21.59	-1.19	13.87
927	15.49	7.33	21.15	-1.17	13.27
933	15.79	7.32	21.56	-1.18	13.63
953	14.70	7.33	21.00	-1.17	12.90
		Av.	21.00 ± 0.34	Av.	13.52 ± 0.36

A comparison of the third law values and the second law values for reactions (19) and (20) is given in Table V.

It is shown in Table V that there is good agreement for reactions (19) and(20) between the third law and the second law enthalpies for the linear symmetrical structure of $Li_2H(g)$. It is seen that the measurements were conducted under equilibrium conditions in the Knudsen cell, and the evaluated reaction enthalpy, ΔH°_0, for $Li_2H(g)$ with linear symmetrical structure has the greater probability of being correct.

Combination of the third law values for linear symmetrical Li_2H with the dissociation energies: $D^{\circ}_0(Li_2) = 1.12 \pm 0.03$ eV, $D^{\circ}_0(LiH) = 2.4288 \pm 0.0002$ eV, and $D^{\circ}_0(Li_3) = 1.8 \pm 0.17$ eV, yields the corresponding heats of atomization:

$$D^{\circ}_0(Li_2H) = 91.8 \pm 0.5 \text{ kcal/mol from reaction (19)}$$

and

$$D^{\circ}_0(Li_2H) = 87.5 \pm 0.7 \text{ kcal/mol from reaction (20)}$$

The average value is:

$$D^{\circ}_0(Li_2H) = 89.7 \pm 5.0 \text{ kcal/mol.}$$

Table V: Summary of Thermodynamic Properties of the Reactions Involving the Molecule $Li_2H(g)$.

Reaction	ΔH_0°(Second Law) kcal/mol		ΔH_0°(Third Law) kcal/mol	
	Linear Symmetrical	Isosceles Triangle	Linear Symmetrical	Isosceles Triangle
$Li_2H(g) + Li(g) \rightleftarrows LiH(g) + Li_2(g)$	11.6 ± 4.8	12.1 ± 4.8	10.8 ± 0.5	3.3 ± 0.6
$Li_2H(g) + Li_2(g) \rightleftarrows LiH(g) + Li_3(g)$	18.3 ± 3.0	18.6 ± 3.0	21.0 ± 0.3	13.5 ± 0.4

Finally, combining the atomization energy of $Li_2H(g)$ with the heat of formation of $Li(g)$, ΔH_0° = 38.5 ± 0.1 kcal/mol, and the dissociation energy $D_0^\circ(H_2)$ = 103.25 kcal/mol, yields the heat of formation:

$$\Delta H_0^\circ(Li_2H) = 38.93 \pm 5.0 \text{ kcal/mol}$$

for the reaction:

$$2Li(s) + 1/2\ H_2(g) \rightarrow Li_2H(g)$$

E1.2.2 Binding Energy of the Ion Molecule Li_2H^+

The ionization potential of the Li_2H molecule was measured as:

$$I.P.(Li_2H^+) = 4.5 \pm 0.2 \text{ eV}.$$

When the measured value for the ionization potential of Li_2H is combined with the atomization energy $D_0^\circ(Li_2H)$ = 89.7 ± 5.0 kcal/mol and the ionization potentials I.P.(H) = 13.598 ± 0.002 eV and I.P.(Li) = 5.392 eV, the binding energies are obtained as follows:

$$Li_2H^+ \rightarrow 2Li + H^+ \qquad \Delta H_0^\circ = 299.0 \pm 4.0 \text{ kcal/mol}$$

$$Li_2H^+ \rightarrow Li + Li^+ + H \qquad \Delta H_0^\circ = 110.0 \pm 5.0 \text{ kcal/mol}$$

Table VI: Comparison of Experimental and Calculated Values of the Binding Energies for Li_2H and Li_2H^+

Molecule	D_0° exp.	D_0° calc.[8,9]	D_0° exp./D_0° calc.
Li_2H	89.7	78.8	1.14
Li_2H^+	299.0	257.6	1.16

Companion[9] has applied the diatomic-in-molecule theory and predicted the atomization energy of the linear molecule as: D_0°(LiHLi) = 78.8 kcal/mol. Wu and Ellison[10] have applied the same theory and predicted the atomization energy of the linear ion as: $D_0^\circ(LiHLi^+)$ = 257.6 kcal/mol for the dissociation to $2Li + H^+$. Table VI shows the comparison of the measured and calculated results. It is seen that the molecules Li_2H and Li_2H^+ are more stable than expected by theory.

E1.2.3 Thermodynamics of the Molecule $LiH_2(g)$

The following gas equilibria have been measured at temperatures between 836 and 998 K, and at a concentration of hydrogen of about 1000 ppm in liquid lithium.

$$Li(g) + LiH_2(g) = 2LiH(g) \qquad (23)$$

$$LiH_2(g) + Li_2(g) = LiH(g) + Li_2H(g) \qquad (24)$$

The gas equilibria were evaluated from the measured ion currents using the following relations:

$$K_{23} = \frac{I^2(LiH)}{I(Li)\,I(LiH_2)} \qquad (25)$$

$$K_{24} = \frac{I(LiH)\,I(Li_2H)}{I(LiH_2)\,I(Li_2)} \qquad (26)$$

where I is the ion current.

At constant temperature the ion currents of Li^+, Li_2^+, and Li_3^+ are practically independent of the concentration of hydrogen in dilute solutions in lithium, whereas the ion currents of LiH and Li_2H are directly proportional to the concentrations of hydrogen in lithium, and the ion current of LiH_2 is proportional to the square of the concentration of hydrogen. To keep the change in the hydrogen concentration in lithium during the measurements as small as possible, the measurements of ion currents were carried out in the following sequence: LiH_2, LiH, Li_2H, Li_2 and Li.

The threshold appearance potentials evaluated by the vanishing current method for Li^+, Li_2^+, Li_3^+, LiH^+, Li_2H^+ and LiH_2^+ are 5.5, 5.0, 4.5, 7.9, 4.5 and 6.3 eV, respectively, the uncertainty being ± 0.3 eV. The appearance potentials for Li^+, Li_2^+, Li_3^+, LiH^+, and Li_2H^+ agree with the known ionization potentials of the corresponding neutral gaseous species given in the literature[49, 50, 32].

Thus the appearance potentials showed that the ions observed are produced by ionization of the corresponding neutrals.

The relative ion intensities of the gaseous species used in the evaluation of the LiH_2 molecule are given in Table VII.

The Gibbs energy functions, as well as the enthalpy increments, for the calculation of ΔH_0° from ΔH_T° were taken from JANAF tables for Li(g), Li_2(g), and LiH(g) ; and those for Li_2H(g) were taken from our previous estimated values.

The Gibbs energy function for LiH_2(g) was calculated by the statistical mechanical method with the estimated parameter given by Companion[9]. The resulting numerical values are given in Table VIII.

The third law results of reactions (23) and (24) are given in Tables IX and X, and the corresponding second law plots are shown in Fig. 3. The reaction enthalpies for the reactions (23) and (24) evaluated by using the second law treatment are:

Table VII: The Relative Ion Abundances as a Function of Temperature

T(K)	$I(Li^+)$	$I(LiH^+)$	$I(Li_2H^+)$	$I(LiH_2^+)$	$I(Li_2^+)$
836	2.88×10^7	6.20×10^1	2.70×10^2	8.00	9.00×10^5
869	3.13×10^7	2.24×10^2	3.90×10^1	2.40×10^2	1.05×10^6
890	5.69×10^7	2.30×10^2	4.60×10^2	2.00×10^1	2.10×10^6
850	2.50×10^7	1.10×10^2	2.75×10^2	1.40×10^1	7.50×10^5
908	2.25×10^7	6.70×10^1	1.92×10^2	4.00	4.10×10^5
924	2.13×10^7	1.66×10^2	2.10×10^2	1.25×10^1	4.24×10^5
936	3.25×10^7	2.60×10^2	3.60×10^2	1.95×10^1	6.90×10^5
946	4.69×10^7	3.25×10^2	4.55×10^2	2.20×10^1	1.05×10^6
962	6.25×10^7	3.00×10^2	4.25×10^2	2.10×10^1	1.52×10^6
967	1.00×10^8	5.80×10^2	9.20×10^2	3.00×10^1	$2.50.10^6$
840	2.43×10^7	8.70×10^1	2.36×10^2	3.50	2.92×10^5
855	2.13×10^7	3.50×10^2	3.65×10^2	1.40×10^1	2.83×10^5
968	6.18×10^7	4.30×10^2	5.00×10^2	1.50×10^1	1.55×10^6
978	6.06×10^7	4.05×10^2	5.55×10^2	1.70×10^1	1.60×10^6
998	8.75×10^7	7.45×10^2	8.30×10^2	3.10×10^1	2.54×10^6

Table VIII: Free Energy Functions $(G_T^\circ - H_0^\circ)/T$ in cal mol^{-1} K^{-1} for $LiH_2(g)$

Temperature (K)	Linear Symmetrical $-(G_T^\circ - H_0^\circ)/T$	Isosceles Triangle $-(G_T^\circ - H_0^\circ)/T$
800	47.45	51.64
850	48.06	52.26
900	48.65	52.85
950	49.19	53.41
1000	49.74	53.94

Table IX: Third Law Enthalpies for Reaction:
$Li(g) + LiH_2(g) = 2\ LiH(g)$

T (K)	-RlnK	Linear Symmetrical $-\Delta[(G_T^\circ - H_0^\circ)/T]$ (cal $mol^{-1}K^{-1}$)	Linear Symmetrical ΔH_0° (kcal/mol)	Isosceles Triangle $-\Delta[(G_T^\circ - H_0^\circ)/T]$ (cal $mol^{-1}K^{-1}$)	Isosceles Triangle ΔH_0° (kcal/mol)
836	21.86	-1.32	19.38	2.88	15.87
840	18.53	-1.30	16.66	2.89	13.37
850	20.41	-1.30	18.45	2.90	14.88
855	15.49	-1.30	14.36	2.90	10.76
869	19.10	-1.30	17.73	2.89	14.09
890	19.82	-1.29	18.79	2.91	15.05
908	19.68	-1.28	19.03	2.92	15.21
924	18.22	-1.28	18.02	2.92	14.14
936	18.17	-1.29	18.21	2.91	14.28
946	18.26	-1.29	18.49	2.91	14.52
962	19.05	-1.28	19.56	2.92	15.52
967	18.08	-1.28	18.72	2.92	14.66
968	16.93	-1.27	17.63	2.93	13.55
978	17.38	-1.27	18.24	2.93	14.14
988	16.87	-1.26	18.09	2.94	13.90
			Av. 18.09±1.26		Av. 14.26±1.20

Table X: Third Law Enthalpies for Reaction:
$LiH_2(g) + Li_2(g) = LiH(g) + Li_2H(g)$

T (K)	-RlnK	Linear Symmetrical $-\Delta[(G_T^\circ - H_0^\circ)/T]$ (cal $mol^{-1}K^{-1}$)	Linear Symmetrical ΔH_0° (kcal/mol)	Isosceles Triangle $-\Delta[(G_T^\circ - H_0^\circ)/T]$ (cal $mol^{-1}K^{-1}$)	Isosceles Triangle ΔH_0° (kcal/mol)
836	10.05	3.19	7.38	7.39	3.87
850	9.88	3.21	7.15	7.41	3.58
869	9.78	3.23	6.97	7.42	4.13
890	10.58	3.24	7.69	7.44	3.96
908	8.75	3.28	5.77	7.48	2.00
924	9.22	3.28	6.20	7.48	2.30
936	9.24	3.28	6.17	7.48	2.25
946	9.50	3.29	6.38	7.49	2.42
962	10.56	3.30	7.88	7.50	3.34
967	9.50	3.30	6.30	7.50	2.25
998	9.60	3.33	6.32	7.53	2.10
			Av. 6.70±0.63		Av. 2.93±0.84

$$\Delta H^{\circ}_{920} = 17.3 \pm 1.2 \text{ kcal/mol}$$

and

$$\Delta H^{\circ}_{920} = 12.3 \pm 4.0 \text{ kcal/mol},$$

respectively.

Using the calculated heat content of $LiH_2(g)$, $H^{\circ}_{920} - H^{\circ}_0 = 9.7$ kcal/mol (linear symmetrical) and $H^{\circ}_{920} - H^{\circ}_0 = 10.6$ kcal/mol (isosceles triangle), and for Li_2H: $H^{\circ}_{920} - H^{\circ}_0 = 11.0$ kcal/mol (linear symmetrical), the corresponding ΔH°_0 values were calculated as: 16.85 ± 1.2 kcal/mol (linear symmetrical) and 17.75 ± 1.2 kcal/mol (isosceles triangle) for reaction (23), and $\Delta H^{\circ}_0 = 11.4 \pm 4.0$ kcal/mol (linear symmetrical), and $\Delta H^{\circ}_0 = 12.3 \pm 4.0$ kcal/mol (isosceles triangle) for reaction (24).

The third law values and second law values for reactions(23) and (24) are given in Table XI. It is seen that the agreements between the third and second law values for $LiH_2(g)$ with the linear symmetrical structure are better than those for $LiH_2(g)$ with the isosceles triangle structure.

Table XI: Summary of Thermodynamic Properties of the Reaction Involving the Molecule $LiH_2(g)$

Reaction	ΔH°_0 (Second Law) kcal/mol		ΔH°_0 (Third Law) kcal/mol	
	Linear Symetrical	Isosceles Triangle	Linear Symmetrical	Isosceles Triangle
$Li(g) + LiH_2(g) = 2\ LiH(g)$	16.85 ± 1.2	17.75 ± 1.2	18.09 ± 1.26	14.26 ± 1.20
$LiH_2(g) + Li_2(g) = LiH(g) + Li_2H(g)$	11.4 ± 4.0	12.30 ± 4.0	6.70 ± 0.63	2.93 ± 0.84

Combining the third law values for reactions (25) and (26) with the dissociation energies, $D_0^\circ(Li_2)$ = 25.5 ± 1.5 kcal/mol[32], $D_0^\circ(LiH)$ = 55.86 ± 0.005 kcal/mol[51], and $D_0^\circ(Li_2H)$ = 89.7 ± 5.0 kcal/mol[50], yields the corresponding atomization energy for LiH_2:

$D_0^\circ(LiH_2)$ = 130.0 ± 1.5 kcal/mol (linear symmetrical)

$D_0^\circ(LiH_2)$ = 126.3 ± 1.5 kcal/mol (isosceles triangle)

from reaction (23) and

$D_0^\circ(LiH_2)$ = 126.9 ± 4.0 kcal/mol (linear symmetrical)

$D_0^\circ(LiH_2)$ = 123.1 ± 4.0 kcal/mol (isosceles triangle)

from reaction (24).

The average values are

$D_0^\circ(LiH_2)$ = 128.5 ± 3.0 kcal/mol (linear symmetrical)

and

$D_0^\circ(LiH_2)$ = 124.7 ± 3.0 kcal/mol (isosceles triangle).

The fact that there is no clear difference in the magnitude of the atomization energies between the linear symmetrical and isosceles triangle structures for the LiH_2(g) molecule shows that the average value $D_0^\circ(LiH_2)$ = 126.6 ± 3.0 kcal/mol should be more reasonable. Combining the atomization energy of LiH_2(g) with the heat of formation of Li(g), ΔH_0° = 38.5 ± 0.1 kcal/mol, and the dissociation energy $D_0^\circ(H_2)$ = 103.25 kcal/mol, yields the heat of formation $\Delta H_0^\circ(LiH_2)$ = 14.75 ± 7.0 kcal/mol.

E1.2.4 Binding Energy of the Ion Molecule LiH_2^+

An accurate evaluation of the threshold appearance potential was made by the extrapolated voltage difference method. The LiH_2^+ threshold was measured against Li^+, and the ionization potential for the LiH_2^+ ion was determined as I.P.(LiH_2^+) = 6.14 ± 0.2 eV.

If the measured values for the ionization potential I.P.(LiH_2^+) = 6.14 eV and the atomization energy $D_0^\circ(LiH_2)$ = 126.6 ± 3.0 kcal/mol are combined with I.P.(Li) = 5.392 eV, and I.P.(H) = 13.598 ± 0.002 eV, the binding energy $D_0^\circ(LiH_2^+)$ = 109.3 ± 3.0 kcal/mol results for the dissociation to $Li^+ + 2H$; and $D_0^\circ(LiH_2^+)$ = 298.13 ± 3.0 kcal/mol results for the dissociation to $Li + H + H^+$.

If the uncertainties in the calculated Gibbs energy function (10 %) and in the assumption that the ionization cross sections and multiplier gains in the isomolecular exchange reactions cancel each other (30 %), are taken into account, the following atomization energies result:

$D_0^\circ(LiH_2) = 127.0 \pm 7.0$ kcal/mol

$D_0^\circ(LiH_2^+) = 109.0 \pm 8.0$ kcal/mol

for the dissociation to $Li^+ + 2H$ and

$D_0^\circ(LiH_2^+) = 298.0 \pm 8.0$ kcal/mol

for the dissociation to $Li + H + H^+$.

A comparison of these experimental results for the atomization energies with the predicted values of Companion [9], and Wu and Ellison [10], by using the diatomic-in-molecule theory is given in Table XII. It is seen that there is good agreement between the experimental values and those predicted by theory.

Switalski, Huang and Schwarz have used the value-only electronic structure theory and ab inito calculations to predict the energy of the reaction:

$LiH_2^+ \rightarrow Li^+ + H_2$ $\quad \Delta E = 3.8$ kcal/mol (valence-only model)

$\Delta E = 5.2$ kcal/mol (ab initio calculation)

If the atomization energy of the molecule LiH_2 and ionization potential I.P.(LiH_2) measured in this work are combined with the ionization potential of lithium, I.P. (Li) = 5.392 eV [49], and the dissociation

Table XII: Comparison of Experimental and Calculated Values of the Atomization Energies for LiH_2 and LiH_2^+

Molecule	D_0° (exp) kcal/mol	D_0° (calc)[1,2] kcal/mol	D_0° (exp)/D (calc)
LiH_2	127.0	124.6	1,02
LiH_2^+	109.0	111.5	0.98

energy of hydrogen $D_0^\circ(H_2)$ = 103.25 kcal/mol, the reaction energy ΔE = 6.5 kcal/mol is obtained. The agreement between these two results is excellent.

E1.2.5 Thermodynamics of the Molecule Li_2H_2

When a dilute solution of hydrogen in lithium with a concentration of 1000 ppm is heated in a molybdenum cell in the temperature range of 830 K to 1000 K, the ions Li^+, Li_2^+, Li_3^+, LiH^+, LiH_2^+, Li_2H^+ and $Li_2H_2^+$ are observed; and the appearance potentials for these ions were found to be 5.5, 5, 4.5, 8, 6.5, 5 and 6 eV, respectively by the linear extrapolation method with an uncertainty of ± 0.5 eV. These agree with the known ionization potentials of the corresponding neutral gaseous species given in the literature. Thus the appearance potentials suggest that the ions observed are produced by ionization of the corresponding neutrals.

The measurements of the gaseous isomolecular exchange equilibria:

$$Li_2H_2(g) + Li_2(g) = 2Li_2H(g) \qquad (27)$$

$$Li_2H_2(g) + Li(g) = LiH_2(g) + Li_2(g) \qquad (28)$$

$$Li_2H_2(g) + Li_2(g) = Li_3(g) + LiH_2(g) \qquad (29)$$

$$Li_2H_2(g) + LiH(g) = Li_2H(g) + LiH_2(g) \qquad (30)$$

were carried out at temperatures between 830 and 1000 K. The equilibrium constants for the reactions were calculated from the measured ion currents using the relations:

$$K_{27} = \frac{I(Li_2H^+)^2}{I(Li_2^+)I(Li_2H_2^+)} \qquad (31)$$

$$K_{28} = \frac{I(LiH_2^+)I(Li_2^+)}{I(Li^+)I(Li_2H_2^+)} \qquad (32)$$

$$K_{29} = \frac{I(Li_3^+)I(LiH_2^+)}{I(Li_2^+)I(Li_2H_2^+)} \qquad (33)$$

and

$$K_{30} = \frac{(Li_2H^+)I(LiH_2^+)}{I(LiH^+)I(Li_2H_2^+)} \qquad (34)$$

where I is the relative ion intensity.

The experimental values for the ionization cross sections and multiplier gains, which are necessary for the evaluation of the equilibrium constants of gas reactions from the measured ion intensities, are not available. Therefore, an assumption that the ionization cross sections and multipler gains for isomolecular reactions can cancel each other out has been made[52].

By using the estimated molecular parameters given by Tyndall and Companion[15] for the D_{2h} diamond-shaped and C_{2v} dimer of LiH, one obtains the Gibbs energy function for the $Li_2H_2(g)$ molecule by the statistical mechanical method; and the resulting numerical values of the Gibbs energy functions as a function of temperature are given in Table XIII.

The Gibbs energy functions for Li(g) and $Li_2(g)$ were taken from the JANAF tables, those for $Li_3(g)$, $Li_2H(g)$ and $LiH_2(g)$ were taken from previous sections.

The measured equilibrium constants as functions of temperature are shown in Fig. 4 and the third law results of reactions (27), (28), (29) and (30) are given in Tables XIV, XV, XVI, and XVII.

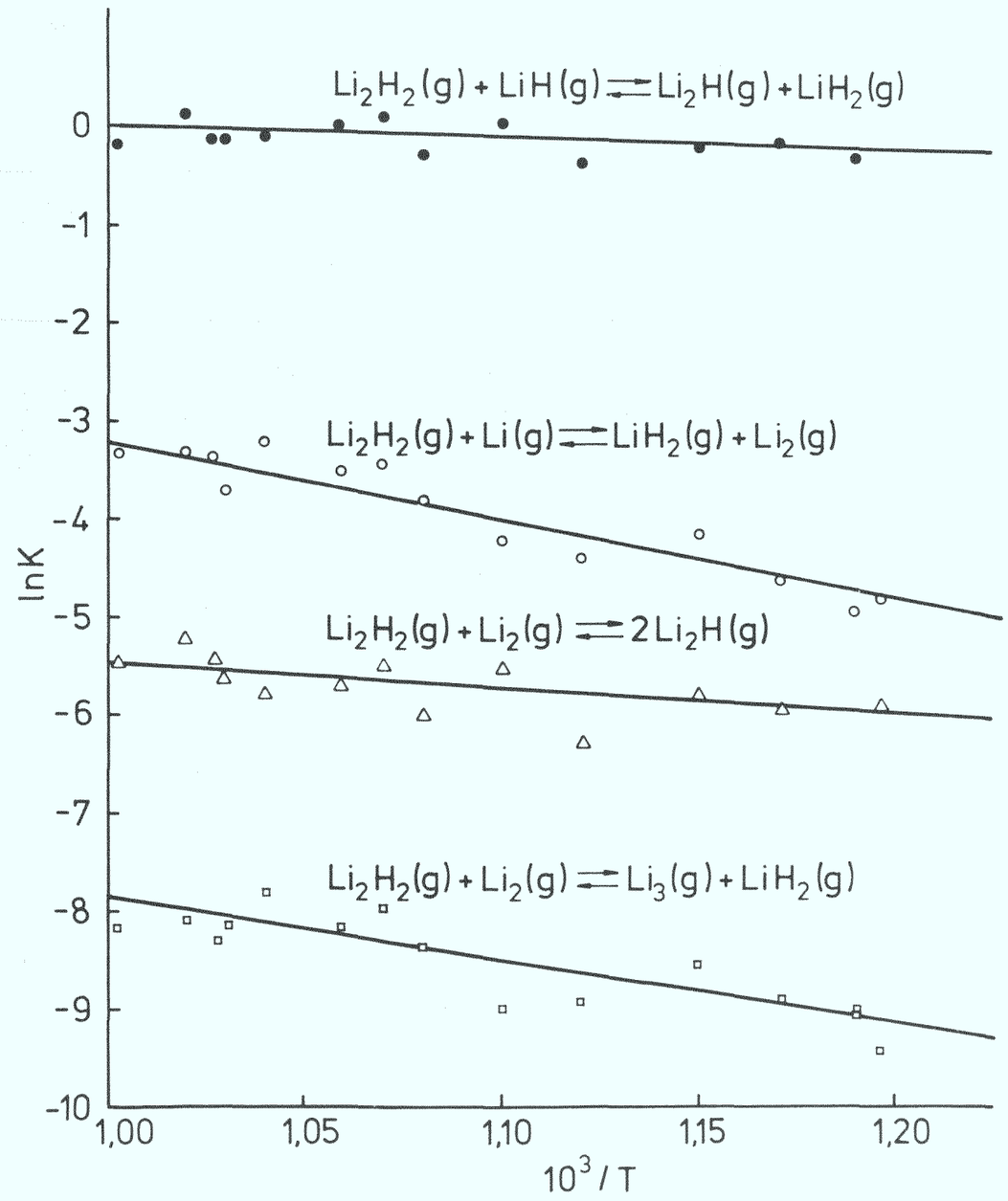


Fig. 4 Equilibrium constants of the reactions involving the molecule Li_2H_2 as a function of temperature.

Table XIII: Free Energy Function $-(G_T^\circ - H_0^\circ)/T$ in cal mol^{-1} K^{-1} for $Li_2H_2(g)$

Temperature (K)	$-(G_T^\circ - H_0^\circ)/T$	
	D_{2h} Dimer	C_{2v} Dimer
298	44.79	42.67
400	47.71	45.81
500	50.19	48.45
600	52.37	50.75
700	54.33	52.79
800	56.11	54.63
900	57.74	56.29
1000	59.25	57.82

Table XIV: Third Law Enthalpies for the Reaction:

$$Li_2H_2(g) + Li_2(g) = 2\ Li_2H(g)$$

T K	$-\Delta[(G_T^\circ - H_0^\circ)/T]$ (cal mol^{-1} K^{-1})		ΔH_0° (kcal mol^{-1})	
(K)	D_{2h} Dimer	C_{2v} Dimer	D_{2h} Dimer	C_{2v} Dimer
836 2.70×10^{-3}	-2.10	-0.63	8.07	9.29
869 2.90×10^{-3}	-2.15	-0.70	8.22	9.48
890 1.68×10^{-3}	-2.18	-0.72	9.35	10.66
850 2.52×10^{-3}	-2.13	-0.66	8.29	9.54
908 4.07×10^{-3}	-2.23	-0.78	7.91	9.22
924 2.23×10^{-3}	-2.25	-0.81	9.13	10.46
936 4.03×10^{-3}	-2.26	-0.82	8.14	9.48
946 3.37×10^{-3}	-2.28	-0.84	8.54	9.91
962 2.99×10^{-3}	-2.31	-0.87	8.89	10.27
967 3.45×10^{-3}	-2.31	-0.88	8.66	10.04
840 5.62×10^{-3}	-2.10	-0.63	6.88	8.12
855 1.41×10^{-3}	-2.15	-0.68	5.40	6.67
968 4.53×10^{-3}	-2.32	-0.88	8.13	9.53
978 5.30×10^{-3}	-2.34	-0.90	7.89	9.30
998 3.91×10^{-3}	-2.39	-0.93	8.61	10.06
			Av.8.14±0.96	9.47±0.98

Table XV: Third Law Enthalpies for the Reaction:

$$Li_2H_2(g) + LiH(g) = Li_2H(g) + LiH_2(g)$$

T K	$-\Delta[(G_T^\circ - H_0^\circ)/T]$ (cal mol^{-1} K^{-1})		ΔH_0° (kcal mol^{-1})	
(K)	D_{2h} Dimer	C_{2v} Dimer	D_{2h} Dimer	C_{2v} Dimer
836 1.16	1.09	2.56	0.66	1.89
869 8.36×10^{-1}	1.08	2.53	1.24	2.51
890 6.67×10^{-1}	1.05	2.52	1.66	2.95
850 8.75×10^{-1}	1.08	2.55	1.14	2.39
908 1.09	1.05	2.50	0.80	2.11
924 6.87×10^{-1}	1.03	2.47	1.64	2.97
936 1.12	1.02	2.46	0.74	2.09
946 9.93×10^{-1}	1.01	2.45	0.97	2.33
962 1.35	0.99	2.43	0.39	1.76
967 8.65×10^{-1}	0.99	2.42	1.25	2.62
840 7.30×10^{-1}	1.10	2.57	2.45	2.68
855 1.08	1.08	2.55	0.79	2.05
968 8.72×10^{-1}	0.99	2.43	1.23	2.62
978 1.11	0.98	2.42	0.76	2.16
998 8.22×10^{-1}	0.94	2.40	1.33	2.78
			Av. 1.07±0.37	2.39±0.37

Table XVI: Third Law Enthalpies for the Reaction:

$$Li_2H_2(g) + Li_2(g) = Li_3(g) + LiH_2(g)$$

T K	$-\Delta[(G_T^\circ - H_0^\circ)/T]$ (cal mol^{-1} K^{-1})		ΔH_0° (kcal mol^{-1})	
(K)	D_{2h} Dimer	C_{2v} Dimer	D_{2h} Dimer	C_{2v} Dimer
836 7.56×10^{-5}	8.32	9.99	22.72	23.95
869 2.10×10^{-4}	8.35	9.80	21.88	23.14
890 1.31×10^{-4}	8.37	9.83	23.26	24.56
850 1.37×10^{-4}	8.33	9.80	22.11	23.35
908 1.22×10^{-4}	8.37	9.82	23.86	25.17
924 2.30×10^{-4}	8.38	9.82	23.12	24.45
936 3.47×10^{-4}	8.38	9.82	22.66	24.01
946 2.84×10^{-4}	8.39	9.83	23.29	24.65
967 2.75×10^{-4}	8.40	9.83	23.88	25.26
940 1.26×10^{-4}	8.33	9.80	21.98	23.22
855 8.79×10^{-4}	8.33	9.80	19.08	20.33
968 2.22×10^{-4}	8.39	9.83	24.30	25.70
978 2.99×10^{-4}	8.40	9.84	23.99	25.39
998 2.64×10^{-4}	8.40	9.84	24.77	26.16
			Av. 22.92±1.41	24.24±1.46

Table XVII: Third Law Enthalpies for the Reaction:

$$Li_2H_2(g) + Li(g) = LiH_2(g) + Li_2(g)$$

T K	$-\Delta[(G^\circ_T - H^\circ_0)/T]$ (cal mol^{-1} K^{-1})		ΔH°_0 (kcal mol^{-1})	
(K)	D_{2h} Dimer	D_{2v} Dimer	C_{2h} Dimer	C_{2v} Dimer
836 8.35×10^{-3}	5.60	7.07	12.63	13.86
869 1.61×10^{-2}	5.61	7.06	12.01	13.27
890 1.23×10^{-2}	5.59	7.05	12.75	14.05
850 1.05×10^{-2}	5.59	7.06	12.45	13.69
908 1.46×10^{-2}	5.61	7.06	12.72	14.04
924 2.20×10^{-2}	5.59	7.03	12.17	13.50
936 3.35×10^{-2}	5.59	7.03	11.55	12.89
946 3.00×10^{-2}	5.59	7.03	11.88	13.24
962 4.20×10^{-2}	5.57	7.01	11.42	12.80
967 2.43×10^{-2}	5.57	7.00	12.53	13.91
840 8.44×10^{-3}	5.60	7.07	12.67	13.91
855 3.41×10^{-2}	5.61	7.08	10.54	11.80
968 3.55×10^{-2}	5.57	7.01	11.81	13.21
978 3.70×10^{-2}	5.57	7.01	11.85	13.26
998 3.53×10^{-2}	5.53	6.99	12.15	13.61
			Av. 12.08±0.60	13.40±0.60

The third law values of reactions (27), (28), (29) and (30) were combined with the following atomization energies :

$D_0^\circ(Li_2)$ = 25.5 ± 1.5 kcal/mol[32]

$D_0^\circ(Li_2H)$ = 89.7 ± 5.0 kcal/mol[50]

$D_0^\circ(Li_3)$ = 45.5 ± 4.0 kcal/mol[32]

$D_0^\circ(LiH)$ = 55.86 kcal/mol[51]

$D_0^\circ(LiH_2)$ = 127.0 ± 7.0 kcal/mol[45].

The atomization energies of $Li_2H_2(g)$ with different configurations,which were obtained from the four independent gas reactions,are given in Table XVIII.

The second law values of the enthalpies of reaction for the reactions (27), (28), (29) and (30) are ΔH_{915}° = 4.8 ± 3.0 kcal/mol, ΔH_{915}° = 15.6 ± 2.2 kcal/mol ΔH_{915}° = 12.6 ± 11.4 kcal/mol and ΔH_{915}° = 2.1 ± 1.5 kcal/mol respectively. These values agree well with the third law values within the limits of error. However, the third law values are much more reliable than those from the second law. Therefore only the third law values have been used for the evaluation of the atomization energy of Li_2H_2.

Table XVIII: The Atomization Energies Obtained from four Gas Reactions

Reaction	Enthalpy of Reaction (kcal mol^{-1})		Atomization Energy of Li_2H_2 (kcal mol^{-1})	
	D_{2h} Dimer	C_{2v} Dimer	D_{2h} Dimer	C_{2v} Dimer
$Li_2H_2(g) + Li_2(g) = 2Li_2H(g)$	8.14 ± 0.96	9.47 ± 0.98	162.0 ± 5.2	163.4 ± 5.2
$Li_2H_2(g) + Li(g) = LiH_2(g) + Li_2(g)$	12.08 ± 0.60	13.40 ± 0.60	164.5 ± 7.1	165.9 ± 7.1
$Li_2H_2(g) + Li_2(g) = Li_3(g) + LiH_2(g)$	22.92 ± 1.41	24.24 ± 1.46	165.9 ± 8.2	167.2 ± 8.2
$Li_2H_2(g) + LiH(g) = Li_2H(g) + LiH_2(g)$	1.07 ± 0.37	2.39 ± 0.37	161.9 ± 8.5	163.2 ± 8.5
			Av. 164.3 ± 10.0	

It is seen that the agreement between the atomization energies derived from four independent isomolecular exchange reactions is excellent. This suggests that the measurements were conducted under equilibrium conditions in the Knudsen cell; and that there is no serious error in the free energy function for $Li_2H_2(g)$ and in the experimentally determined atomization energies of $Li_2H(g)$, $LiH_2(g)$ and $Li_3(g)$ given in this work.

By using the same error treatment as mentioned elsewhere[50], an estimated uncertainty of ±10 kcal/mol is obtained for the atomization energy of $Li_2H_2(g)$.

Finally, combining the atomization energy of $Li_2H_2(g)$, $D_0^\circ(Li_2H_2) = 164 \pm 10$ kcal/mol, and of LiH(g), $D_0^\circ(LiH) = 55.86$ kcal/mol, with the heat of formation of Li(g), $\Delta H_0^\circ = 38.5 \pm 0.1$ kcal/mol, and the dissociation energy $D_0^\circ(H_2) = 103.25$ kcal/mol, yields the heat of formation: $\Delta H_0^\circ(Li_2H_2) = 16.0 \pm 10$ kcal/mol, and the heat of dimerization:

$$2LiH \rightarrow Li_2H_2 \qquad \Delta H_0^\circ = -(52.6 \pm 10) \text{ kcal/mol}$$

Kollman, Bender and Rothenberg[16] have predicted a heat of dimerization: $\Delta H_0^\circ = -47.2$ kcal/mol, by electronic structure calculation.

Milne and Cubicciotti[53] have applied ionic models to calculate the heats of dimerization for gaseous alkali halide dimer molecules, and the results are as follows:

$$2LiF \rightarrow Li_2F_2 \qquad \Delta H_0^\circ = -57.6 \text{ kcal/mol} \qquad (35)$$

$$2LiCl \rightarrow Li_2Cl_2 \qquad \Delta H_0^\circ = -54.7 \text{ kcal/mol} \qquad (36)$$

$$2LiBr \rightarrow Li_2Br_2 \qquad \Delta H_0^\circ = -52.3 \text{ kcal/mol} \qquad (37)$$

$$2LiI \rightarrow Li_2I_2 \qquad \Delta H_0^\circ = -48.9 \text{ kcal/mol} \qquad (38)$$

The calculated stability of Li_2H_2[16] agrees well with our experimental results, which place the dimerization energy of LiH close to that of LiBr given above. This supports the statement that the LiH dimer is similar to the alkali halide dimers.

In previous studies of vapor-solid equilibria involving Li_2I_2, Li_2Br_2, Li_2Cl_2[54] and other alkali halides[55], using a velocity selector with a molecular beam technique, it was concluded that the vapors in equilibrium with solid lithium halides consisted predominantly of dimeric species Li_2X_2. From the phase diagram of the Li-H system (see page 32) it is seen that at 850 K, when the atom fraction of hydrogen exceeds 10^5ppm, the LiH(g) phase exists, and by using the following relations determined from our previous work[48]:

$$\ln \frac{P_{Li_2D_2}}{X_D} = - \frac{1.225 \times 10^4}{T} + 11.5 \qquad (39)$$

and

$$\ln \frac{P_{LiD}}{X_D} = - \frac{2.368 \times 10^4}{T} + 14.8 \qquad (40)$$

Further, when it is assumed that $P_{Li_2H_2}/P_{LiH} \simeq P_{Li_2D_2}/P_{LiD}$, one obtains the partial pressure ratio of the dimer Li_2H_2 to the monomer LiH:

$P_{Li_2H_2}/P_{LiH} \simeq 138.7$ ($P_{Li_2H_2} = 2.96 \times 10^{-5}$ atm), $P_{LiH} = 2.13 \times 10^{-7}$ atm at $X_H = 10^5$ ppm and T = 850 K).

This means that the dimer Li_2H_2 is predominant. This is in accord with the statements made for alkali halide systems by other authors.

E1.2.6 Binding Energy of the Ion Molecule $Li_2H_2^+$

A more accurate determination of the ionization potential has been carried out by the extrapolated voltage difference method. Fig. 5 shows an ionization efficiency curve for Li^+ and $Li_2H_2^+$. Five determinations of $Li_2H_2^+$ gave: I.P.($Li_2H_2^+$) = 6.6 eV, with a reproducibility of 0.05 eV; the estimated accuracy is 0.3 eV.

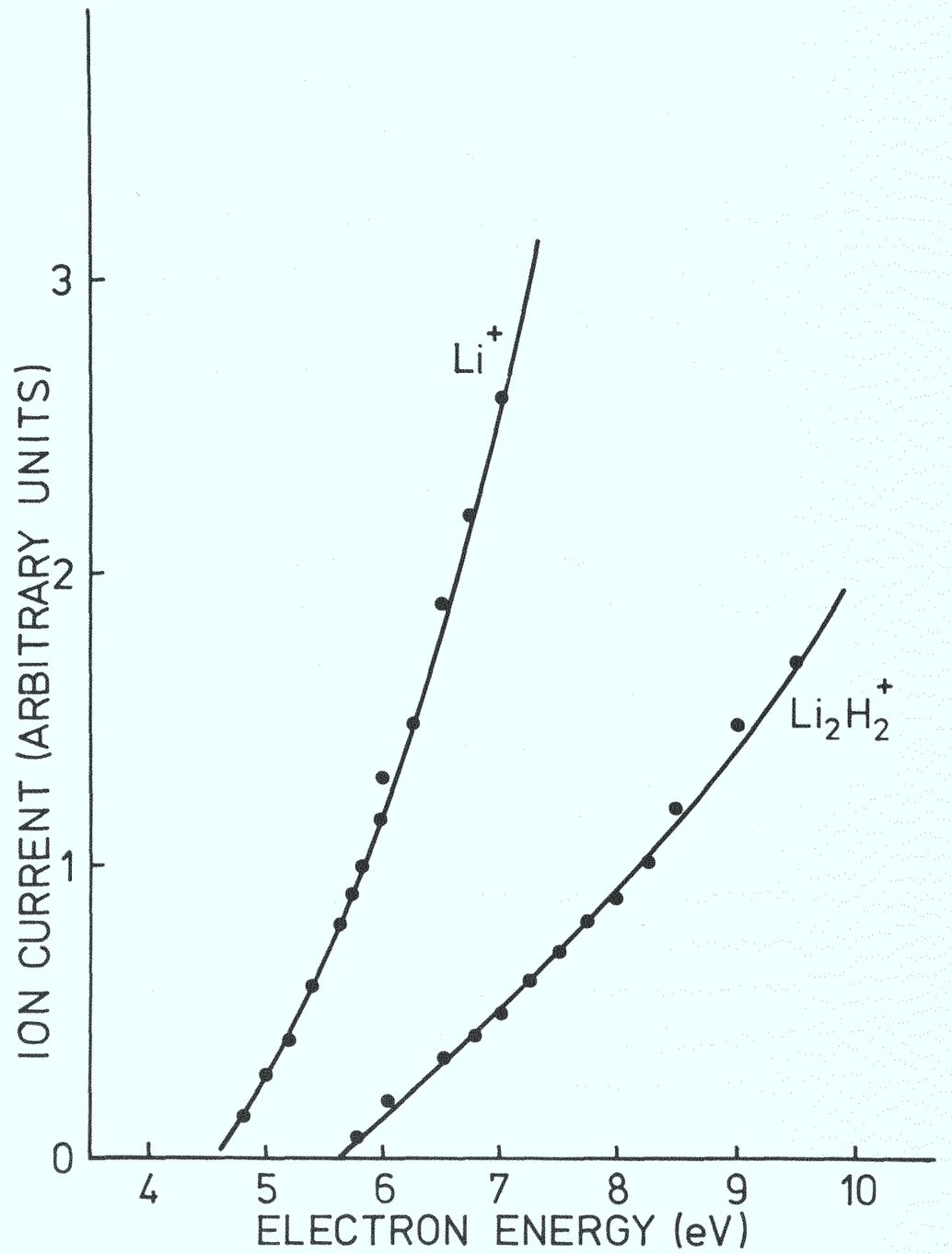


Fig. 5 Ionization efficiency curves for Li^+ and $Li_2H_2^+$.

Table XIX: Thermochemistry of the Molecule $Li_2H_2^+$

Ionization Potential	Binding Energy	Products of Reaction
I.P.	$D_0^\circ(Li_2H_2^+)$	
(eV)	(kcal/mol)	
	136.5 ± 11	$Li^+ + Li + 2H$
6.6 ± 0.3		
	325.3 ± 11	$H^+ + H + 2Li$

When the measured values for the ionization potential: I.P.(Li_2H_2) = 6.6 eV, and the atomization energy: $D_0^\circ(Li_2H_2)$ = 164.3 ± 10 kcal/mol are combined with the ionization potentials:
I.P.(H) = 13.598 ± 0.002 eV[49], and I.P.(Li) = 5.392 eV[49], one obtains the binding energies for the ions, and these are given in Table XIX.

Finally, by using the thermodynamic properties of $Li_2H(g)$, $LiH_2(g)$ and $Li_2H_2(g)$ measured in this work, the energies of some reactions which are probably interesting for the study of molecular beam kinetics and the theoretical chemistry of the Li-H system[56, 57, 58] were calculated:

$Li^+ + 2H \rightarrow LiH_2$	(exothermic by 10.91 eV)	(41)
$Li + 2H \rightarrow LiH_2$	(exothermic by 5.52 eV)	(42)
$Li + H_2 \rightarrow LiH_2$	(exothermic by 1.04 eV)	(43)
$Li^+ + H_2 \rightarrow LiH_2$	(exothermic by 6.43 eV)	(44)
$Li_2 + 2H \rightarrow LiH_2 + Li$	(exothermic by 4.41 eV)	(45)
$Li_2 + H_2 \rightarrow LiH_2 + Li$	(exothermic by 0.07 eV)	(46)
$Li_2^+ + 2H \rightarrow LiH_2 + Li$	(exothermic by 9.27 eV)	(47)
$Li_2^+ + H_2 \rightarrow LiH_2 + Li$	(exothermic by 4.79 eV)	(48)
$2Li + H \rightarrow Li_2H$	(exothermic by 3.90 eV)	(49)

$Li_2 + H \rightarrow Li_2H$ (exothermic by 2.80 eV) (50)

$Li_2^+ + H \rightarrow Li_2H$ (exothermic by 7.66 eV) (51)

$2Li + 2H \rightarrow Li_2H_2$ (exothermic by 7.14 eV) (52)

$2Li + H_2 \rightarrow Li_2H_2$ (exothermic by 2.65 eV) (53)

$Li_2 + 2H \rightarrow Li_2H_2$ (exothermic by 6.03 eV) (54)

$Li_2^+ + 2H \rightarrow Li_2H_2$ (exothermic by 10.89 eV) (55)

E2 The Alkali Metal Systems

The importance of the available physical chemical properties for the technical application of alkali metal vapors has been described in detail before.

Using low temperature matrix spectroscopic techniques, several groups have reported ultra violet and visible absorption spectra of Ag_n ($n = 1 \sim 6$)[59], Cu_n($n = 1 \sim 4$)[60] and Ni_n($n = 1 \sim 3$)[61].

Raman and IR measurements have been carried out on Ag clusters[62], and an ESR spectrum of Na clusters has been observed[63].

Some good results concerning cluster investigation were obtained by matrix spectroscopic techniques, but the interpretation of the spectra is made difficult by many problems[62]:

1. Several different clusters are present in the matrix at the same time. The assignments of spectroscopic features to one species rely heavily on additional hypotheses (non-overlapping of bonds, statistical growth of cluster).

2. The spectrum of the metal cluster is more or less perturbed by surrounding rare gas atoms (matrix shift) and neighbouring metal atoms and clusters. The amount and direction of spectral shifts as compared with the gas phase is very difficult to account for.

3. Low sensitivity of the matrix spectroscopic techniques.

We used the quadrupole mass spectrometer with high sensitivity to investigate the existence of lithium clusters.

E2.1 Thermodynamics of the Lithium Clusters $Li_2(g)$ and $Li_3(g)$

E2.1.1 Experimental

The apparatus used and the experimental procedure has been described elsewhere. The Knudsen cells used were machined from molybdenum. The inside diameter of the cell was 13 mm and the orifice diameter was 0.6 mm. The cells were degassed by heating under vacuum before loading with 0.5 g of 99.99 % lithium (Research Organic/Inorganic Chemical Corporation, Sun Valley, CA).

The measurements of the gaseous equilibria $Li(s,l) \rightarrow Li(g)$ (56), $2Li(s,l) \rightarrow Li_2(g)$(57), $Li_2(g) \rightarrow 2Li(g)$(58), $3Li(s,l) \rightarrow Li_3(g)$(59) and $2Li_2(g) \rightarrow Li_3(g) + Li(g)$(60) were carried out in a temperature range from 550 to 1050 K.

For the evaluation of third law enthalpy changes in pressure dependent reactions, a knowledge of ionization cross sections and multiplier gains is essential; whereas in pressure independent reactions, the assumption that these factors mutually cancel each other is a reasonable approximation.

Partial pressures P_i were determined from the relation

$$P_i = K \frac{I_i T}{\sigma_i \beta \gamma_i}$$

where I_i is the ion intensity, σ_i is the relative ionization cross section, β is the isotopic abundance for which the following values are used: ^7Li = 92.6 %, $^7Li^7Li$ = 85.7 % and $^7Li^7Li^7Li$ = 79.4 %, γ_i is the multiplier gain and K is the pressure calibration constant. The pressure calibration constant K was obtained from a direct comparison of the partial pressure of lithium with the Li^+ ion current at a number of temperatures before the ions Li_2^+ and Li_3^+ were observed. The multiplier gains were measured as 1.25×10^5 and 1.20×10^5 for Li and Li_2. The multiplier gain for triatomic lithium $\gamma_{Li_3} = \gamma_{Li} = 1.25 \times 10^5$ was assumed. Atomic ionization cross sections were taken from Mann, while the molecular ionization cross section was calculated by taking 0.75 of the sum of Mann's atomic cross sections[38]. It was assumed that a similar relation holds between the trimer and the dimer[67] and deduced that $\sigma_{Li_3} = 1.88\sigma_{Li}$.

E2.1.2 Thermodynamics of the Molecules Li_2 and Li_3

The Gibbs energy functions for Li(s,l), Li(g), and Li_2(g) were taken from the data of Stull and Sinke[64], and from the JANAF tables. The Gibbs energy function for Li_3(g) was calculated on the basis of the two proposed kinds of molecular structure: one with a bond angle of 137° and the other with a bond angle of 34°, and estimated molecular parameters given by Companion, Steible and Starshak[65]. The resulting numerical values of the free energy function at 800, 900, 1000, 1100, and 1200 K for Li_3(g), with bond angle 137°, are 59.99, 61.31, 62.50, 63.57 and 64.56, and those for Li_3(g) with bond angle 34° are 64.29, 65.81, 67.18, 68.43, and 69.58, respectively.

A comparison of the second and third law values of ΔH_0^o for reactions (56), (57), (58), (59) and (60) is given in Table XX.

Table XX: The Third and Second Law Enthalpies for the Gas Reactions Involving Li(g), $Li_2(g)$ and $Li_3(g)$

Reaction	ΔH_0°(Second Law) kcal/mol		ΔH_0°(Third Law) kcal/mol	
	Bond Angle 34°	Bond Angle 137°	Bond Angle 34°	Bond Angle 137°
$3Li(s,l) = Li_3(g)$	75.2 ± 2.5	77.4 ± 2.5	72.89 ± 0.35	68.35 ± 0.52
$2Li_2(g) = Li_3(g) + Li(g)$	10.7 ± 0.65	12.9 ± 0.65	10.68 ± 0.14	6.15 ± 0.33
$Li(s,l) = Li(g)$	39.3 ± 1.0		38.5 ± 0.1	
$2Li(s,l) = Li_2(g)$	51.68 ± 1.4		51.55 ± 0.19	
$Li_2(g) = 2Li(g)$	24.50 ± 0.80		25.45 ± 0.17	

It is shown in Table XX that there is good agreement for reactions (59) and (60) between the third and second law enthalpies for the structure with a bond angle of 34^{o}. Because of this agreement and of the fact that the second law enthalpies are independent of any chosen structure, it may be concluded that the measurements were conducted under equilibrium conditions in the Knudsen cell, and the value of ΔH_0^o evaluated for $Li_3(g)$ with a bond angle of 34^{o} has a greater probability of being correct.

From the evaluation of the third law enthalpies, the average values, with estimated errors, of the atomization energies are obtained:

$$D_0^o(Li_2) = 25.5 \pm 1.5 \text{ kcal/mol}$$

and

$$D_0^o(Li_3) = 41.5 \pm 4.0 \text{ kcal/mol.}$$

The following heats of formation were also obtained:

$$\Delta H_0^o(Li) = 38.5 \pm 1.0 \text{ kcal/mol}$$

$$\Delta H_0^o(Li_2) = 51.5 \pm 2.0 \text{ kcal/mol}$$

and

$$\Delta H_0^o(Li_3) = 73.0 \pm 4.0 \text{ kcal/mol}$$

E2.1.3 The Binding Energies of the Ion Molecules Li_2^+ and Li_3^+

The Li_2^+ and Li_3^+ thresholds were measured against Li^+, and the results were evaluated by the extrapolated voltage difference method.

The ionization potentials for Li_2 and Li_3 were determined as:

$$I.P.(Li_2) = 4.86 \pm 0.1 \text{ eV}$$

and

$$I.P.(Li_3) = 4.35 \pm 0.2 \text{ eV}.$$

The binding energies of Li_2^+ and Li_3^+ were:

$$Li_2^+ \rightarrow Li^+ + Li \qquad D_0^\circ(Li_2^+) = 37.7 \pm 2.0 \text{ kcal/mol}$$

$$Li_3^+ \rightarrow Li^+ + Li + Li \qquad D_0^\circ(Li_3^+) = 65.5 \pm 4.3 \text{ kcal/mol}$$

E2.2 Thermodynamics of the Lithium Cluster $Li_4(g)$

E2.2.1 Identification of the Molecule Li_4

The apparatus used for this work has been described in detail earlier. To minimize the interference contributed by impurities such as nitrogen, oxygen and hydrogen[66] in the lithium sample in the identification of gas species, three different compositions of lithium have been used in this series of experiments: enriched ^6Li > 97 % and natural lithium (^7Li = 93 %, ^6Li = 7.0 %), as well as a mixture of ^6Li and natural lithium (^6Li = 56.8 %, ^7Li = 43.2 %).

The isotopic abundance and relative ion intensities for three different kinds of sample at a temperature of about 1000 K are given in Tables XXI, XXII and XXIII.

The measured relative intensities for the isotopes of Li_4 agree very well with the theoretical values for lithium samples of three different compositions, so that the presence of Li_4 is undoubtedly proved.

The threshold appearance potentials evaluated by the vanishing current method for Li^+, Li_2^+, and Li_3^+ are 5.5, 5.0 and 4.5 eV, respectively, the uncertainty being ± 0.3 eV.

Table XXI: Isotopic Abundance and Relative Intensity of the Lithium Species for Sample A (^{6}Li = 7.0%, ^{7}Li = 93.0%)

	Calculation		Experimental	
Molecule	Isotopic Abundance(%)	Relative Intensity	m/e	Relative Intensity
$^{6}Li_2$	$5.0x10^{-1}$	$5.78x10^{-3}$	12	$5.70x10^{-3}$
$^{6}Li^{7}Li$	13.0	$1.50x10^{-1}$	13	$1.47x10^{-1}$
$^{7}Li_2$	86.5	1	14	1
$^{6}Li_3$	$3.43x10^{-2}$	$4.27x10^{-4}$	18	
$^{6}Li_2{}^{7}Li$	1.37	$1.70x10^{-2}$	19	$1.72x10^{-2}$
$^{6}Li^{7}Li_2$	18.2	$2.26x10^{-1}$	20	$2.1\ x10^{-1}$
$^{7}Li_3$	80.4	1	21	1
$^{6}Li_4$	$2.4\ x10^{-3}$	$3.21x10^{-5}$	24	
$^{6}Li_3{}^{7}Li$	$1.28x10^{-1}$	$1.71x10^{-3}$	25	
$^{6}Li_2{}^{7}Li_2$	2.54	$3.4\ x10^{-2}$	26	$3.0\ x10^{-2}$
$^{6}Li^{7}Li_3$	22.5	$3.0\ x10^{-1}$	27	$3.2\ x10^{-1}$
$^{7}Li_4$	74.8	1	28	1

Table XXII: Isotopic Abundance and Relative Intensity of the Lithium Species for Sample B (^{6}Li = 56.8%, ^{7}Li = 43.2%)

	Calculation		Experimental	
Molecule	Isotopic Abundance(%)	Relative Intensity	m/e	Relative Intensity
$^{6}Li_2$	32.30	$6.58x10^{-1}$	12	$6.35x10^{-1}$
$^{6}Li^{7}Li$	49.10	1	13	1
$^{7}Li_2$	18.70	$3.81x10^{-1}$	14	$3.75x10^{-1}$
$^{6}Li_3$	18.30	$4.38x10^{-1}$	18	$4.2\ x10^{-1}$
$^{6}Li_2{}^{7}Li$	41.80	1	19	1
$^{6}Li^{7}Li_2$	31.80	$7.61x10^{-1}$	20	$7.80x10^{-1}$
$^{7}Li_3$	$8.06x10^{-1}$	$1.93x10^{-1}$	21	$2.1\ x10^{-1}$
$^{6}Li_4$	10.40	$2.88x10^{-1}$	24	$4.0\ x10^{-1}$
$^{6}Li_3{}^{7}Li$	31.70	$8.78x10^{-1}$	25	$8.8\ x10^{-1}$
$^{6}Li_2{}^{7}Li_2$	36.10	1	26	1
$^{6}Li^{7}Li_3$	18.30	$5.07x10^{-1}$	27	$5.0\ x10^{-1}$
$^{7}Li_4$	$3.48x10^{-1}$	$9.64x10^{-2}$	28	

Table XXIII: Isotopic Abundance and Relative Intensity of the Lithium Species for Sample C (^{6}Li = 97.0%, ^{7}Li = 3.0%)

	Calculation		Experimental	
Molecule	Isotopic Abundance(%)	Relative Intensity	m/e	Relative Intensity
$^{6}Li_2$	94.10	1	12	1
$^{6}Li^{7}Li$	5.82	6.18×10^{-2}	13	6.00×10^{-2}
$^{7}Li_2$	9.00×10^{-2}	9.56×10^{-4}	14	9.50×10^{-4}
$^{6}Li_3$	91.30	1	18	1
$^{6}Li_2{}^{7}Li$	8.47	9.28×10^{-2}	19	9.14×10^{-2}
$^{6}Li^{7}Li_2$	2.62×10^{-1}	2.87×10^{-3}	20	2.85×10^{-3}
$^{7}Li_3$	2.70×10^{-3}	2.96×10^{-5}	21	
$^{6}Li_4$	88.5	1	24	1
$^{6}Li_3{}^{7}Li$	11.0	1.24×10^{-1}	25	1.20×10^{-1}
$^{6}Li_2{}^{7}Li_2$	5.08×10^{-1}	5.76×10^{-3}	26	
$^{6}Li^{7}Li_3$	1.05×10^{-2}	1.19×10^{-4}	27	
$^{7}Li_4$	8.1×10^{-5}	9.15×10^{-7}	28	

These appearance potentials agree with the known ionization potentials of the corresponding neutral gaseous species given in the literature; thus the appearance potentials showed that the ions observed are produced by ionization of the corresponding neutrals.

Depending on the purity of the lithium sample (in most cases for enriched ^{6}Li), the mass numbers (m/e) 25 and 26 are sometimes observed. It could be deduced from the intensity ratios that these spectra are caused by the presence of magnesium as impurity. However, the contribution to the intensity of mass number (m/e) 24 caused by 24 Mg could be calculated by using the isotopic abundance of magnesium. In most of these measurements magnesium has not been observed.

E2.2.2 Equilibrium Measurements, Atomization Energy, and Heat of Vaporization of $Li_4(g)$

The measurements of the gaseous exchange equilibria:

$$4Li(s,l) \rightarrow Li_4(g) \qquad (61)$$

$$Li_4(g) + Li_2(g) \rightarrow 2Li_3(g) \qquad (62)$$

and

$$Li_4(g) + Li(g) \rightarrow Li_3(g) + Li_2(g) \qquad (63)$$

were carried out at temperatures between 980 K and 1135 K. For the dissociation reaction (61), the absolute pressures necessary were calculated from the relation $Pi = K\, I_i^+ T/\sigma_i \gamma_i C_i$, where K is the pressure calibration constant, σ_i the ionization cross section, γ_i the multiplier gain and C_i the relative isotope abundance for the Li sample. The sensitivity constant was determined by using the known dissociation energy of Li_2, $D_0^\circ(Li_2) = 25.5$ kcal mol[32].

The ionization cross section for Li_4 was calculated as: $\sigma_{Li_4} = 0.75(\sigma_{Li_2} + \sigma_{Li_2})$, $\sigma_{Li_2} = 0.75(\sigma_{Li} + \sigma_{Li})$. The atomic cross section for lithium was taken from Mann's compilation[38]. The multiplier gains were measured as 1.20×10^5 for Li and Li_2; that for Li_4 was assumed to be: $\gamma_{Li_4} = \gamma_{Li_2} = 1.20 \times 10^5$. The free energy functions for Li(s,l), Li(g) and $Li_2(g)$ were taken from the JANAF tables[41], and that for $Li_3(g)$ was taken from previous work[32]. For the $Li_4(g)$ cluster the free energy function has been calculated for four different structures:

square planar (D_{4h}), dispenoid (D_{2d}), rhombic (D_{2h}) and linear cluster. The fundamental vibrational frequencies of the square, disphenoid and rhombic structures, which are needed for the calculation of the free energy function, have been taken from the literature[27,31]; those for the linear cluster have been estimated. Table XXIV shows the free energy function for $Li_4(g)$ as a function of temperature.

A typical set of relative ion currents measured at 1100 K: Sample A: ^7Li = 93%, ^6Li = 7.00%

$^7Li = 1$ $\qquad$ $^7Li^7Li = 4.67 \times 10^{-2}$

$^7Li^7Li^7Li = 4.70 \times 10^{-5}$ $\qquad$ $^7Li^7Li^7Li^7Li = 6.70 \times 10^{-6}$

The third law results for the dissociative reaction (61), and the isomolecular reactions (62) and (63), are given in Tables XXV, XXVI and XXVII. The error terms quoted are standard deviation. The reaction enthalpies for reactions(62) and (63), calculated by using the second law treatment, are $\Delta H^{\circ}_{1030} = 20.5 \pm 3.0$ kcal/mol (62) and $\Delta H^{\circ}_{1090} = 9.80 \pm 6.0$ kcal/mol (63).
(Because of the small range of temperature in the measurement of the reaction (61), the second law value has not been evaluated).

Table XXIV: Free Energy Functions, $-(G_T^\circ - H_0^\circ)/T$, in cal mol^{-1} K^{-1} for $Li_4(g)$

Temperature K	Free Energy Function, $-(G_T^\circ - H_0^\circ)/T$			
	Square	Dispenoid	Rhombic	Linear
900	71.95	67.90	72.85	68.38
1000	73.67	69.60	74.76	70.00
1100	75.34	71.15	76.49	71.49
1200	76.70	72.49	78.09	72.85
1300	78.13	73.89	79.57	74.12
1400	79.56	75.29	80.94	75.29
1500	80.99	76.69	82.27	76.39

Table XXV: Third Law Enthalpies for the Reaction: $4Li(s,l) \rightarrow Li_4(g)$

T	-RlnK	$-\Delta[G_T^\circ - H_0^\circ)/T]$ (cal mol^{-1} K^{-1})				ΔH_0° (kcal mol^{-1})			
(K)		Square	Disphenoid	Rhombic	Linear	Square	Disphenoid	Rhombic	Linear
986	4.42	33.34	29.30	34.40	29.69	76.27	72.29	77.32	72.67
998	4.32	33.21	29.14	34.30	29.54	76.24	72.18	77.33	72.58
1008	4.27	33.12	29.04	34.22	29.44	76.48	72.37	77.59	72.77
1018	4.23	33.03	28.94	34.14	29.34	76.73	72.56	77.86	72.97
						76.43 ±0.23	72.35 ±0.16	77.53 ±0.26	72.75 ±0.17

Table XXVI: Third Law Enthalpies for the Reaction: $Li_4(g) + Li_2(g) \rightarrow 2Li_3(g)$

T	-RlnK	$-\Delta[(G_T^\circ - H_0^\circ)/T]$(cal mol^{-1} K^{-1})				ΔH_0°(kcal mol^{-1})			
(K)		Square	Disphenoid	Rhombic	Linear	Square	Lisphenoid	Rhombic	Linear
1093	10.60	11.44	15.62	10.29	15.28	24.04	28.60	23.00	28.23
1053	10.56	11.44	15.57	10.29	15.57	23.17	27.20	22.00	27.20
1135	8.94	11.50	15.70	10.29	15.35	23.20	28.00	21.83	27.57
986	11.36	11.42	15.48	10.29	15.11	22.46	26.46	21.34	26.10
998	11.72	11.43	15.50	10.29	15.12	23.10	27.20	21.97	26.78
1008	11.91	11.43	15.50	10.29	15.13	23.50	27.60	22.37	27.25
1018	11.98	11.43	15.52	10.29	15.15	23.80	28.00	22.67	27.62
993	12.19	11.42	15.49	10.29	15.12	23.45	27.48	22.32	27.12
1013	11.54	11.43	15.50	10.29	15.15	23.27	27.39	22.11	27.04
1018	11.47	11.43	15.52	10.29	15.15	23.32	27.48	22.15	27.10
1028	11.30	11.43	15.54	10.29	15.16	23.37	27.57	22.20	27.20
1043	10.81	11.43	15.55	10.29	15.18	23.19	27.49	22.01	27.11
					Av.	23.32 ±0.40	27.54 ±0.50	22.16 ±0.42	27.19 ±0.50

Second law value ΔH°_{1030} = 20.5 ± 3.0 kcal/mol

Table XXVII: Third Law Enthalpies for the Reaction: $Li_4(g) + Li(g) \rightarrow Li_3(g) + Li_2(g)$

T	-RlnK	$-\Delta[(G_T^\circ - H_0^\circ)/T]$ (cal mol^{-1} K^{-1})				ΔH_0° (kcal mol^{-1})			
(K)		Square	Disphenoid	Rhombic	Linear	Square	Disphenoid	Rhombic	Linear
1130	2.11	8.61	12.75	7.23	12.40	12.11	16.79	10.55	16.39
1093	1.94	8.60	12.70	7.33	12.33	11.78	16.27	10.13	15.60
1053	2.51	8.59	12.68	7.38	12.31	11.69	16.00	10.41	15.61
1135	0.48	8.61	12.75	7.23	12.41	10.32	15.02	8.75	14.63
						11.48	16.02	9.96	15.55
						±0.80	±0.74	±0.83	±0.72

Second law value: $\Delta H_{1090}^\circ = 9.8 \pm 6.0$ kcal/mol

It is shown that the second law enthalpy of the reaction (62) agrees very well with that of the third law values for the square and rhombic structures. Good agreement between the second and third law enthalpies in the reaction (63) has been found for square and rhombic Li_4. It follows that of the four possible structures for Li_4, the square and rhombic configuration are the most probable; but from the results of calculation and experiments made up till now, it is not possible to decide between these two.

The heat of vaporization for $Li_4(g)$ has been obtained directly from reaction (61); the selected value of the heat of vaporization of Li_4: $\Delta H_0^\circ(Li_4)$ = 77.0 ± 3.0 kcal/mol, was obtained from the average value of the square and the rhombic structures.

Combining the third law values of reactions (61), (62) and (63) with the atomization energies: $D_0^\circ(Li_2)$ = 25.5 ± 1.5 kcal/mol, $D_0^\circ(Li_3)$ = 41.5 ± 4.0 kcal/mol, and the heat of formation: $\Delta H_0^\circ(Li)$ = 38.5 ± 1.0 kcal/mol, yields the corresponding atomization energies for Li_4. These are:

$D_0^\circ(Li_4)$ = 76.6 ± 1.0 kcal/mol (rhombic),

$D_0^\circ(Li_4)$ = 77.6 ± 1.0 kcal/mol (square) from reaction (61),

$D_0^\circ(Li_4)$ = 78.5 ± 3.5 kcal/mol(rhombic),

$D_0^\circ(Li_4)$ = 79.5 ± 3.5 kcal/mol (square) from reaction (62)

and

$D_0^\circ(Li_4)$ = 77.0 ± 3.0 kcal/mol (rhombic),

$D_0^\circ(Li_4)$ = 78.0 ± 3.0 kcal/mol (square) from reaction (63)

respectively. The atomization energies for Li_4 obtained from these three reactions are in good agreement. The selected mean value for the rhombic and square structures is: $D_0^\circ(Li_4)$ = 77.8 ± 3.0 kcal/mol.

E2.2.3 Ionization Potential of Li_4 and Binding Energy of Li_4^+

The ionization potentials of Li, Ag, Au, H_2O, N_2 and Ar were used to calibrate the electron energy of the mass spectrometer.

Fig. 6 shows an ionization efficiency curve for Li^+ and Li_4^+. An evaluation of the threshold appearance potential was made by the extrapolated voltage difference method. The Li_4^+ threshold was measured against Li^+(I.P. = 5.39 eV), Li_2^+(I.P. = 4.86 eV) and Li_3^+(I.P. = 4.35 eV).

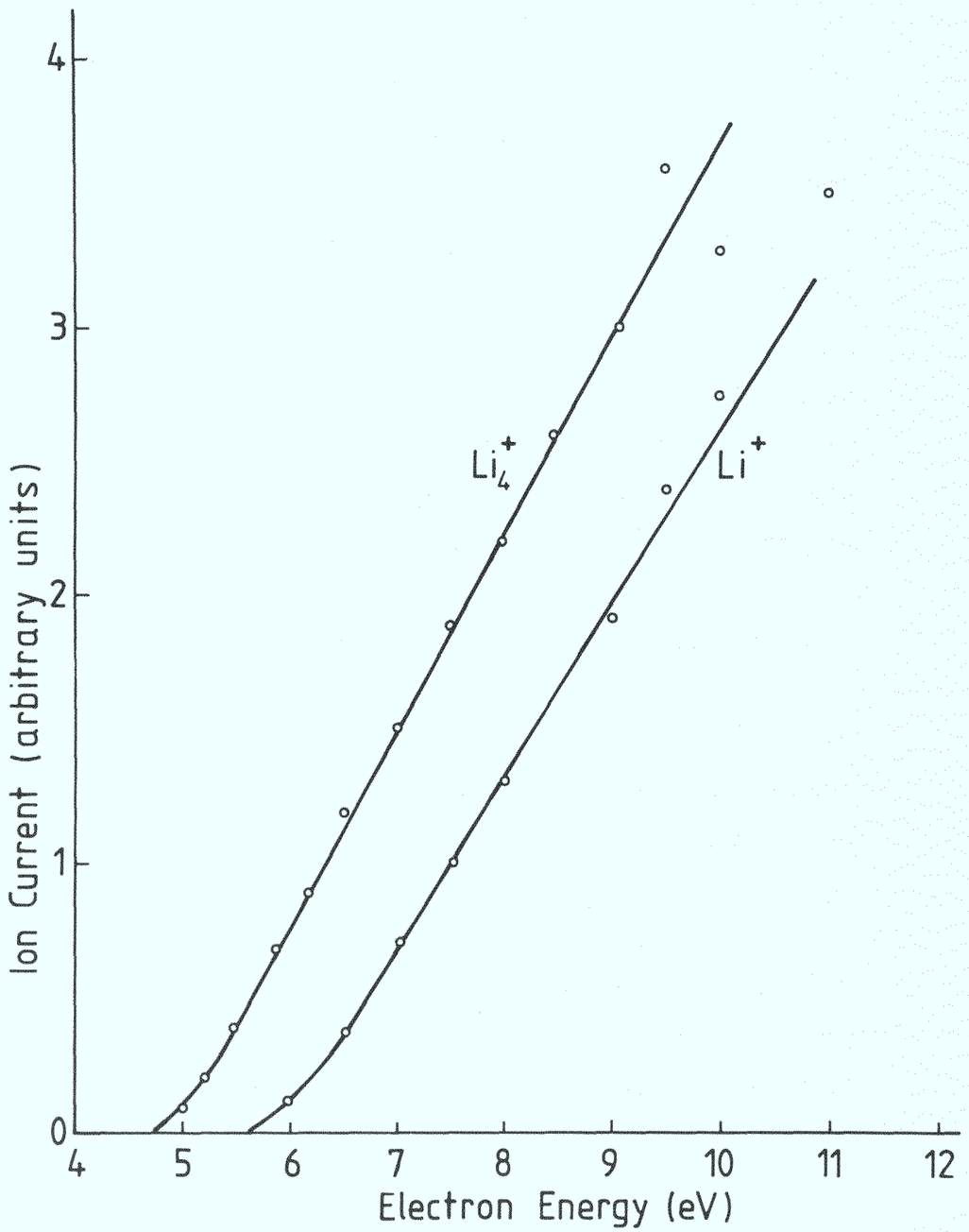


Fig. 6 Ionization efficiency curves for Li^+ and Li_4^+.

Three determinations of the ionization potential gave : I.P.(Li_4) = 4.69 eV, with a reproducibility of 0.05 eV; the estimated accuracy is 0.2 eV.

There is no information about the electronic spectrum of gaseous Li_4; therefore no correction for the measured ionization potential due to thermal population is possible. The fact that the measured threshold appearance potentials for Li^+, Li_2^+ and Li_3^+ are very close to the known ionization potentials of the respective neutrals shows that one can expect that the measured appearance potential of Li_4^+ is close to the ionization potential.

If the measured value for the ionization potential I.P.(Li_4) = 4.69 eV, and the atomization energy $D_0^\circ(Li_4)$ = 77.8 ± 3.0 kcal/mol, are combined with I.P.(Li) = 5.39 eV, a binding energy: $D_0^\circ(Li_4^+)$ = 94.0 ± 3.0 kcal/mol is obtained for the reaction $Li_4^+ \rightarrow Li^+ + 3Li$.

E2.2.4 Discussion

By using the method of diatomics-in-molecule (DIM), A.L. Companion[27] has predicted the atomization energy of Li_4, and given: $D_0^\circ(Li_4)$ = 63.94 kcal/mol.

B.T. Pickup[29] has used the same method 'DIM' to calculate the atomization energy and given a value of $D_0^o(Li_4)$ = 68.16 kcal/mol for square Li_4. Many years later, A.L. Companion[67] has recalculated by DIM, with more accurate $^3\Sigma_u^+$ potential, an atomization energy of: $D_0^o(Li_4)$ = 71 kcal/mol. The atomization energies of Li_4 obtained by using the DIM method are lower than the value presented in this work. One should mention, that by using more accurate input data for the DIM calculation, a higher value of the atomization energy is obtained. Companion's latest value of $D_0^o(Li_4)$ = 71 kcal/mol, is very close to the results presented here.

Beckmann et al.[31] have used the ab initio C.I. method to study the properties of the Li_4 cluster, and predicted the ionization potentials of Li_4 to be: I.P.(Li_4) = 4.54 eV for the rhombic structure and: I.P.(Li_4) = 4.67 eV, for the square structure. These are in excellent agreement with the measured value: I.P.(Li_4) = 4.69 eV, obtained in this work. This supports the statement, deduced from the experiment, that the square and rhombic structures are the most favorable for the Li_4 cluster.

In Table XXVIII are shown the properties of some lithium clusters. It is seen that the energy per Li-Li bond decreases with increasing number of atoms in the cluster; this has been found also for the Na and Li clusters by theoretical calculation (Na to Na_4) [68].

The ionization potential of Li_3 is lower than that of Li_4. Herrmann, Schumacher and Wöste [33] made a similar investigation by means of photoionization study in the Na and K system, and found that: $I.P.(Na_3) < I.P.(Na_4)$, and $I.P.(K_3) < I.P.(K_4)$.

Fig. 7 shows the ionization potential, heat of formation and bond energy per Li-Li bond as a function of the number of lithium atoms n in a cluster. It seems that all of these three properties each tend to a quasi constant value above Li_4. Further detailed study on lithium clusters with higher numbers of atoms is necessary to confirm the observations made in this work.

The heat of formation of lithium clusters can be calculated by the equation:

$$\Delta H_0^\circ(Li_n) = n \cdot \Delta E - D_0^\circ(Li_n), \qquad (64)$$

Table XXVIII: Some Thermochemical Properties of the Lithium Clusters

Cluster	Enthalpy of Formation (eV)	Atomization Energy per Atom (eV)	Ionization Potential (eV)	Energy per Li-Li Bond (eV)
Li	1.67	-	5.39	-
Li_2	2.24	0.56	4.86	1.11
Li_3	3.17	0.60	4.35	0.90
Li_4	3.35	0.85	4.69	0.85

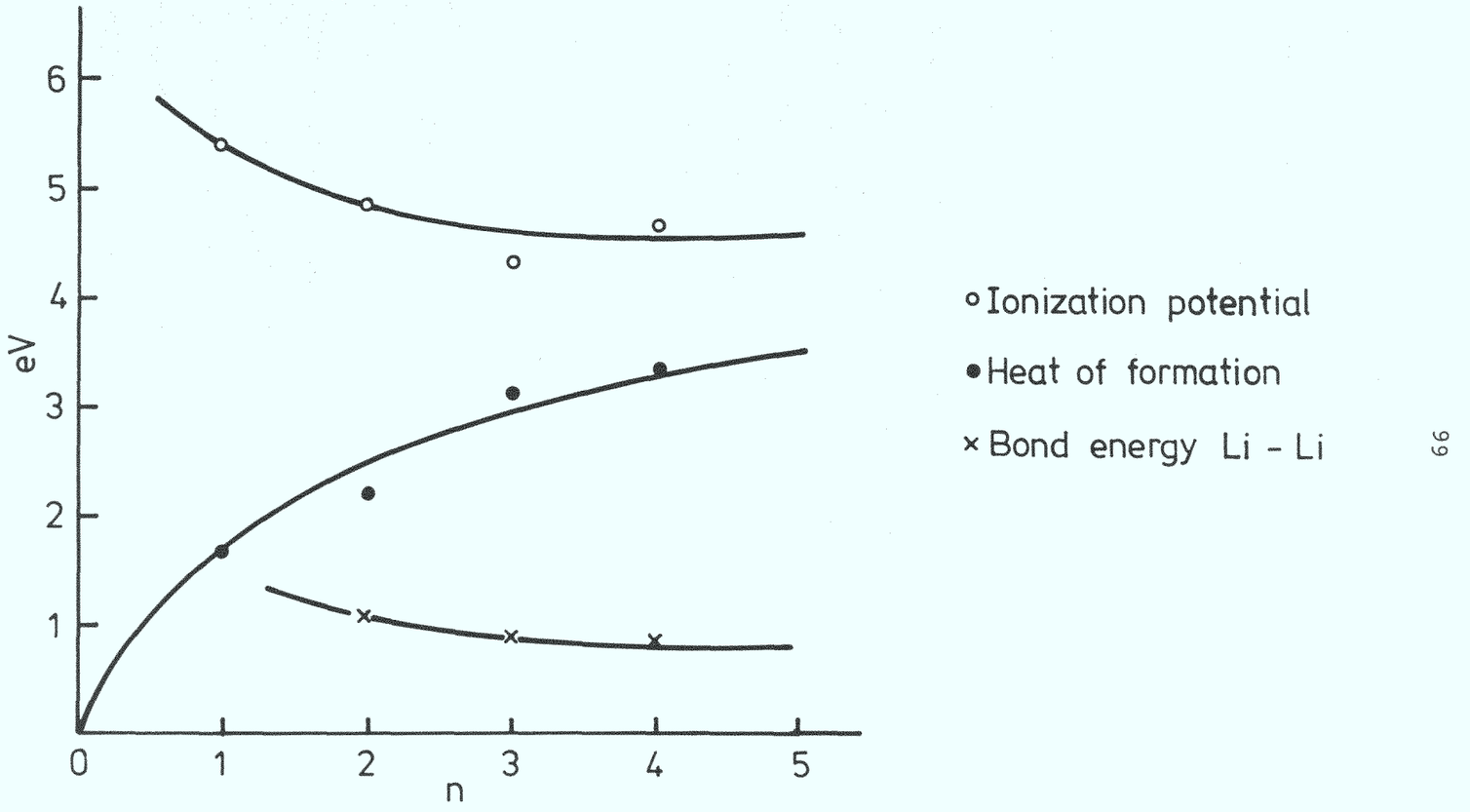


Fig. 7 Ionization potential, heat of formation and bond energy of the Li-Li bond as a function of the number of Li atoms in the lithium clusters.

where $\Delta H_0^\circ(Li_n)$ is the heat of formation of the lithium cluster in eV. $\Delta E = \Delta H_0^\circ(Li)$ is the cohesive energy of atomic lithium in eV. $D_0^\circ(Li_n)$ is the atomization energy of the lithium cluster in eV. n is the number of lithium atoms in the lithium cluster.

By using the literature values of $\Delta E = 1.66$ eV[32], $D_0^\circ(Li_2) = 1.11$ eV[32], $D_0^\circ(Li_3) = 1.80$ eV[32], and the here measured $D_0^\circ(Li_4) = 3.38$ eV, one obtains the heats of formation from equation (64): $\Delta H_0^\circ(Li_2) = 2.21$ eV, $\Delta H_0^\circ(Li_3) = 3.18$ eV and $\Delta H_0^\circ(Li_4) = 3.26$ eV; these agree well with the measured values (see Table XXVIII), suggesting that the measured values of the atomization energies and heats of formation of lithium clusters are consistent.

From the equation:

$$-\ln \frac{P_{Li}{}^4}{P_{Li_4}} = \frac{D_0^\circ(Li_4)}{RT} + \frac{\Delta[(G_T^\circ - H_0^\circ)/T]}{R} \qquad (65)$$

where P_{Li} is the equilibrium partial pressure of atomic lithium over metallic lithium in atm, P_{Li_4} is the equilibrium pressure of Li_4 over metallic lithium in atm., $D_0^\circ(Li_4)$ is the atomization energy in kcal/mol, $\Delta[(G_T^\circ - H_0^\circ)/T]$ is the change in the free energy function in (cal mol^{-1} K^{-1}) for the reaction $Li_4(g) \rightarrow 4Li(g)$;

one obtains the partial pressure of Li_4 as a function of temperature, which together with the measured partial pressures of Li, Li_2 and Li_3 [32] is given by the following equations:

$$\ln P_{Li} = - \frac{(1.869 \pm 0.19) \times 10^4}{T} + (11.6 \pm 0.12) \quad (66)$$

$$\ln P_{Li_2} = - \frac{(2.463 \pm 0.43) \times 10^4}{T} + (14.0 \pm 0.7) \quad (67)$$

$$\ln P_{Li_3} = - \frac{(3.594 \pm 1.20) \times 10^4}{T} + (17.8 \pm 1.2) \quad (68)$$

$$\ln P_{Li_4} = - \frac{(3.48 \pm 0.14) \times 10^4}{T} + (14.40 \pm 0.16) \quad (69)$$

e.g. the equilibrium partial pressures of lithium clusters at 1000 K are Li = 8.334×10^{-4} atm, $Li_2 = 4.869 \times 10^{-5}$ atm, $Li_3 = 1.324 \times 10^{-8}$ atm, and $Li_4 = 1.382 \times 10^{-9}$ atm.

In order to obtain a reasonable second law value for the reaction $Li_4 + Li_2(g) \rightarrow 2Li_3(g)$, the measurement of the equilibrium constant has been extended to high temperatures. The lithium pressure ranges from 5×10^{-4} to 10^{-2} atm in this experiment, so one may expect that the transition from molecular to viscous flow could occur in the high pressure region and the assumption of Knudsen effusion will no longer be justified.

By critical investigation in the measurement of the Li partial pressure ($p_{Li} \sim I_{Li} \times T$), it has been found that the plot of $\ln I_{Li} \times T$ vs. 1000/T deviates from the extrapolated line at a temperature of about 1137 K (see Fig. 8), at which the Li partial pressure is about $\sim 10^{-2}$ atm. The deviation may be caused mainly by the transition from molecular to viscous flow. The deviation remains constant with a factor of

$$(I \times T)_{meas.}/(I \times T)_{extrapol.} \approx 1.8).$$

Another investigation has been made by measuring the equilibrium constant for the reaction $Li_4(g) + Li_2(g) \rightarrow 2Li_3(g)$. As is shown in Fig. 9, the transition has occured at a temperature of 1137 K also. Consequently, the evaluation of thermodynamic data has been made by using the measured results below 1137 K. One should point out that the slope of the second law plot is the same for both molecular and viscous flow.

The quadrupole mass spectrometric system used has a high sensitivity, and ion currents of $\sim 3.5 \times 10^{-16}$ A can be detected. This detection limit corresponds to an effusion rate of 2.1×10^{8} particles $\times$ sec^{-1}. Furthermore, the dynamic range of the system is 10^{7}.

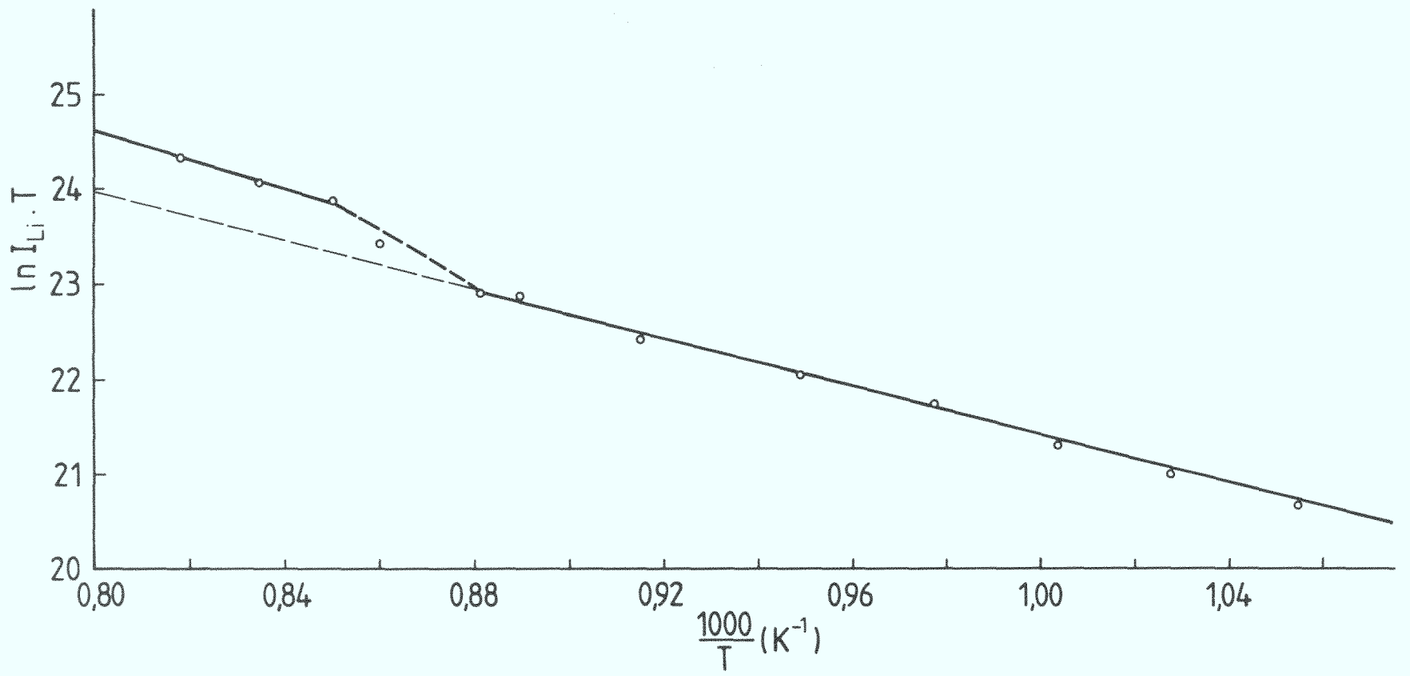


Fig. 8 Relative ion intensity of lithium as a function of temperature.

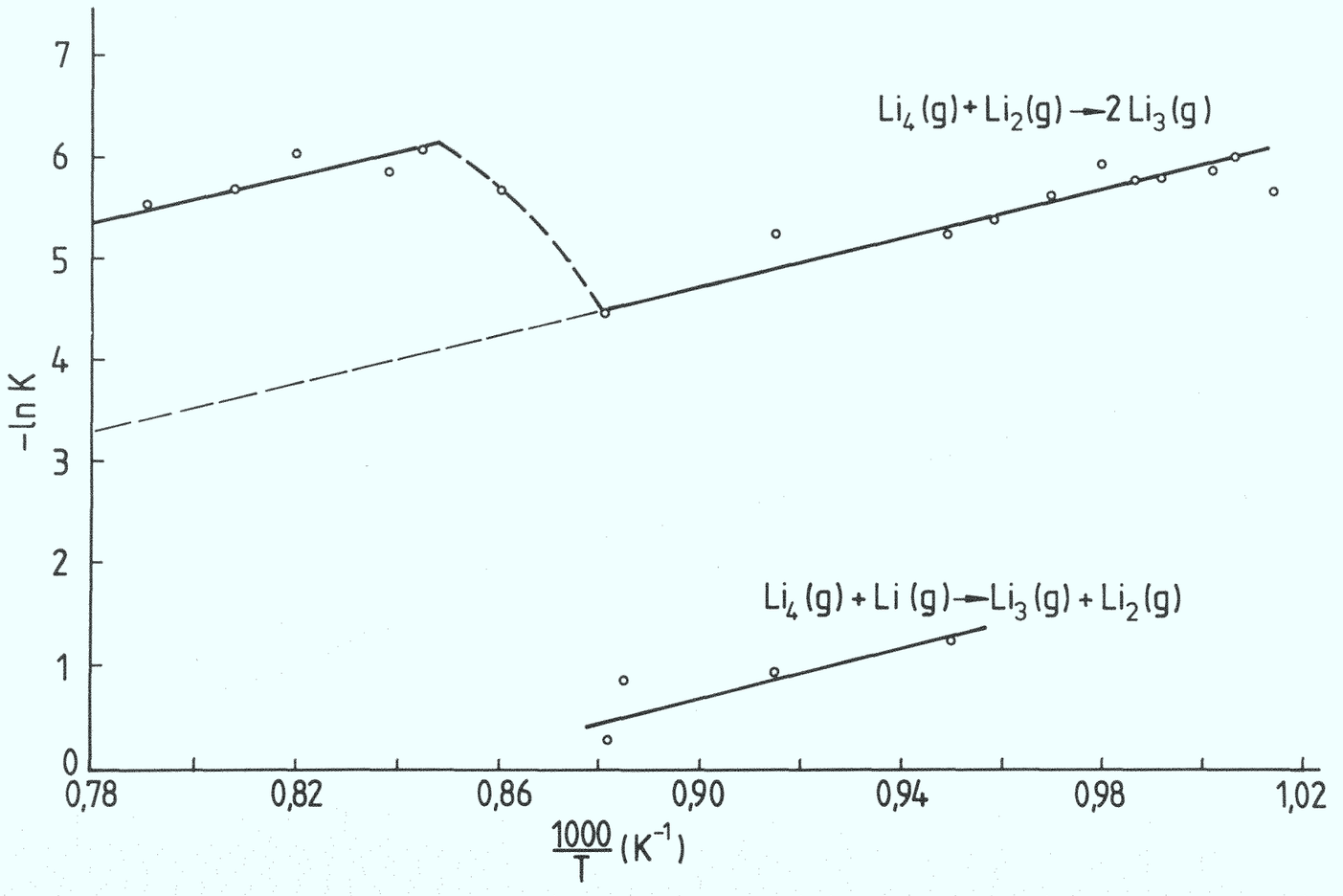


Fig. 9 Second law plot of the reactions
$Li_4(g) + Li_2(g) \rightarrow 2Li_3(g)$ and $Li_4(g) + Li(g) \rightarrow Li_3(g) + Li_2(g)$

During the measurement of the ionization potential of Li_4 molecules, a vacuum of $\leq 10^{-9}$ Torr was maintained, so a good reproducibility of ~0.05 eV has been achieved. The same experiences were made in the measurements of the ionization potential for the low intensity species LiH, Li_2H and LiH_2 in the Li-H system [44, 45, 50]. An accurancy of ± 0.2 eV for Li_4 is confident.

Finally, by using the atomization energies of Li_2, Li_3 and Li_4, and ionization potentials of Li, Li_2, Li_3 and Li_4, the energies of some interesting reactions for the study of molecular beam kinetics and the theoretical chemistry of the lithium cluster system were calculated:

$$Li^+ + Li \rightarrow Li_2 \qquad \text{(exothermic by 6.5 eV)} \quad (70)$$

$$Li^+ + 2Li \rightarrow Li_3 \qquad \text{(exothermic by 7.2 eV)} \quad (71)$$

$$Li^+ + Li_2 \rightarrow Li_3 \qquad \text{(exothermic by 6.1 eV)} \quad (72)$$

$$Li + Li_2 \rightarrow Li_3 \qquad \text{(exothermic by 0.7 eV)} \quad (73)$$

$$Li + Li_3 \rightarrow Li_4 \qquad \text{(exothermic by 1.58 eV)} \quad (74)$$

$$2Li_2 \rightarrow Li_4 \qquad \text{(exothermic by 1.17 eV)} \quad (75)$$

$$Li_2 + 2Li \rightarrow Li_4 \qquad \text{(exothermic by 2.27 eV)} \quad (76)$$

$$4Li \rightarrow Li_4 \qquad \text{(exothermic by 3.38 eV)} \qquad (77)$$

$$Li^+ + Li_3 \rightarrow Li_4^+ \qquad \text{(exothermic by 2.28 eV)} \qquad (78)$$

$$Li_2^+ + Li_2 \rightarrow Li_4^+ \qquad \text{(exothermic by 1.34 eV)} \qquad (79)$$

$$Li_2^+ + 2Li \rightarrow Li_4^+ \qquad \text{(exothermic by 2.44 eV)} \qquad (80)$$

$$Li^+ + 3Li \rightarrow Li_4^+ \qquad \text{(exothermic by 4.08 eV)} \qquad (81)$$

$$Li_3^+ + Li \rightarrow Li_4^+ \qquad \text{(exothermic by 3.04 eV)} \qquad (82)$$

E2.3 Experimental and Predicted Stability of Heteronuclear Diatomic Alkali Metal Molecules - Application of the Pauling Model.

The Pauling model has been successfully used to predict the stability of diatomic molecules. A number of workers have predicted the stability of these intermetallic compounds[37].

The dissociation energy of the heteronuclear diatomic molecule, D(A-B) can be estimated by the formula for the Pauling model of a polar bond:

$$D(A\text{-}B) = 1/2[D(A\text{-}A) + D(B\text{-}B)] + 23(X_A - X_B)^2 \qquad (83)$$

where D(A-B) is the dissociation energy of a compound AB, D(A-A) and D(B-B) are the dissociation energies of the dimers A_2 and B_2 and X_A and X_B are the corresponding electronegativities.

The dissociation energies of the alkali metal molecules Li_2, Na_2, K_2, Rb_2 and Cs_2, together with the electronegativities, are given in Table XXIX.

In the previous work[69], the dissociation energies and the ionization potentials of the molecules NaLi, NaK and KLi have been determined; and the following relation was found:

$$I.P.(A\text{-}B) \simeq 1/2\ [I.P.(A_2) + I.P.(B_2)] \qquad (84)$$

where I.P.(A-B) is the ionization potential of the heteronuclear diatomic alkali metal molecules, $I.P.(A_2)$ and $I.P.(B_2)$ are the ionization potentials of the dimeric alkali metal molecules A_2 and B_2.

Finally, the calculated dissociation energies and the ionization potentials for alkali metal compounds,together with the experimentally determined values,are given in Table XXX. The binding energies of the alkali metal ion molecules were deduced by using the values given in Table XXIX ; and the calculated results are shown in Table XXXI.

It is seen that there is good agreement between the experimental values and those calculated from the equation of the Pauling model.

Table XXIX: The Dissociation Energy and Electronegativity of the Alkali Metals

Molecule	Dissociation Energy [51] D_0^o (kcal/mol)	Electronegativity [76]
Li_2	25.5	1.0
Na_2	17.3	0.9
K_2	11.8	0.8
Rb_2	10.8	0.8
Cs_2	10.4	0.7

Table XXX: Comparison of the Calculated Ionization Potentials and Dissociation Energies of Alkali Compound Molecules with those of Experimental Values

Molecule	$I.P._{calc}$ (eV)	$I.P._{expt}$ (eV)	D_{calc} (kcal/mol)		$D^{\circ}_{0}{}_{expt}$ (kcal/mol)
NaLi	4.88	4.94	21.63	21.40	20.7
NaK	4.45	4.5 4.57	14.78	14.60	14.6
NaRb	4.18		14.28	14.05	
NaCs	4.05		14.77	13.85	
RbLi	4.16		19.07	18.15	
CsLi	4.03		20.02	17.95	
CsK	3.60		11.33	11.10	
CsRb	3.33		10.83	10.60	
RbK	3.73		11.3	11.30	
KLi	4.43	4.69	19.57	18.70	18.70

Table XXXI: The Binding Energies of the Heteronuclear Diatomic Alkali Metal Ions

Ion Molecule	Binding Energy D_0° (kcal/mol	Dissociation Products
$LiNa^+$	31.10	$Li^+ + Na$
LiK^+	34.84	$Li^+ + K$
$LiRb^+$	47.39	$Li^+ + Rb$
$LiCs^+$	51.33	$Li^+ + Cs$
NaK^+	27.69	$Na^+ + K$
$NaRb^+$	36.34	$Na^+ + Rb$
$NaCs^+$	39.82	$Na^+ + Cs$
KRb^+	25.35	$K^+ + Rb$
KCs^+	28.37	$K^+ + Cs$
$RbCs^+$	30.28	$Rb^+ + Cs$

F THERMOCHEMISTRY OF THE SYSTEMS Li-O AND Li-C-N

The chemical elements O, C and N could be present in lithium as impurities; or when the concentrations of O, C and N in lithium exceed a certain limit, new phases such as Li_2O, Li_2C_2 and Li_3N could be formed. Therefore, knowledge of the physical chemical properties of the systems Li-O, Li-C and Li-N is important for the interest of basic science, as well as for fusion technology.

F1 Thermodynamics of the Molecules $Li_2O_2(g)$ and $Li_3O(g)$

When the platinum Knudsen cell loaded with pretreated lithium oxide was heated to above 1170 K, the ions Li^+, Li_2^+, LiO^+, Li_2O^+, Li_3O^+ and $Li_2O_2^+$ were observed; and the experimental results suggested that the ions were formed by direct ionization of the corresponding neutrals.

The measurements of the gaseous isomolecular exchange equilibra:

$$Li_2O(g) + Li_2(g) = Li_3O(g) + Li(g) \qquad (85)$$

$$2Li_2O(g) = Li_3O(g) + LiO(g) \qquad (86)$$

$$Li_2O_2(g) + Li_2(g) = 2Li_2O(g) \qquad (87)$$

and

$$Li_2O_2(g) + Li_2(g) = Li_3O(g) + LiO(g) \qquad (88)$$

were carried out at temperatures between 1360 and 1670 K. The equilibrium constants for the reactions were calculated from the measured ion intensities using the relations:

$$K_{85} = \frac{I(Li_3O^+)\,I(Li^+)}{I(Li_2O^+)\,I(Li_2^+)} \qquad (89)$$

$$K_{86} = \frac{I(Li_3O^+)\,I(LiO^+)}{I^2(Li_2O^+)} \qquad (90)$$

$$K_{87} = \frac{I^2(Li_2O^+)}{I(Li_2O_2^+)\,I(Li_2^+)} \qquad (91)$$

and

$$K_{88} = \frac{I(Li_3O^+)\,I(LiO^+)}{I(Li_2O_2^+)\,I(Li_2^+)} \qquad (92)$$

The Gibbs energy functions of Li_3O and Li_2O_2 were calculated by using the estimated molecular parameters [23,24]. The third law results together with the second law enthalpies for reactions (85), (86), (87) and (88) are given in Table XXXII.

Table XXXII: The Third and Second Law Enthalpies for Reactions Involving the Molecules LiO(g), $Li_2O(g)$, $Li_3O(g)$ and $Li_2O_2(g)$

Reaction	ΔH_0° (Second Law) (kcal/mol)	ΔH_0° (Third Law) (kcal/mol)
$Li_2O(g) + Li_2(g) = Li_3O(g) + Li(g)$	-(35.2 ± 10.7)	-(23.57 ± 0.77)
$2Li_2O(g) = Li_3O(g) + LiO(g)$	43.14 ± 1.60	46.10 ± 0.40
$Li_2O_2(g) + Li_2(g) = 2Li_2O(g)$	-(28.47 ± 5.80)	-(51.44 ± 0.84) (without O-O bond) -(37.07 ± 0.52) (with O-O bond)
$Li_2O_2(g) + Li_2(g) = Li_3O(g) + LiO(g)$	14.4 ± 4.5	-(5.22 ± 0.66) (without O-O bond) 9.11 ± 0.36 (with O-O bond)

By combining the third law values with the dissociation energies: $D_0^\circ(Li_2)$ = 25.5 ± 1.5 kcal/mol, $D_0^\circ(LiO)$ = 80.5 ± 1.5 kcal/mol and $D_0^\circ(Li_2O)$ = 178.3 ± 1.1 kcal/mol, the following atomization energies were obtained:

$D_0^\circ(Li_2O_2)$ = 279.1 ± 4.0 (without O-O bond)

$D_0^\circ(Li_2O_2)$ = 293.4 ± 4.0 (with O-O bond)

and

$D_0^\circ(Li_3O)$ = 228.7 ± 2.0 kcal/mol

It is seen that within the experimental error of the measurements, there is good agreement between the second and third law values for the reactions involving the Li_2O_2 molecule with an O-O bond. The fact that there is excellent agreement on the vibration frequencies between the theoretical work of Yates and Pitzer[24], and the infrared work of Andrews[23] makes it reasonable to recommend the structure of Li_2O_2 with an O-O bond, and an atomization energy $D_0^\circ(Li_2O_2)$ = 293.4 ± 4.0 kcal/mol.

By using the same error treatment as mentioned previously, the final results of the atomization energies were obtained:

$D_0^\circ(Li_2O_2)$ = 293.0 ± 12 kcal/mol (with O-O bond)

$D_0^\circ(Li_3O)$ = 229.0 ± 10 kcal/mol

F1.1 Binding Energies of the Ion Molecules Li_3O^+ and $Li_2O_2^+$

The ionization potentials of Li_2O_2 and Li_3O were measured as I.P. (Li_3O) = 4.54 ± 0.2 eV and I.P.(Li_2O_2) = 7.88 ± 0.2 eV.

The binding energies of the ions were found to be as follows:

$Li_3O^+ \rightarrow 3Li + O^+$	$D_0^\circ(Li_3O^+)$ = 438.0 ± 15 kcal/mol
$Li_3O^+ \rightarrow Li^+ + 2Li + O$	$D_0^\circ(Li_3O^+)$ = 249.0 ± 10 kcal/mol
$Li_2O_2^+ \rightarrow 2Li + O^+ + O$	$D_0^\circ(Li_2O_2^+)$ = 425.0 ± 16 kcal/mol
$Li_2O_2^+ \rightarrow Li^+ + Li + 2O$	$D_0^\circ(Li_2O_2^+)$ = 236.0 ± 10 kcal/mol

Finally, combining the atomization energy of $Li_2O_2(g)$ and $Li_3O(g)$ with the heat of formation of Li(g), ΔH_0° = 38.5 ± 0.1, and the dissociation energy $D_0^\circ(O_2)$ = 117.97 ± 0.1 kcal/mol, yields the following heats of formation: $\Delta H_0^\circ(Li_2O_2)$ = -(98.0 ± 12) kcal/mol and $\Delta H_0^\circ(Li_3O)$ = -(54.5 ± 10) kcal/mol.

Table XXXIII: The Thermochemical Properties of the Molecules in the Li-O System

Molecule	Heat of Formation ΔH_0° (kcal/mol)	Atomization Energy D_0° (kcal/mol)	Ionization Potential I.P.(eV)
LiO	8.3 ± 3.3[a]	89.2 ± 3.3[a]	8.96 ± 0.2[a]
	16.5 ± 1.5[b]	80.5 ± 1.5[b]	8.45 ± 0.2[b]
	16.0 ± 5.0[c]	80.9[c]	8.60 ± 0.2[c]
Li_2O	-42.3 ± 1.1[a]	178.3 ± 1.1[a]	6.41 ± 0.2[a]
	-43.7 ± 2.5[c]	178.9[c]	6.19 ± 0.2[b]
			6.9 ± 0.3[c]
Li_3O	-54.5 ± 10[a]	229.0 ± 10[a]	4.54 ± 0.2[a]
Li_2O_2	-98.0 ± 12[a]	293.0 ± 12[a]	7.88 ± 0.2[a]

[a] this work
[b] Hildenbrand
[c] White et al.

The thermochemical properties of the neutral molecules in the Li-O system are given in Table XXXIII.

F2 Thermodynamics of the Gas Molecules LiNC and Li_2NC

The alkali cyanides in both the gas and solid phases provide a rich and topical field of study. Near Hartree Fock molecular orbital calculations on the gas molecules LiNC and LiCN have been carried out by B. Bak et al.[70]. In further theoretical calculations, E. Clementi et al.[80] have shown that the equilibrium configuration is the linear iso-cyanide LiNC.

An ab initio molecular orbital study of NaCN and KCN has been made by M.L. Klein et al.[72]; and the rotational spectrum and structure of KCN have been investigated experimentally by T. Törring et al.[73].

The existence of the gas molecules LiNC and Li_2NC has been proved experimentally by mass spectrometric measurements.

The experimental procedure in this study is the same as described in the paragraph on the $Li_4(g)$ molecule. To minimize the interference contributed by impurities such as Na, K and Mg in the lithium sample in the identification of gas species, three different compositions of lithium have been used in this series of experiments: enriched ^6Li > 97 % and natural lithium (^7Li = 93 %, ^6Li = 7.0 %), as well as mixtures of ^6Li and natural lithium (^6Li = 56.8 %, ^7Li = 43.2 %).

The commercial lithium contained a few hundred ppm of nitrogen, and some tens of ppm carbon as impurity. One could expect that the nitrogen pressure will not be too high when lithium is vaporized for mass spectrometric analysis.

The experiments were carried out at temperatures between 973 and 1313 K, and the following gaseous equilibria were measured:

$$LiNC(g) + Li(g) = Li_2(g) + NC(g) \qquad (93)$$

$$Li_2NC(g) + Li(g) = LiNC(g) + Li_2(g) \qquad (94)$$

$$Li_2NC(g) + Li_2(g) = LiNC(g) + Li_3(g) \qquad (95)$$

and the equilibrium constants were evaluated from the measured ion intensities, using the following relations:

$$K_{93} = \frac{I(Li_2^+) \times I(NC^+)}{I(LiNC^+) \times I(Li)}$$

$$K_{94} = \frac{I(LiNC^+) \times I(Li_2^+)}{I(Li_2NC^+) \times I(Li^+)}$$

and

$$K_{95} = \frac{I(LiNC^+) \times I(Li_3^+)}{I(Li_2NC^+) \times I(Li_2^+)}$$

F2.1 Gibbs Energy Functions and Enthalpies of the Molecules LiNC and Li_2NC

The existence of stable molecules LiNC and Li_2NC has not been demonstrated experimentally prior to this investigation; and the structures of these molecules are not known.

For the calculation of Gibbs energy functions and the enthalpies, a linear configuration of LiNC and two different structures for Li_2NC, Li-NC-Li and $NC\lessdot^{Li}_{Li}$ ($<110^o$) are assumed. The parameters of the molecules which have been used for the calculation and the thermodynamic functions are given in Tables XXXIV, XXXV, XXXVI, XXXVII.

F2.2 The Thermochemistry of the Molecules LiNC(g) and $Li_2NC(g)$

The measured equilibrium constants and the third law enthalpies of the reactions (93), (94), and (95) as a function of temperature are given in Tables XXXVIII, XXXIX and XL.

Combining the third law values for reactions (93), (94) and (95) with the atomization energies:

$$D_0^o(NC) = 178.0 \pm 5 \text{ kcal/mol}^{51)}$$

$$D_0^o(Li_2) = 25.5 \pm 1.5 \text{ kcal/mol}^{32)}$$

and

$$D_0^o(Li_3) = 41.5 \pm 4.0 \text{ kcal/mol}^{32)}$$

yields the atomization energies for LiNC and Li_2NC:

$$D_0^o(LiNC) = 232.0 \pm 8 \text{ kcal/mol}$$

$$D_0^\circ(Li_2NC) = 270.0 \pm 10 \text{ kcal/mol}$$

for linear configuration, and

$$D_0^\circ(Li_2NC) = 265.0 \pm 10 \text{ kcal/mol}$$

for the structure $N\text{-}C\begin{smallmatrix}Li\\Li\end{smallmatrix}$ ($< 110^\circ$).

The stabilities predicted by B. Bak et al.[70] ~254.0 kcal/mol and ~262.8 kcal/mol, respectively, agree well with the results of this experiment.

F2.3 Binding Energies of the Ion Molecules $LiNC^+$ and Li_2NC^+

The accurate determination of the ionization potentials of LiNC and Li_2NC has been carried out by the extrapolated voltage difference method.

The ionization potentials of LiNC and Li_2NC were determined as 8.79 ± 0.2 eV and 7.70 ± 0.2 eV respectively. When the measured ionization potentials and atomization energies of LiNC and Li_2NC are combined with the following ionization potentials:

I.P.(N) = 14.53 ± 0.12 ev

I.P.(C) = 11.3 ± 0.2 eV

and

I.P.(Li) = 5.392 eV,

the binding energies that are deduced are given in Table XLI.

Table XXXIV: The Parameters of the Molecules LiNC and Li_2NC

Molecule	Vibrational Frequencies and Degeneracies	Bond Distance	Bond Angle
LiNC	ω_1 = 250 cm^{-1} (2) ω_2 = 787 cm^{-1} (1) ω_3 = 2371 cm^{-1} (1)	Li-N 1.764Å N-C 1.156Å	Li-N-C 180°
Li_2NC	ω_1 = 120 cm^{-1} (1) ω_2 = 210 cm^{-1} (1) ω_3 = 230 cm^{-1} (1) ω_4 = 652 cm^{-1} (1) ω_5 = 815 cm^{-1} (1) ω_6 = 2363 cm^{-1} (1)	N-C 1.156Å Li-C 1.921Å	N-C(Li,Li) < 110°
Li_2NC	ω_1 = 127 cm^{-1} (2) ω_2 = 330 cm^{-1} (2) ω_3 = 625 cm^{-1} (1) ω_4 = 830 cm^{-1} (1) ω_5 = 2396 cm^{-1} (1)	Li-N 1.764Å N-C 1.159Å C-Li 1.921Å	Li-N-C-Li 180°

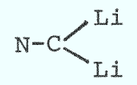
Table XXXV: Thermodynamic Functions of the Molecule LiNC

T (K)	$H_T^\circ - H_0^\circ$ cal mol^{-1}	$\frac{-(G_T^\circ - H_0^\circ)}{T}$ cal mol^{-1} K^{-1}
298	2735.5	45.0998
300	2756.2	45.1567
400	3904.8	47.8822
500	5102.9	50.1101
600	6338.5	52.0036
700	7605.7	53.6553
800	8900.4	55.1235
900	10219.1	56.4474
1000	11558.8	57.6545
1100	12916.5	58.7649
1200	14289.6	59.7939
1300	15676.1	60.7530
1400	17073.9	61.6518
1500	18481.5	62.4975

Table XXXVI: Thermodynamic Functions of the Molecule
Li-N-C-Li

T	$H_T^\circ - H_0^\circ$	$\frac{-(G_T^\circ - H_0^\circ)}{T}$
(K)	cal mol^{-1}	cal mol^{-1} K^{-1}
298	3550.3	50.0890
300	3579.3	50.1627
400	5203.3	53.7499
500	6915.8	56.7449
600	8689.0	59.3263
700	10508.3	61.5998
800	12364.8	63.6342
900	14252.2	65.4771
1000	16165.4	67.1630
1100	18100.4	68.7176
1200	20053.7	70.1606
1300	22022.5	71.5074
1400	24004.6	72.7705
1500	25997.8	73.9599

Table XXXVII: Thermodynamic Functions of the Molecule



(< 110°)

T	$H_T^\circ - H_0^\circ$	$\frac{-(G_T^\circ - H_0^\circ)}{T}$
(K)	cal mol^{-1}	cal mol^{-1} K^{-1}
298	3603.2	55.3710
300	3631.1	55.4459
400	5188.4	59.0522
500	6822.4	62.0220
600	8511.0	64.5591
700	10242.4	66.7804
800	12008.8	68.7596
900	13804.6	70.5470
1000	15625.1	72.1782
1100	17466.5	73.6796
1200	19325.5	75.0710
1300	21199.5	76.3683
1400	23086.2	77.5836
1500	24983.7	78.7270

Table XXXVIII: Third Law Enthalpies for the Reaction
$LiNC(g) + Li(g) = Li_2 + NC(g)$

T (K)	K	$-\Delta[(G_T^\circ - H_0^\circ)/T]$ (cal mol^{-1} K^{-1})	ΔH_0° (kcal mol^{-1})
1263	1.055×10^{-3}	-7.242	26.35
1223	7.949×10^{-4}	-7.266	26.23
1183	1.321×10^{-4}	-7.290	29.61
1123	2.435×10^{-5}	-7.327	31.93
1093	3.968×10^{-5}	-7.345	30.04
1023	5.357×10^{-5}	-7.383	27.54
			28.62

Table XXXIX: Third Law Enthalpies for the Reaction:

$$Li_2NC(g) + Li(g) = LiNC(g) + Li_2(g)$$

T	K	$-\Delta[(G_T^\circ - H_0^\circ)/T]$		ΔH_0°	
(K)		(cal mol^{-1} K^{-1})		(kcal/mol)	
		Li-NC-Li	NC(Li)(Li)	Li-NC-Li	NC(Li)(Li)
1263	1.00×10^{-1}	5.323	4.511×10^{-1}	12.487	6.333
1223	8.174×10^{-2}	5.359	4.631×10^{-1}	12.640	6.652
1183	6.019×10^{-2}	5.394	4.751×10^{-1}	12.987	7.168
1163	5.183×10^{-2}	5.410	4.811×10^{-1}	13.130	7.398
1123	4.025×10^{-2}	5.442	4.931×10^{-1}	13.280	7.722
1093	3.424×10^{-2}	5.467	5.029×10^{-1}	13.300	7.878
1023	3.759×10^{-2}	5.537	5.410×10^{-1}	12.333	7.223
973	2.539×10^{-2}	5.587	5.530×10^{-1}	12.538	7.640
				12.837	7.252

Second law value: $\Delta H_{1118}^\circ = 6.449 \pm 0.220$ kcal/mol

Table XL: Third Law Enthalpies for the Reaction:
$Li_2NC(g) + Li_2(g) = LiNC(g) + Li_3(g)$

T	K	$-\Delta[(G_T^\circ - H_0^\circ)/T]$		ΔH_0°	
(K)		(cal mol^{-1} K^{-1})		(kcal/mol)	
		Li-NC-Li	$NC\begin{smallmatrix}Li\\Li\end{smallmatrix}$	Li-NC-Li	$NC\begin{smallmatrix}Li\\Li\end{smallmatrix}$
973	1.943×10^{-3}	8.414	3.382	20.26	15.36
1023	1.170×10^{-3}	8.405	3.401	22.32	17.20
1093	8.428×10^{-4}	8.391	3.427	24.55	19.12
1123	8.214×10^{-4}	8.385	3.437	25.29	19.71
1163	1.198×10^{-3}	8.377	3.449	25.29	19.56
1183	5.885×10^{-4}	8.373	3.455	27.39	21.57
1223	4.627×10^{-4}	8.384	3.488	28.91	22.93
1263	3.692×10^{-4}	8.408	3.536	30.46	24.30
1283	3.263×10^{-4}	8.420	3.560	31.27	25.03
1313	6.307×10^{-3}	8.447	3.602	24.31	17.95
				23.47	18.55

Table XLI: The Binding Energies of the Ions $LiNC^+$ and Li_2NC^+

Ion Molecule	Products of Reaction	Binding Energy D_0° (kcal/mol)
$LiNC^+$	$Li^+ + N + C$	154.0 ± 8.0
	$Li + N^+ + C$	364.0 ± 6.0
	$Li + N + C^+$	290.0 ± 7.0
Li_2NC^+	$Li^+ + Li + N + C$	217.0 ± 7.0 (linear) 212.0 ± 7.0 (< 110°)
	$2Li + N^+ + C$	427.0 ± 7.0 (linear) 422.0 ± 7.0 (< 110°)
	$2Li + N + C^+$	353.0 ± 8.0 (linear) 348.0 ± 8.0 (< 110°)

G. CONCLUSIONS ON AND IMPLICATIONS OF THE USE OF LITHIUM AND LITHIUM OXIDE AS BREEDING MATERIALS IN FUSION REACTORS

It is seen that the quadrupole mass filter combined with RF heating has been successfully applied to high temperature chemistry[74]. The favorable advantages of the quadrupole mass spectrometer are:

1. High sensitivity, combined with high efficiency, particularly for the identification of molecules of which the concentrations are very low.

2. High dynamic range; in a usual case a dynamic range of 10^7 can be attained easily, and it may even be extended to 10^9.

3. The optimal geometrical arrangement in the apparatus can easily be achieved. The distance between the cell orifice and the electron beam of the ion source is only about ~3 cm; this makes it possible to identify the molecules at low concentrations. The disadvantage of the quadrupole mass spectrometer, i.e. that the sensitivity is strongly mass dependent, could be eliminated by calibration of this mass spectrometer.

The molecules LiH^+, LiH_2, Li_2H, Li_2H_2, Li_3O, Li_2O_2, Li_3, Li_4, LiNC and Li_2NC have been detected here experimentally for the first time; the ionization potentials of these molecules were determined, and the ion binding energies were deduced. These results are compared with those predicted theoretically, so far as such are available.

The application of the Pauling model has been demonstrated for the heteronuclear diatomic alkali metal molecules. The values which were calculated by using Pauling's model are in good agreement with the measured values.

In previous work[48] we have found that the validity of Sievert's law was confirmed for extremely dilute solutions of deuterium in lithium; and values for Sievert's constant were measured between 773 and 973 K over a concentration range of

$$0.5 \times 10^{-6} \leq X_D \leq 10^{-4}.$$

However, at these low concentrations of deuterium (or tritium) which are of interest for fusion reactor blankets, and at high temperatures, it is not D_2 but rather the lithium containing species LiD, Li_2D, LiD_2, Li_2, Li_3 and Li_4, which are detected and measured.

The partial pressures of the gas species in equilibrium with liquid lithium as a function of temperature at a deuterium concentration of $X_D = 10^{-5}$ are given in Fig. 10.

The partial pressures as functions of temperature and the deuterium concentration in liquid lithium are given in Table XLII.

From these results, it can be deduced that at high temperatures the ratio of the deuterium atomic fraction in the gas to that in the liquid exceeds unity, and deuterium is enriched in the gas phase upon distillation. This finding has been confirmed by Rayleigh distillation experiments[75]; the enrichment factor, $R = X_{D(g)}/X_{D(l)}$, is independent of the concentration in dilute solutions of tritium in lithium. Therefore, thermodynamically, it is possible to separate tritium from the lithium blanket at very low concentrations of tritium (X_T from 1 to 10 ppm).

From this study it is found that the gas phase composition over solid lithium oxide (Li_2O) is quite complex.

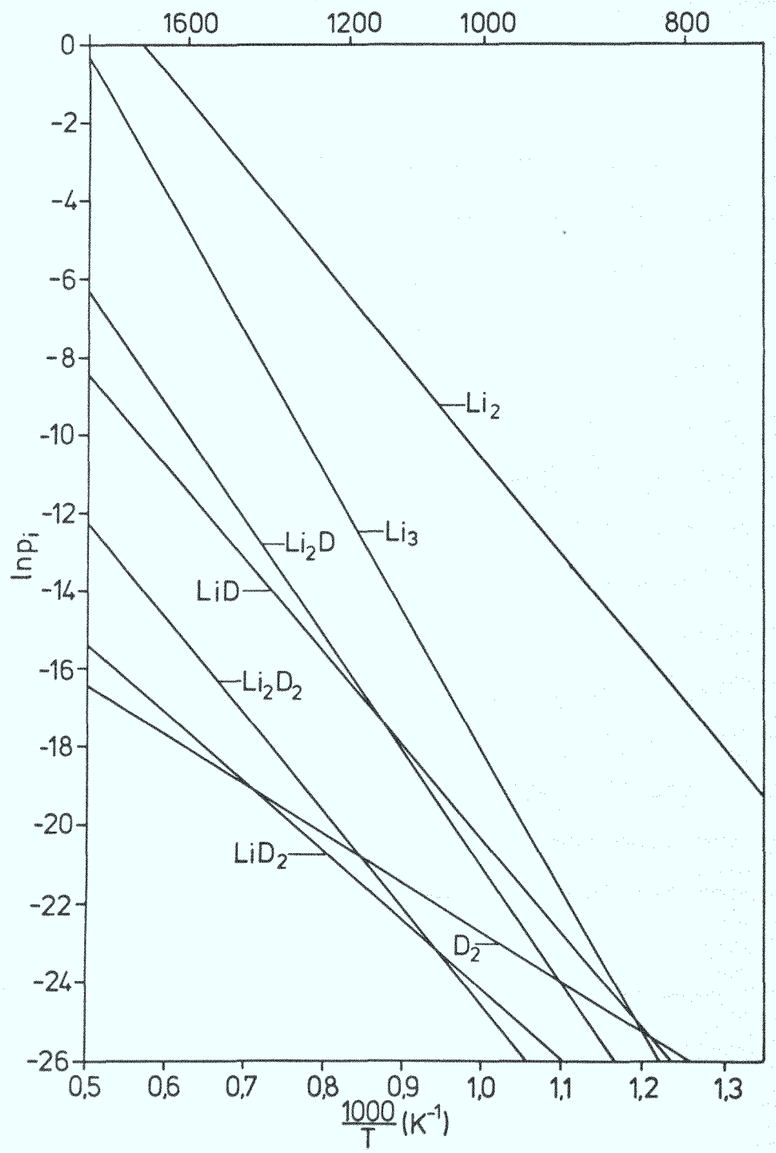


Fig. 10 Partial pressures over a solution of 10 ppm deuterium in liquid lithium.

LiO, Li_2O, Li_3O and Li_2O_2 are present if Li_2O is used as fusion blanket containing low concentrations of tritium. One can expect that the tritum will react with these lithium-oxygen species to form $Li_xO_yT_z$ species, which complicates tritium recovery from a Li_2O blanket.

The compatibility of lithium oxide with structual materials has been studied by means of vaporization. It is found that the partial pressures of the gas species over solid Li_2O are dependent on the choice of the structural materials. Fig. 11 shows the partial pressures of lithium over Li_2O as a function of temperature for different materials used as Knudsen cells. The very pronounced increase in the lithium pressure in the presence of molybdenum or graphite is probably caused by formation of the volatile oxides Li_2MoO_4 and CO, with an associated reduction of oxygen pressure in the system.

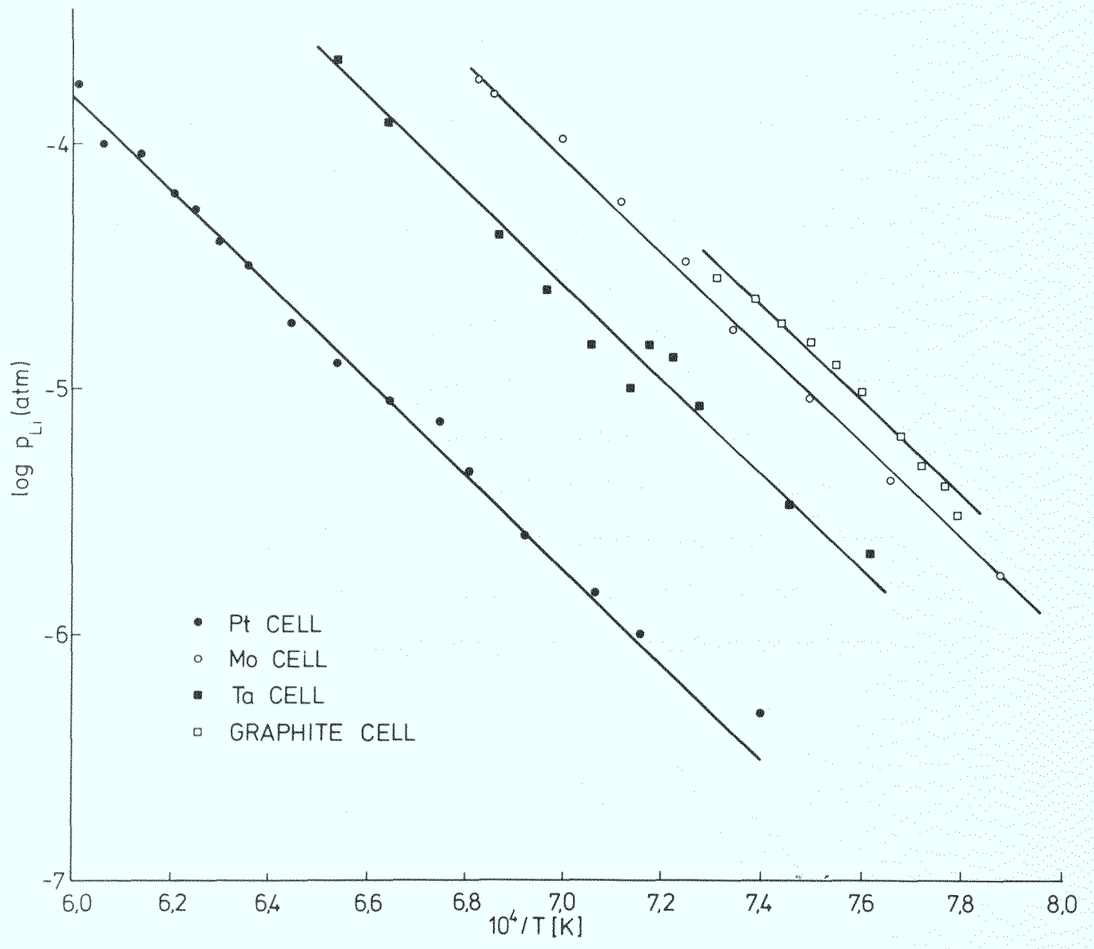


Fig. 11 Partial pressures of lithium over Li_2O as a function of temperature for different materials used as Knudsen cells.

REFERENCES

1. E.L. Muetterties, T.N. Rhodin, E. Brand, C.F. Brucker, and W.R. Pretzer
Chem. Rev., 79, 91 (1979)

2. E.L. Muetterties
Science, 196, 839 (1977)

3. H. Stoll and H. Preuss
Phys. Status Solid B, 64, 103 (1974)

4. W.C. Stwalley and K.R. Way
J. Chem. Phys. 60, 3611 (1974)

5. P.G. Wilkinson,
Astrophys. J. 138, 778 (1963)

6. R.P. Hurst, O. Plats and F.A. Matsen
J. Chem. Phys. 31, 501 (1959)

7. J.C. Browne
J. Chem Phys. 41, 3495 (1964)

8. S. Fraga and B.J. Ransil
J. Chem. Phys. 35, 669 (1961)

9. A.L. Companion
J. Chem. Phys. 48, 1186 (1968)

10. A.A. Wu and F.O. Ellison
J. Chem. Phys. 47, 1458 (1967)

11. W.B. England, N.H. Sabell, and A.C. Wahl
J. Chem. Phys. 63, 4596 (1975)

12. P. Siegbahn and A.F. Schaefer
J. Chem. Phys. 62, 3488 (1975)

13. A.L. Companion
J. Chem. Phys. 48, 1186 (1968)

14. J.D. Switalski, J.T. Huang, and M.E. Schwartz
J. Chem. Phys. 60, 2252 (1974)

15. J.R. Tyndall and A.L. Companion
J. Chem. Phys. 52, 2036 (1970)

16. P. Kollman, C.F. Bender, S. Rothenberg
J. Amer. Chem. Soc. 94, 8016 (1972)

17. J.D. Lee
"Tritium Breeding and Direct Energy Conversion"
pp. 51-90 in the Chemistry of Fusion Technology,
Edited by D.M. Gruen, Plenum Press, New York-London, 1972

18. L Brever
Chem. Rev. 52, 1 (1953)

19. L. Brewer and J.L. Margrave
J. Phys. Chem. 59, 421 (1955)

20. J. Berkowitz, W.A. Chupka, G.D. Blue, and J.L. Margrave
J. Phys. Chem. 63, 644 (1959)

21. D. White, K.S. Seshadri, D.F. Dever, D.E. Mann, and
M.J. Linevsky
J. Chem. Phys. 39, 2463 (1963)

22. D.L. Hildenbrand
J. Chem. Phys. 57, 4556 (1972)

23. L. Andrews
J. Chem. Phys. 50, 4288 (1969)

24. J.H. Yater and R.M. Pitzer
J. Chem. Phys. 66, 3592 (1977)

25. J.R. Powell
Tritium Recovery from Fusion Blankets Using Solid Lithium Compounds: I, Design and Minimization of Tritium Inventory, Proc. of Radiation Effects and Tritium Technology for Fusion Reactors, October, 1975, Gatlinburg pp. III 197-230

26. W.C. Stwalley and M.E. Koch
Optical Engineering 19, 71 (1980)

27. A.L. Companion
J. Chem. Phys. 50, 1165 (1969)

28. F.O. Ellison
J. Am. Chem. Soc. 85, 3540 (1963)

29. B.T. Pickup
Proc. R. Soc. London Ser. A: 333, 69 (1973)

30. J. E. Inglesfield
J. Chem. Phys. 67, 505 (1977)

31. H.O. Beckmann, J. Koutecký and Bonacić-Koutecký
J. Chem. Phys. 73, 5182 (1980)

32. C.H. Wu
J. Chem. Phys. 65, 3181 (1976)

33. A. Herrmann, E. Schuhmacher, and L. Wöste
J. Chem. Phys. 68, 2327 (1978)

34. W.A. Chupka and M.g. Inghram
J. Chem. Phys. 21, 371 (1953)
22, 1472 (1954)

35. R.E. Honig
J. Chem. Phys. 22, 126 (1953)

36. J. Drowart and P. Goldfinger
Angew. Chem. 79, 589 (1967)

37. K.A. Gingerich
J. Crystal Growth 9, 31 (1971)

38. J.B. Mann
J. Chem. Phys. 46, 1646 (1967)

39. R.F. Pottie
J. Chem. Phys. 44, 916 (1966)

40. J.E. Mayer and M.G. Mayer
Statistical Mechanics, New York 1940

41. JANAF Thermochemical Tables, second edition,
Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. 37 (1971)

42. R.W. Kiser
Introduction to Mass Spectrometry and Its Applications,
Prentice-Hall, Englewood Cliffs. N.J. 1965

43. J.W. Warren
Nature, 165, 810 (1950)

44. H.R. Ihle and C.H. Wu
J. Chem. Phys. 63, 1605 (1975)

45. C.H. Wu
J. Chem. Phys. 71, 783 (1979)

46. H.R. Ihle and C.H. Wu
"Experimental Determination of the Partial Pressures
Of D_2, LiD and Li_2D in Equilibrium with Dilute Solutions
of Deuterium in Liquid Lithium",
Proc. 8th Symp. on Fusion Technology
Noordwijkerhout/Netherlands 1974, pp. 787-799,
EUR 5182 C

47. C.H. Wu
J. Chem. Phys. 66, 4400 (1977)

48. H.R. Ihle and C.H. Wu
"The Solubility of Deuterium in, and Its Separation
from, Liquid Lithium by Distillation",
Proc. 2nd Int. Congr. Hydrogen in Metals (Paris, June 1977),
Pergamon Press, New York (1977) Paper ID8

49. J.L. Franklin, J.D. Dillard, H.M. Rosenstock,
J.T. Herron, K. Draxl, and F.H. Field
Nat. Stand. Ref. Data Ser. Nat. Bur. Stand. 26 (1969)

50. C.H. Wu and H.R. Ihle
J. Chem. Phys. 66, 4356 (1977)

51. A.G. Gaydon
Dissociation Energies and Spectra of Diatomic Molecules,
Chapman and Hall, London, 1968

52. J. Kordis, K.A. Gingerich, and R.J. Seyse
J. Chem. Phys. 61, 5114 (1974)

53. T.A. Milne and D. Cubicciotti
J. Chem. Phys. 29, 846 (1958)

54. J. Berkowitz and W.A. Chupka
J. Chem. Phys. 29, 653 (1958)

55. R.C. Miller and P. Kusch
J. Chem. Phys. 25, 860 (1956)

56. R.A. La Budde and R.B. Berstein
J. Chem. Phys. 55, 5499 (1971)

57. W.A. Lester, Jr. and J. Schaefer
J. Chem. Phys. 59, 3676 (1973)

58. A.F. Wagner, A.C. Wahl, A.M. Karo, and R. Krejci
J. Chem. Phys. 69, 3756 (1978)

59. W. Schulze, H.V. Becker and H. Abe
Chem. Phys. 35, 177 (1978)

60. M. Moskovits and J. E. Hulse
J. Chem. Phys. 67, 4271 (1977)

61. M. Moskovits and J.E. Hulse
J. Chem. Phys. 66, 3988 (1977)

62. W. Schulze, H.V. Becker, R. Minkwitz, and K. Manzel
Chem. Phys. Letters 55, 59 (1978)

63. D.M. Lindsay, D.R. Herschbach, and A.L. Kwiram
Mol. Phys. 32, 1199 (1976)

64. D.G. Stull and G.C. Sinke
Thermodynamic Properties of the Elements,
American Chemical Society, Washington, D.C., 1956

65. A.L. Companion, D.J. Steible, and A. Starsbak
J. Chem. Phys. 49, 3637 (1968)

66. A.J. Blair and C.H. Wu
Z. Anal. Chem. 275, 261 (1975)

67. A.L. Companion
Chem. Phys. Letter 56, 500 (1978)

68. C.T. Ewing, J.P. Stone, J.R. Spann, and R.R. Miller
J. Phys. Chem. 71, 473 (1967)

69. K.F. Zmbov, C.H. Wu and H.R. Ihle
J. Chem. Phys. 67, 4603 (1977)

70. B. Bak, E. Clementi, and R.N. Kortseborn
J. Chem. Phys. 52, 764 (1970)

71. E. Clementi, H. Kistenmacher, and H. Popkie
J. Chem. Phys. 58, 2460 (1973)

72. M.L. Klein, G.D. Goddard and D.G. Bounds
J. Chem. Phys. 75, 3909 (1981)

73. T. Törring, J.P. Bekooy, W. Meerts, J. Hoeft,
E. Tilmann, and A. Dymanus
J. Chem. Phys. 73, 4875 (1980)

74. C.H. Wu
Jül-739-PC, März 1971

75. H.R. Ihle and C.H. Wu
J. Phys. Chem. 79, 2386 (1975)

76. L. Pauling
The Nature of the Chemical Bond, 3rd Ed., Cornell
Univ. Press, Ithaca, N.Y. (1960)

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Professor O. Knacke, Professor P. von R. Schleyer, Professor K.A. Gingerich and Dr. H.R. Ihle for their constant interest, discussion and encouragement during the course of this work.

The author thanks also Professor G. Stöcklin for the support of this work.

The valuable discussions with Dr. A. Neubert, critical reading of the manuscript by Dr. J.A. Blair and the experimental assistance of F. Fröschen and W. Michelsen are gratefully acknowledged.

The author also wishes to express his thanks to Mrs. I. Kearns for her patience in the preparation of this manuscript.