

VAPORIZATION THERMODYNAMICS OF KCl. COMBINING VAPOR PRESSURE AND GRAVIMETRIC DATA

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ABSTRACT

The presence of complex species in the vapors above alkali halides at high temperature introduces special problems in the assessment of thermodynamic properties of the vapor and the vaporization process, coupling pressure measurements and calibration methods. This work presents a new review of the literature for potassium chloride, including a review of the methods used for currently accepted assessments. Of particular importance is that a new assessment method, using non-linear least squares refinement and the Maximum Likelihood method, has been used to treat simultaneously all the available total pressure data, using the partial pressure studies to select among cases. This assessment treats the presence of both statistical and systematic errors among the various studies in a general way. New values for thermodynamic properties of the monomer and dimer vapor are recommended, including a need to change the value of the dimer entropy by approximately $10 \text{ J mol}^{-1} \text{ K}^{-1}$. Recommended values include $\Delta_f H^\circ(\text{KCl, g, 298.15 K}) = -214.95 \pm 0.5 \text{ kJ mol}^{-1}$, $\Delta_f H^\circ(\text{K}_2\text{Cl}_2, \text{ g, 298.15 K}) = -604.19 \pm 5.4 \text{ kJ mol}^{-1}$ and $S^\circ(\text{K}_2\text{Cl}_2, \text{ g, 298.15 K}) = 360.70 \pm 3.8 \text{ J mol}^{-1} \text{ K}^{-1}$. Comparison of the reevaluated partial pressures with mass spectral intensities also provides new information on ionization cross sections.

1. INTRODUCTION

The vapor pressure of a substance is an important system property in many applications. Its value is intimately connected with the vaporization rate, which controls the working temperature interval of a given substance and constrains the choice of materials one can work with in a given temperature interval. When the vapor is complex, containing multiple species, the derivation of a full thermodynamic understanding requires detailed species-specific information and, even with such data, can be a complex task.

In high temperature chemistry situations, vapor pressures are typically less than 100 kPa. The molar volume of a condensed phase under such conditions is negligible compared with the molar volume of the gas phase. If the gas phase consists of molecules of the same stoichiometry as the condensed phase and the pressure is low enough, the equation of state of a perfect gas may be used. Then,

integration of the Clausius-Clapeyron equation, relating pressure p and temperature T to the transition thermodynamic functions enthalpy $\{\Delta_{trs}H^\circ\}$ and entropy $\{\Delta_{trs}S^\circ\}$

$$R \ln\left(\frac{p}{p^\circ}\right) = -\Delta_{trs}\frac{H^\circ}{T} + \Delta_{trs}S^\circ \quad (1)$$

The index $^\circ$ shows that the thermodynamic quantity so marked is referenced to the standard state (In this work, standard state condition is $p = 101325$ Pa). The subscript $_{trs}$ denotes that the change is for a transition, typically sublimation from the solid or vaporization from the liquid for the cases discussed here. R is the gas constant ($R = 8.31441$ J mol $^{-1}$ K $^{-1}$).

Equation (1) is generally used to process experimental data and extrapolate vapor pressures to higher and lower temperatures, commonly with the realistic assumption that $\Delta_{trs}H^\circ$ and $\Delta_{trs}S^\circ$ are independent of temperature over spans of a few hundred kelvins. The assumption of ideal or near-ideal gas behavior implies no dependence on pressure. However, when a substance vaporizes with several gaseous species as products, the thermodynamic description gets more complicated. Take the common case of potassium chloride, as an example, where monomers (KCl) and dimers (K $_2$ Cl $_2$) are formed in the vapor phase. The ideal associated solution model is usually used in this case. Monomers (m) and dimers (d) separately are assumed to obey the equation of state of a perfect gas, and the total vapor pressure (p_{tot}) at a given temperature is the sum of the partial pressures at that temperature,

$$p_{tot}(T) = p_m(T) + p_d(T) \quad (2)$$

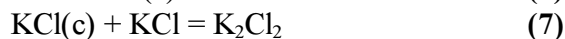
In spite of the existence of two species in the vapor, the system is still one-component because the species are linked by a homogenous gas-phase chemical reaction. In this example, it is not possible to apply Eqn. (1) directly to the temperature dependence of the total vapor pressure p_{tot} . One should use Eqn. (1) to describe monomers and dimers separately, and then apply Eqn (2). Then

$$p_{tot} = \exp\left\{\frac{\Delta S_m^\circ(T)}{R}\right\} \exp\left\{-\frac{\Delta H_m^\circ(T)}{RT}\right\} + \exp\left\{\frac{\Delta S_d^\circ(T)}{R}\right\} \exp\left\{-\frac{\Delta H_d^\circ(T)}{RT}\right\} \quad (3)$$

or in the alternative form

$$\ln p_{tot} = \frac{\Delta S_m^\circ(T)}{R} - \frac{\Delta H_m^\circ(T)}{RT} + \ln \left\{ 1 + \exp\left[\frac{\Delta S_{dm}^\circ(T)}{R}\right] \exp\left[-\frac{\Delta H_{dm}^\circ(T)}{RT}\right] \right\} \quad (4)$$

where ΔH_m° , ΔH_d° , ΔH_{dm}° and ΔS_m° , ΔS_d° , ΔS_{dm}° are the enthalpies and entropies of the reactions



and where (c) indicates a condensed phase (all species not so identified are gases). Note that reaction (7) is not independent; it is obtained by subtracting reaction (5) from (6).

The goal of the present work is to consider the solution to problems arising when multiple gas species coexist, and equations such as (3) and (4) must be used for processing and extrapolating experimental vapor pressure experimental data. Potassium chloride is taken as an example.

It should be mentioned that the standard state of KCl (and of K_2Cl_2) is the ideal associated solution model in the hypothetical state of the gas consisting only of monomers (or dimers), obeying the equation of state of a perfect gas at the standard state p and T . However, it is impossible to obtain a vapor consisting of only monomer or only dimer molecules in thermodynamic equilibrium with the condensed phase. Therefore, practically all experimental results represent a summed characteristic of the vapor, coupling the measured values of the various species together experimentally. Where only total pressure is measured, the existence of dimer molecules is commonly inferred by comparison with different methods. High temperature molecular beam mass spectrometry techniques provide an exception to this approach, giving direct evidence for the existence of complex molecular species. Here, as in the other methods, a gas phase ideal solution of monomers and dimers is the system investigated. The individual concentrations of monomers and dimers in the vapor can be estimated from measurements of the individual mass spectral ion currents derived from the separate species.

2. MEASUREMENT APPROACHES

2a. High temperature mass spectrometry

To apply mass spectrometry (MS) to high temperature vapors, a molecular beam is formed from the vapor under study, taking care that the beam composition corresponds to that of the vapor source. In one form of the method, an effusion cell (generally referred to as a *Knudsen* effusion source) is used to directly produce a molecular beam. For total pressures greater than about 5 Pa (typical for sublimation from the liquid), another method (the Transpiration MS technique) utilizes a supersonic nozzle arrangement to extract a molecular beam, relying on ultra-rapid gasdynamic cooling to "freeze-in" the high temperature composition from a transpiration cell [12].

The mass spectrometer is located downstream of the molecular beam source. There, neutral molecules in the molecular beam are converted to ions for mass analysis in the MS ion source, usually by electron bombardment ionization there with a crossed, approximately monoenergetic, electron beam. Most ambiguities in mass spectrometry arise at the ion source stage due to lack of detailed knowledge of the various ionization processes involved, including fragmentation pathways and ionization cross sections. To study ionization processes, one should already know the vapor composition accurately, but to determine the vapor composition, one needs to have information about ionization pathways of molecules. Intercomparison of mass spectrometric data, mass transport (*i.e.* total pressure), and clues from velocity analysis, angular distributions, appearance potential measurements, and thermodynamically structured experiments (double-oven experiments, special mixtures with activity constraints, etc.) are used to distinguish the dominant ionization pathways and

identify the vapor species. This paper presents a unified approach to provide new insight into the vapor composition.

In 1955, Hobson [1] was the first to observe the mass spectrum of the vapors over KCl(c), reporting the negative ions, K^- , Cl^- , KCl^- , KCl_2^- , and K_2Cl^- from electron impact ionization of the neutral vapors. Milne, *et al* [2], in 1958, reported the mass spectrum of the positive ions K^+ , KCl^+ , K_2Cl^+ , and $K_3Cl_2^+$. The cross sections for formation of positive ions by electron bombardment of the neutral vapor are typically far larger than for formation of negative ones, even in the KCl case, and later studies used essentially only positive ions for quantitative studies [3-13], with only Hobson [1] and Ebinghaus [15] reporting negative ion spectra. Worthy of note is that negative and positive ions exist in the equilibrium vapor of potassium chloride without any external ionization [16], but the ion concentration is six to eight orders of magnitude less than the concentration of neutral monomers and dimers at reasonable experimental temperatures. Hence, thermally produced ions have negligible effect on the measured total vapor pressure.

Refs. [3, 10, 11, and 13] give quantitative mass spectra of positive ions, and [5, 7, 9, and 12] also report the temperature dependence of the various observed ion currents. Grimley and Muenow [6] and Grimley, *et al* [8] measured the angular distribution of the ion currents. Potts, *et al* [14] obtained mass spectra of the positive ions using photo-ionization.

With the exception of Ref. [12], Knudsen effusion cells were used to generate a molecular beam. The Knudsen effusion condition requires that the collision rate in the gas phase be negligible with respect to the gas-condensed phase collision rate. This condition generally implies that the total vapor pressure not exceed a few pascals and hence all the effusion measurements were made below 1000 K over solid KCl. Hastie *et al* [12] overcame this pressure limit using a transpiration cell with saturated flowing gas, generating a supersonic molecular beam (the Transpiration MS method) and obtaining mass spectra directly of vaporizing liquid potassium chloride.

In a specially designed mixed halide experiment, Milne [4] showed that there were no (<0.1 percent) ion-molecule reactions in the typical ionization source area, where electron bombardment occurred. So, the identification of the ions K_2Cl^+ and $K_3Cl_2^+$ provided strong evidence that there are indeed complex molecules in the vapor of KCl(c). No parent ions, such as $K_2Cl_2^+$ were observed at all. The parent ion dimers are very unstable and rapidly decompose with the loss of Cl (see quantum mechanical calculations for Na_2Cl_2 [17, 18]). This process is common for all alkali halides, but, in the KCl case, there is no doubt as to the presence of dimer molecules, in spite of the absence of parent ions. In the absence of collisions, only higher polymeric $(KCl)_n$ species are reasonable sources of K_2Cl^+ and $K_3Cl_2^+$, besides K_2Cl_2 and K_3Cl_3 . Neutral molecules like K_2Cl are rather unlikely from a chemical point of view (see theoretical studies of Li_2F , LiF_2 , Na_2F , Na_2Cl [19-22]). Also, it should be kept in mind that potassium chloride is known to vaporize congruently, which means that the gas phase should have the same overall stoichiometric composition as the condensed phase. Cl-only containing species are quite negligible.

As well as the question of the existence of polymeric species, it is also necessary to determine the extent of fragmentation and the appropriate correction coefficients. The ion current of $K_3Cl_2^+$ is small (of the order of a hundredth of a percent of the total). Thus the concentration of trimers can be assumed to be negligibly small and only ions K^+ , KCl^+ , and K_2Cl^+ arising from neutral atomic K and the molecules KCl and K_2Cl_2 need to be taken into account. While the ion K_2Cl^+ is formed unambiguously from the dimer molecule, the K^+ and KCl^+ ions can potentially arise by fragmentation from both monomer and dimer molecules. Thus, we have to write $I(K^+) = I_m(K^+) + I_d(K^+)$ where the subscripts m and d indicate the part of the K^+ ion current formed only from monomers or dimers. A similar expression can be written for KCl^+ . Thus the first analysis task is the apportionment of ion currents $I(K^+)$ and $I(KCl^+)$ to their constituents.

There are several methods used to determine fragmentation corrections [23-24] including:

- comparing the temperature dependencies of ion currents,
- measuring ion currents as a function of ionizing electron energy,
- changing the ratio of dimer and monomer molecules by superheating vapors (dual Knudsen cell) or lowering the activity of condensed phase,
- angular distribution measurements of ion currents.

If the monomer sublimation enthalpy (ΔH_m) differs from the dimer sublimation enthalpy (ΔH_d), the temperature dependence of ion currents formed from different molecules should be different. The slope of KCl^+ is close to that of K^+ and both differ markedly from the slope of K_2Cl^+ (see Table 1). Consideration of the ion current dependencies on energy leads to the same conclusion.

Grimley & Muenow and Grimley, *et al* measured angular distributions of ion currents for K^+ , KCl^+ and K_2Cl^+ . According to theoretical analyses (see Liu & Wahlbeck [25] and Voronin [26-28]) monomers and dimers should have different angular distributions due to collisions with the wall of the orifice. Ions K^+ and KCl^+ showed the same angular distribution, which fitted the theoretical distribution of monomer molecules. K_2Cl^+ had a different distribution, which fitted the theoretical distribution for dimer molecules.

Based on the above arguments, we can say that ions K^+ and KCl^+ are formed mainly from monomer species and K_2Cl^+ arises mainly from the dimer. Thus, the total ion current for the monomer is $I_m = I(K^+) + I(KCl^+)$, and the total ion current for the dimer is $I_d = I(K_2Cl^+)$, where mass discrimination corrections for multiplier, mass analyzer and ion source have been applied to the observed ion current data. The slopes from the temperature dependent plots of the ion currents (see Table 1) then immediately yield the enthalpies of reactions (5) and (6). The expression for the ratio of the total ion currents is

$$I_d / I_m = \frac{I(K_2Cl^+)}{[I(K^+) + I(KCl^+)]} \quad (8)$$

and the ratio of partial pressures may be determined as

$$P_d/P_m = (I_d/I_m) (\sigma_m/\sigma_d) , \quad (9)$$

where the ion current I corresponds to the observed ion current for the named species, and σ_m/σ_d is the ratio of the electron bombardment ionization cross sections for monomers and dimers, independent of instrument-dependent factors.

Unfortunately, the ratio of total cross sections σ_m/σ_d is not known and this uncertainty makes the application of Eqn (9) difficult. It is impossible to determine the cross section ratio without *a priori* knowledge of the true ratio of partial pressures, and the accuracy of theoretical values of cross sections is no better than 50 percent. The only experimental method available to control the monomer/dimer ratio is the application of the dual effusion chamber technique [24] but no one has reported such experiments with potassium chloride.

The mass spectrometric studies have shown clearly that only monomers and dimers should be taken into account where the vapors of KCl are considered. The concentration of other polymer molecules has been shown to be negligible. However, there is insufficient data to make a quantitative determination of the partial vapor pressures with good accuracy only from mass spectrometry.

2b. Total pressure and mass loss measurements

This group of methods is considered together because of one common feature. The property measured is the sum of all molecules existing in the vapor, the total vapor pressure. There is extensive literature on these methods — the review by Wahlbeck [29] is an excellent reference.

The total vapor pressure is determined as the sum of the partial pressures of monomers and dimers (Eqn 2). Various manometric techniques including the boiling point method, the Rodebush and Dixon method, and the torsion-effusion method have all been applied to measurement of the total vapor pressure over potassium chloride [30-43].

The mass loss, or gravimetric method, generally used for determining lower total pressures (less than ~5 Pa), utilizes a microbalance to determine the vaporization rate $\{\rho = m/(At)$, where m is the mass lost in time t through an orifice of area $a\}$ from a Knudsen effusion cell. When a substance produces both monomer and dimer molecules in its equilibrium vapor, the Hertz-Knudsen equation can be written as

$$\rho = \rho_m + \rho_d = (2\pi MRT)^{-1/2} M (p_m + \sqrt{2} p_d) ,$$

where M is the molecular mass of KCl and the rates and pressures are at temperature T . Let us define an apparent pressure obtained *via* the weight-loss Knudsen effusion method as

$$p_{KE} = \rho (2\pi RT)^{1/2} M^{-1/2} ,$$

which can be calculated from the vaporization rate, ρ . Then

$$p_{KE} = p_m + \sqrt{2} p_d . \quad (10)$$

For potassium chloride, such measurements are found in Refs. [13, 35, 44-57].

At vapor pressures greater than ~ 5 – 10 Pa, the measurement of saturated vapor transport rate in the flow of an inert gas is commonly used (the transpiration method). In this method, when the carrier gas is saturated with the vapor of KCl, the ratio of the mass of material vaporized (m) to the number of moles of carrier gas (n_c) transpired is as follows:

$$m/n_c = (m_m + m_d)/n_c = M (p_m + 2 p_d)/p_c$$

The partial pressure of the carrier gas, p_c , can be expressed in terms of the total pressure in the experimental system p_{sys} and the partial pressures of monomers and dimers by

$$p_c = p_{sys} - p_m - p_d$$

Typically, p_{sys} is of the order of 0.1 MPa, and p_m is rarely more than a few percent of p_{sys} . Introducing the apparent pressure obtained from the transpiration method, p_{TR} , which is calculated assuming only monomers to be in the vapor by

$$p_{TR} = p_{SYS} / \left(\frac{M}{m} \frac{n_c}{C} + 1 \right)$$

The following equation can also be obtained:

$$p_{TR} = \frac{(p_m + 2 p_d)}{(1 + p_d/p_{sys})} . \quad (11)$$

Usually, the partial pressure of dimer molecules is negligibly small compared with the system pressure p_{sys} , so the following approximation is valid within measurement error limits:

$$p_{TR} = p_m + 2 p_d$$

The transpiration method was applied to potassium chloride in Refs. [40, 58-64]. The authors of the original works ascribed an accuracy of 2-5 percent to the experimentally determined quantities p_{tot} , p_{KE} , and p_{TR} .

To conclude this section, we list other reported methods that also give information on the composition of the vapor of KCl:

- analysis of the velocity distribution of vapor molecules [49],
- p-V-T measurements of the superheated vapor [65],
- analysis of the angular distribution of vapor molecules [27, 28],
- electron diffraction on the molecular beam formed from the KCl vapor [66].

3. DETERMINING THE PARTIAL PRESSURES OF MONOMERS AND DIMERS

As has been mentioned, mass spectrometry shows unambiguously that KCl and K_2Cl_2 are the main components of the vapor over potassium chloride, but the accuracy of determining the partial pressures of monomers and dimers is generally dependent on estimates of relative ionization cross sections. We have shown that p_m and p_d can be calculated from total pressure measurements when the experimentally determined quantities p_{tot} , p_{KE} , and p_{TR} are taken together (see Eqns 2, 10, and 11). The accuracy of partial pressures obtained by this means is reasonable, and one can expect that the accuracy of the calculated partial pressures of monomers and dimers would be as good or better than partial pressures derived from mass spectrometric ion current measurements. Nevertheless, applying p_{tot} , p_{KE} , and p_{TR} to determine p_m and p_d is only possible when one has *a priori* knowledge of the significant species existing in the vapor. For example, if we were to include trimer molecules K_3Cl_3 into Eqns (2), (10), and (11), one would not expect comparably good results. Mass spectrometry partial pressure results provide the necessary knowledge of significant vapor species and quantitative checks on the results of calculations from total pressure data.

A similar approach has been used by Lau, *et al* to investigate the vaporization of alkali chromates and sulfates [67, 68]. Mass spectrometry was applied to determine the qualitative vapor composition, and quantitative data were obtained by measuring total vapor pressures and vaporization rates as a function of temperature. In general, it is necessary to combine mass spectrometric data with some form of total pressure measurement (*e.g.*, integrating ion currents observed and correlating with gravimetric measurements, or separate total pressure measurements) to obtain reliable partial pressure data where accurate cross section data are not available, as is generally the case.

Let us consider the existing procedure for the determination of the partial pressures from the total vapor pressure and vaporization rate data at a given qualitative composition. As an example, work by Barton & Bloom [37, 63] will be used. In 1956, they measured the total vapor pressure p_{tot} over KCl in the temperature interval from 1275 to 1539 K (11 measurements, boiling point method) [37] and fitted the results with the equation $\ln p = A - B/T$. In 1959, they determined the transpiration vaporization rate at temperatures from 1250 to 1473 K (7 measurements) [63]. They used the earlier equation for the total vapor pressure and extrapolated values of p_{tot} for each of the temperatures from the transpiration experiment. A simultaneous solution of Eqns (2) and (11) for each temperature of the second experiment gave the partial pressures of monomers and dimers. Then with equations

similar to (1), they obtained the enthalpies and entropies of reactions (5) and (6). A similar approach has been used in other original papers.

In JANAF [69] and Gurvich's [70] reference books, the same method was used, in principle, to estimate thermodynamic values of potassium chloride. First, the equilibrium constants of reaction (7), ($K_{dm}^o = p_d / p_m$) were estimated from the experimental data. To obtain this ratio, the transpiration data were processed as described above, the total pressure data of Barton & Bloom [37] being used to process the transpiration data of Barton & Bloom [63], the total pressure data of Schrier & Clark [40] being used to process transpiration data of Schrier & Clark [40], and so forth. The enthalpies of reaction (7) for each experiment, including the mass spectrometry data were estimated according to the Second and the Third Law and the recommended value of ΔH_{dm}^o inferred.

The next step was partitioning the experimental total pressures to obtain the partial pressures of the monomer, using the values of the equilibrium constant K_{dm}^o of reaction (7), calculated from the recommended value of ΔH_{dm}^o . Then, the partial pressures values of the monomer, p_m (from the equilibrium constant of reaction 5) were processed by both Second and the Third Law methods, and the enthalpy of reaction (5) ΔH_m^o was estimated.

The advantage of this procedure is its relative simplicity. Only ordinary linear regression techniques are required in all the steps. Partitioning the task into steps avoids the simultaneous solution of non-linear equations like (3) and (4) (the equivalent equations for p_{KE} and p_{TR} are analogous).

The disadvantages of the stepwise procedure are a consequence of its advantages. Let us return to the data of Barton & Bloom. Some ambiguity may be seen immediately. For example, it would have been possible to extrapolate the apparent transpiration pressures, p_{TR} , instead, recalculating them at the temperatures of the experimental total pressures. In other words, the choice of temperatures at which Eqns (2) and (7) should be solved is not obvious, and the accuracy of the solution is dependent on the reliability of extrapolated data.

More uncertainties arise from the stepwise method described and used for deriving the values given in thermodynamic references (*e.g.* [69] and [70]). In addition to the question of temperature, it is not clear which comparison method results in the selected combination of experiments on total pressure and vaporization rate. In particular, why were only the total vapor pressures determined by the same authors used when processing their transpiration data, as is the general case? From a general point of view, such a preference appears to have no explanation, as the total pressure determinations, and the transpiration measurements were two independent sets of experiments made on different apparatus. Also, averaging data of different experiments at the derived enthalpy level, and not at the level of the primary experimental quantities, makes it unclear how the weights should have been chosen to average the enthalpies.

The above questions result in the following problems. First, there are no guaranties that the recommended values are optimal. Second, reliable estimation of the true accuracy of the recommended values becomes impossible.

In this work, a simultaneous processing approach is chosen, in which more sophisticated procedures (the non-linear least squares and the maximum likelihood methods) are applied, and through which the above disadvantages can be overcome.

4. THE ORDINARY NON-LINEAR LEAST SQUARES METHOD

Before examining the data in detail, it is necessary to review the techniques being applied. This review will be relatively brief, and serves to link the nomenclature of the experimental discussion with that of the data reduction process.

We begin by noting that there is the set of experimentally measured values of p_{tot} , p_{KE} , and p_{TR} at different temperatures, which are themselves functionally related to the enthalpies and entropies of vaporization reactions of potassium chloride. This set results in an overdetermined system of non-linear equations, h_i , with unknown parameters (Q_1, \dots, Q_k) to solve where the experimental values y_i are assumed to contain measurement errors e_i :

$$y_i = h_i(Q_1, \dots, Q_k) + e_i \quad .$$

To get a reliable estimation of the parameters and their confidence limits, it is necessary to choose the proper error model. The simplest solution is obtained with the following assumptions: errors are random $\{\text{mean}(e_i) = 0\}$ with identical variance $\{\text{dispersion}(e_i) = \sigma^2\}$ and non-correlated $\{\text{cov}(e_i, e_j) = 0; i \neq j\}$. In this case the solution can be found when the sum of squares,

$$SS = \sum_i (y_i - h_i)^2 \quad ,$$

is minimized. This solution bears the special name - ordinary least squares (OLS).

In the KCl case, the OLS hypotheses can be assumed to hold, as a first approximation, for the logarithms of p_{tot} , p_{KE} , and p_{TR} . The temperature interval for all the experimental data is in the range between 700 and 1700 K (see Tables 2 to 4), over which the numerical values of the apparent experimental pressures change by almost ten orders of magnitude. So, if the pressures themselves are used $\{\text{Equations similar to (3)}\}$ the hypothesis about identical variances is clearly not applicable. However, the relative errors of the measured pressures by the various methods are similar, meaning that the absolute errors of the logarithms of the values should be close to each other.

Based on such considerations, the sum of squares function to be minimized is

$$SS = \sum_{i,j} \left(\ln p_{ij} - \ln p_{ij}^{calc} \right)^2, \quad (12)$$

where summation over the different experiments is shown by index i ($i = 1, \dots, L$), and summation over the experimental pressures within a particular experiment is indicated by index j ($j = 1, \dots, N_i$).

$\ln p_{ij}^{calc}$ is related to the partial pressures of monomers and dimers by the following relationships: (1) for the case of the total vapor pressures (where $\ln p_i = \ln p_{tot}$),

$$\ln p_{ij}^{calc} = \ln p_m + \ln (1 + p_d / p_m), \quad (13)$$

(2) for the case of Knudsen effusion apparent pressures ($\ln p_i = \ln p_{KE}$),

$$\ln p_{ij}^{calc} = \ln p_m + \ln (1 + \sqrt{2} p_d / p_m). \quad (14)$$

and (3) for the case of transpiration apparent pressures ($\ln p_i = \ln p_{TR}$),

$$\ln p_{ij}^{calc} = \ln p_m + \ln (1 + 2 p_d / p_m) - \ln \left[1 + \frac{p_m (p_d / p_m)}{P_{sys}} \right]. \quad (15)$$

The partial pressure of monomer molecules p_m and the ratio of partial pressures p_d / p_m depend upon the unknown enthalpies and entropies of Reactions (5) and (7) as

$$\ln p_m = - \left[\frac{\Delta H_m(T)}{RT} \right] + \left[\frac{\Delta S_m(T)}{T} \right] \quad (16)$$

and

$$\ln (p_d / p_m) = \left[\frac{\Delta H_{dm}(T)}{RT} \right] + \left[\frac{\Delta S_{dm}(T)}{T} \right]. \quad (17)$$

In the KCl data, the temperature ranged over a 1000 K interval, and to neglect the dependence of the enthalpies and entropies on temperature would be unrealistic. To deal with the temperature dependence, the melting temperature of solid potassium chloride (1044 K) was selected as the reference point. Then, ΔH_m° , ΔS_m° , ΔH_{dm}° , and ΔS_{dm}° at 1044 K, and the corresponding sublimation processes were taken as the unknown parameters. For temperatures below and above the melting point, the following equations were used

$$\left. \begin{aligned} \Delta H(T) &= \Delta H_{1044} - \int_T^{1044} \Delta C_{\bar{p}} dT \\ \Delta S(T) &= \Delta S_{1044} - \int_T^{1044} \frac{\Delta C_{\bar{p}}}{T} dT \end{aligned} \right\} \quad (18)$$

$$\left. \begin{aligned} \Delta H(T) &= \Delta H_{1044} - \int_T^{1044} \Delta C_{\bar{p}} dT - \Delta H_{fus} \\ \Delta S(T) &= \Delta S_{1044} - \int_T^{1044} \frac{\Delta C_{\bar{p}}}{T} dT - \Delta H_{fus} \end{aligned} \right\} \quad (19)$$

where the subscripts m and dm are applied depending on the quantities being considered.

The temperature dependence of the heat capacity ($\Delta C_{\bar{p},m}^{\circ}$ or $\Delta C_{\bar{p},dm}^{\circ}$) for Reactions (5) and (7), and the enthalpy of melting of KCl ($\Delta_{fus}H^{\circ}$) were considered as *a priori* known quantities, and were taken from [70]. Note that these quantities are essentially the same in JANAF [69].

Substituting Eqns (13)-(19) into (12) gives the resultant sum of squares, with four unknown parameters – ΔH_m° , ΔS_m° , ΔH_{dm}° , and ΔS_{dm}° at 1044 K. It should be mentioned that, when only one type of experimental data (only total vapor pressures, for example) was employed, a reliable solution for all four parameters could not be obtained. Individually, $\ln p_{tot}$, $\ln p_{KE}$, and $\ln p_{TR}$ (Eqns 13-17), as functions of inverse temperature, don't differ significantly from straight lines.

Tables 2 through 4 identify the papers and the experimental data that were used for the minimization of (12). Data given in [32, 34, 36, 52, 58, 59, 60] were not utilized as they are in considerable disagreement with others. Refs. [45, 46] were unavailable. Refs. [51, 56] were devoted to the investigation of the vaporization of potassium chloride under non-equilibrium conditions and [53, 55], where the effusion rates were measured in the transitional flow regime, were not been considered. Also, in the papers of Ewing & Stern [54], and van der Kemp [13], only those effusion rates for temperatures up to 950 K were used. At higher temperatures, molecular effusion enters into transition flow, and the Hertz-Knudsen equation should not be applied.

In the papers of Barton & Bloom [37], Pugh & Barrow [38], Schrier & Clark [40], Kushkin, *et al* [41], and Burylev & Mironov [43], there were no primary experimental data. Only an approximating equation was available. To include these data into the minimization of (12), the following procedure was applied: The experimental temperature interval was equally divided into the number of intervals corresponding to the reported number of experimental points. In Ref. [41, 43] where the number of experimental points was unavailable, N_i was arbitrarily set to ten as a reasonable approximation to

typical numbers of experimental measurements. At each such temperature, the logarithm of pressure was computed according to the approximating equation given and the resulting data were used as pseudo-experimental values in Eqn. (12).

Overall, 460 experimental points from 29 separate experiments were included in the sum of squares (Eqn. 12). To find minimum of Eqn. 12 in terms of the unknown parameters, the finite difference Levenberg-Marquardt algorithm was applied. The parameters estimated are given in Table 5 and this solution will be referred to as OLS. The minimum of the sum of squared deviations (12) was $SS = 7.69$ (for p_i 's in Pa). The corresponding standard deviation of the fit was

$$s_f = \left[\frac{SS_{\min}}{\sum_i N_i - 4} \right]^{1/2} = 0.13 \text{ .}$$

In other words, on average, the apparent pressures differed from the fitting equations by about 15 percent, which is far more than the reproducibility errors within each experiment ($\approx 3\text{-}5$ percent).

5. ANALYSIS OF RESIDUALS

Having estimated the parameters by the ordinary least squares method (OLS), the residuals e_{ij} of the experimental data from the fitting equations were analyzed

$$e_{ij} = \ln p_{ij} - \ln p_{ij}^{calc} \text{ .} \quad (20)$$

The residuals for logarithms of the total vapor pressure, p_{tot} , the apparent Knudsen effusion pressures, p_{KE} , and the apparent transpiration pressures, p_{TR} , from the corresponding fitting equations, are shown in Figures 1 to 3. In Figure 4, the fitting equations for the Knudsen effusion and transpiration data are drawn, corrected to the total vapor pressure, and a portion of the experimental data is also presented. Note that the residuals in Figures 1 to 4 are shown for the recommended solution ML(III-1). The basis for that solution and its choice will be described later. The residuals obtained from fitting by the ordinary least squares method were similar to the ML(III-1) solution.

The residuals show that there is definite disagreement based on the assumption of the simple error model of the ordinary least squares method. The results for different studies vary from each other more than the statistical spread within each separate experiment, indicating in particular that the OLS hypotheses of equivalence and non-correlation of variances are clearly incorrect.

The following interpretation seems to be quite reasonable. The complete error e_{ij} for an apparent experimental pressure contains not only a reproducibility or random error but also a systematic error term. The behavior of the residuals in Figs. 1–4 suggests that in each i -th experiment, the residuals

tend to spread over different straight lines, each of which is shifted and tilted relative to the fitting equation. Thus, the behavior of the residuals may be explained by the following equation

$$e_{ij} = e_{r,ij} + e_{a,i} + e_{b,i} x_{ij} \quad , \quad (21)$$

where

$$x_{ij} = 10^3 \left(\frac{1}{T_{ij}} - \frac{1}{T_i} \right)$$

and T_i is the mean temperature of i -th experiment in Kelvins, in the following sense,

$$\frac{1}{T_i} = N_i^{-1} \sum_j \left(\frac{1}{T_{ij}} \right) \quad ,$$

and the constant, 10^3 , conveniently normalizes the abscissa values to be near unity. In Eqn. (21), $e_{r,ij}$ is the "true" reproducibility error of the j -th point in the i -th experiment; $e_{a,i}$ and $e_{b,i}$ are the systematic errors connected with i -th experiment. $e_{a,i}$ is the error associated with a parallel or constant shift of the $\ln p_i$ values relative to the fitting equation (the shift error), $e_{b,i}$ is the error related to the tilt or rotation of the line that best fits $\ln p_i$ about the point corresponding to the mean temperature (T_i) of the i -th experiment (the tilt error).

When the enthalpies and entropies of Reaction (5) and (7) are determined, the residuals e_{ij} are also determined. It is then possible to estimate $e_{a,i}$ and $e_{b,i}$, if one assumes that the sum of squares of the "true" reproducibility errors, given by

$$\sum_j e_{r,ij}^2 = \sum_j (e_{ij} - e_{a,i} - e_{b,i} x_{ij})^2 \quad , \quad (22)$$

should be minimal. Minimization of (22) gives

$$e_{a,i} = \frac{\sum_j e_{ij}}{N_i}$$

and

$$e_{b,i} = \frac{\sum_j e_{ij} x_{ij}}{P_i} \quad ,$$

where

$$P_i = \sum_j x_{ij}^2 \quad .$$

The estimated values of $e_{a,i}$, $e_{b,i}$, and $s_{r,i} = (\sum_j e_{r,ij}^2)_{\min} / (N_i - 2)$ are shown in Tables 2 to 4.

The estimated values of $s_{r,i}$, $e_{a,i}$, and $e_{b,i}$ are given for the recommended solution ML(III-1). Figure 5 shows a graphic representation of the systematic errors $e_{a,i}$ and $e_{b,i}$ in each experiment. Note that the appearance of Fig. 5, in the case of the ordinary least squares fit, would show a similar dispersion. Note also that it is not $e_{b,i}$ itself, but the term $e_{b,i} \cdot (P_i/N)$ that is used as the ordinate. This term is conveniently dimensionless, has the same sense as $e_{a,i}$, and shows how much, on the average, the full error e_{ij} differs from $e_{r,ij}$ due to the shift and tilt error for each experiment.

Therefore, we conclude that the error model should be modified. Without modifying the error model, the statistical information obtained regarding the precision of the fit are not a reliable guide to the accuracy of the data. To retain the techniques of the ordinary least squares method, the following procedure is usually used. The outlying data sets are discarded, and a smaller set of experimental data is processed. In the KCl case, even that method could not be used, as the data of the twelve experiments that are best in accord with each other (the central group shown within the tolerance circle in Fig. 5) differ from each other more than their reproducibility error. Even for this small group of data, the error model of the ordinary least squares method could still not be applied. In such cases, the analyst is often reduced to assessing the quality of the available data and selecting one consistent set one which to base assessed thermodynamic quantities.

6. THE MAXIMUM LIKELIHOOD METHOD

To get reliable estimated values, it is necessary to change the error model of the ordinary least squares method to a more realistic one, and to redetermine the enthalpies and entropies of Reactions (5) and (7) with that new model. The residual analysis discussed above showed that Eqn. (21) described all the experimental data reasonably well and this equation was chosen as the error model.

Let us make a statistical hypotheses about $e_{r,ij}$, $e_{a,i}$, and $e_{b,i}$, considering them to be random quantities.

Let us also assume that their expectancies are zero and that they are not correlated with each other. Take their dispersion estimates to be given by

$$D(e_{r,ij}) = \sigma_{r,i}^2$$

$$D(e_{a,i}) = \sigma_{a,i}^2$$

$$D(e_{b,i}) = \sigma_{b,i}^2$$

where $\sigma_{r,i}^2$, $\sigma_{a,i}^2$, and $\sigma_{b,i}^2$ are the variance components that we will call reproducibility variance, shift variance, and tilt variance.

The analysis of residuals (see section 5 above, Figs. 1–5, and Tables 2–4) showed that the variances $\sigma_{r,i}^2$, $\sigma_{a,i}^2$, and $\sigma_{b,i}^2$ could not be assumed to be the same for all experiments. Nevertheless, groups of experiments could be chosen for which the hypothesis can be accepted that the variances are sufficiently equal.

Based on Figure 5, three groups of experiments were chosen. The solid line encloses the central group of 12 experiments (labeled WA [31], FR [33], BB1 [37], PB [38], NP [39], SC1 [40], BV1 [48], BV2 [48], BV3 [48], BB2 [63], SC2 [40], MM [64], and identified in Figs. 1-3). These experiments most closely agree with each other. The second group is comprised of the experiments lying near the abscissa axis outside the central circle (D1 [35], D2 [35], MK [49], KK2 [57], KK3 [57]). In this group, the temperature dependence agrees well with the first group, but the values of $\ln p_{ij}$ are shifted away from the fitting equation. The experiments near the ordinate axis are taken as a third group (BD [42], MW [44], NS [50]). Here, the apparent pressures are in agreement with the central group but the temperature dependent behaviors of the $\ln p_{ij}$ are not in reasonable agreement, experiment to experiment.

Three sets were formed. The first set, Q, includes experiments from all three groups listed above. The reproducibility variances were assumed to be the same, $\sigma_{r,i}^2 = \sigma_r^2$, for all the data in this set. The second set, Q_a, includes the first and third groups of experiments. For the studies inside this set, the shift variances were assumed to be the same, $\sigma_{a,i}^2 = \sigma_a^2$. The third set, Q_b, consisting of the experiments from the first and second groups, combined studies assuming the same tilt variances, $\sigma_{b,i}^2 = \sigma_b^2$. For studies not included in any of these sets, it was assumed that their corresponding variances differed among each other and from σ_r^2 , σ_a^2 , and σ_b^2 .

The assumptions made result in a block-diagonal dispersion matrix of all the experimental values, $\ln p_{ij}$

$$D(\bar{y}) = D(\bar{\epsilon}) = \text{diag}(V_i) \quad , \quad (25)$$

where $\bar{\epsilon}$ is the vector of all differences e_{ij} (of length $\sum_i N_i$) and V_i is the dispersion matrix of the i -th experiment,

$$V_i = \sigma_{r,i}^2 \mathbf{I}_i + \sigma_{a,i}^2 \vec{1}_i \vec{1}_i^T + \sigma_{b,i}^2 \vec{x}_i \vec{x}_i^T \quad . \quad (26)$$

where \mathbf{I}_i is the i -dimensioned unit array, and $\vec{1}_i$ is the vector of length N_i , consisting of ones; \vec{x}_i is the j -th vector from x_{ij} .

If the variance components $\sigma_r^2, \sigma_{r,i}^2, \sigma_a^2, \sigma_{a,i}^2, \sigma_b^2$, and $\sigma_{b,i}^2$ are known *a priori*, the general least squares method could be used to estimate the parameters - minimizing the general sum of squares

$$SS = \bar{\mathbf{e}}' \mathbf{D}(\bar{\mathbf{e}})^{-1} \bar{\mathbf{e}} \quad (27)$$

However, in the current case, the dispersion matrix $\mathbf{D}(\bar{\mathbf{e}})$ contains unknown values — the variance components. Thus, the task we have to solve is the simultaneous determination of the enthalpies and entropies of Reactions (5) and (7), and also the variance components $\sigma_r^2, \sigma_{r,i}^2, \sigma_a^2, \sigma_{a,i}^2, \sigma_b^2$, and $\sigma_{b,i}^2$.

Much attention has been paid to determining variance components in the last twenty years [71, 72] and a number of methods have been devised. We selected the Maximum Likelihood method primarily because it is relatively simple to apply. The simple structure of the dispersion matrix $\mathbf{D}(\bar{\mathbf{y}})$ in this case makes it possible to apply the Levenberg-Marquardt algorithm for non-linear systems as the means to realize the Maximum Likelihood method.

One claimed disadvantage of the Maximum Likelihood method is that it introduces a bias in the estimated variance components. However, in many situations, it has been reported that the method is very effective for obtaining variance components [73, 74].

To estimate the parameters and the variance components., the Maximum Likelihood function is maximized. Assuming a multivariate normal distribution for all the errors, the maximum of the likelihood function coincides with the maximum of the following function

$$L = - \det [\mathbf{D}] - (\bar{\mathbf{y}} - \bar{\mathbf{h}})' \mathbf{D}(\bar{\mathbf{y}})^{-1} (\bar{\mathbf{y}} - \bar{\mathbf{h}}) \quad (28)$$

where $\bar{\mathbf{h}}$ is the resultant fitted values corresponding to the observed $\bar{\mathbf{y}}$.

In our situation, the function L can be expressed as

$$L = - \sum_i \left[N_i \ln \sigma_{r,i}^2 + \ln \left(1 + N_i \frac{\sigma_{a,i}^2}{\sigma_{r,i}^2} \right) + \ln \left(1 + P_i \frac{\sigma_{a,i}^2}{\sigma_{r,i}^2} \right) \right] - SS \quad (29)$$

where $P_i = \bar{x}_i \bar{x}_i$ and SS is the general sum of squared deviations (Eqn 27) that in turn is given by

$$SS = \sum_i \sigma_{r,i}^{-2} \left\{ \sum_j \epsilon_{ij}^2 - \gamma_{a,i} (1 + N_i \gamma_{a,i})^{-1} \cdot (\sum_j \epsilon_{ij})^2 - \gamma_{b,i} (1 + P_i \gamma_{b,i})^{-1} \cdot (\sum_j \epsilon_{ij} x_{ij})^2 \right\}$$

Function L depends on the variance components and the parameters (the enthalpies and entropies of Reactions 5 and 7), with the unknown parameters being the residuals e_{ij} (Eqns 20 and 13-19).

Initially, all four parameters, the enthalpies and entropies of Reactions (5) and (7), were also allowed to be unknown quantities. This approach corresponds to the Second Law treatment and the solution obtained will be referred to as ML(II).

In another approach, the entropies of Reactions (5) and (7) were calculated from the absolute entropies of substances involved, in order to analyze the data according to the Third Law treatment (see Ref. [69] for a discussion of the Second Law and Third Law treatments for simple vaporization cases and the relative *pros* and *cons* of each treatment). The entropy of condensed potassium chloride was obtained from the experimentally measured heat capacity, and the entropies of monomer and dimer vapor were estimated from their molecular constants (see the discussion in Ref. 69 for the methods). The entropies of KCl and K₂Cl₂, estimated in JANAF [69] and in Gurvich's [70] tables, are in agreement, the difference being less than 2 J mol⁻¹ K⁻¹ at 1000 K. In these calculations, the entropies were taken from Gurvich [70] because the set of experimental molecular constant data used there is more complete.

When the Third Law treatment was applied, the calculations were performed two ways. In the first case, only the entropy of Reaction (5) was kept constant. This condition corresponds to processing Reaction (5) according to the Third Law and Reaction (7) according to the Second Law. For the second calculation, both entropies were held constant, making this calculation a completely Third Law treatment. The corresponding solutions will be referred to as ML(III-1) and ML(III-2), respectively.

The values of the parameters obtained are presented in Table 5 and the variance components are given in Table 6. The full errors obtained are presented in Table 5.

8. DISCUSSION

The enthalpies and entropies of Reaction (5) and (7), obtained in the present work {the solutions OLS, ML(II), ML(III-1), ML(III-2)} and those calculated according to the data in the reference tables [69, 70] are given in Table 5. The maximized value of function L (Eqn 28) has been computed for each solution set of parameters to allow for comparison among the sets.

The most reliable values of the parameters and their confidence limits were obtained by the Maximum Likelihood method. The ordinary least squares method produced less reliable results because the error model for OLS has been shown to be unrealistic in the KCl case. The dispersion matrix $D(\bar{e})$ is equal to $\sigma^2 \mathbf{I}$ in the ordinary least squares method, which means that each experimental point is given the same weight. As a result, the fitting curve is biased by the experiments with the larger number of points. In the Maximum Likelihood method, the weights are determined by both statistical and

systematic errors. It should be kept in mind that when the number of points in an experiment is increased, the systematic error does not.

The set of parameters obtained with the complete Third Law treatment ML(III-2) may be compared with the values from the reference tables [69, 70], where the Third Law treatment was preferred. The values of L show that the enthalpies and entropies of Reactions (5) and (7) in JANAF [69] and Gurvich [70] are not optimal, as can be expected.

Therefore, only the results obtained by the Maximum Likelihood method, corresponding to the Second and Third Law {ML(II), ML(III-1), ML(III-2)} treatments will be intercompared.

The entropy of Reaction (5), determined in the present work by the Second Law approach, is essentially the same as that calculated from the absolute entropies, while the entropy for Reaction (7) differs by about $10 \text{ J mol}^{-1} \text{ K}^{-1}$. This result implies that the entropy of K_2Cl_2 , calculated from its molecular constants, is less by about $10 \text{ J mol}^{-1} \text{ K}^{-1}$ than the entropy deduced from the ML(II) solution.

The uncertainty in the entropy of K_2Cl_2 at 1000 K in Gurvich [70] is estimated to be $6.3 \text{ J mol}^{-1} \text{ K}^{-1}$. Such a large uncertainty for the entropy of the four-atom dimer molecule (compared to the uncertainty for KCl, $0.05 \text{ J mol}^{-1} \text{ K}^{-1}$) is caused by the fact that the three lowest vibrational frequencies were not experimentally determined. Instead, ion model results were used and there is significant uncertainty in structure and bonding for the dimer. In particular, the lowest vibrational frequencies are relatively very low, and thus contribute strongly to the entropy. Relatively small errors in such low vibrational frequencies result in relatively larger entropy uncertainties.

Since the errors for ΔS°_{dm} , calculated by us and reported in Ref. [70] overlap, it is not strictly reasonable to speak about the disagreement between spectroscopy and thermodynamics. However, in choosing recommended values for the parameters, we have to increase the entropy of the dimer, compared to Refs. [69, 70]. To show this more clearly, let us compare the ML(III-1) and ML(III-2) solutions.

The fit for the ML(III-2) solution, as compared with the ML(III-1) solution, is shown in Figs. 1 to 3. The curves for ML(III-2) go below the central group of experimental data for the total pressure and transpiration data sets (Figs. 1 and 3) and above the central group of Knudsen effusion data (Fig. 2). The variance components, obtained for the ML(III-1) and ML(III-2) solutions, are presented in Table 6. The shift variance for the central group of twelve experiments, $\sigma_{a,i}^2$, is 0.017 in ML(III-1) and 0.055 in ML(III-2). These values mean that for the ML(III-2) solution to be accepted, one would have to say that the systematic errors are about six percent, whereas in the case of ML(III-1) they are less than two percent.

The strongest difference between the results for the Second and for the Third Law treatments of Reaction (7) is seen in the ratio of partial pressures of dimers to monomers, p_d/p_m . That ratio is

presented in Fig. 6, where the results of the mass spectrometric and other methods, not included in our processing, are also presented.

Miller & Kusch [49] calculated p_d/p_m from measurements of the velocity distribution in a potassium chloride molecular beam. Voronin [27, 28] calculated p_d/p_m using the experimental data of Grimley [6, 8] for the angular distribution of molecules KCl and K_2Cl_2 . Mawhorter, *et al* [66] determined the ratio p_d/p_m from their electron diffraction investigation of potassium chloride molecular beams. Determining p_d/p_m from the data of these three methods is not straightforward. Sophisticated treatment of the primary experimental data is required. The results of Miller & Kusch and of Mawhorter, *et al* [66] support the ML(III-1) solution, while the result of Voronin more closely supports the ML(III-2) solution.

Datz [65] measured the density of superheated vapor of potassium chloride and estimated the equilibrium constants of the homogeneous reaction, $K_2Cl_2 = 2 KCl$. Combining the equilibrium constants of reaction (5) with the data of Ref. [65] gives the values for p_d/p_m presented in Fig. 6. Datz's method seems to be trustworthy but the values obtained are not close to either of the ML(III) solutions, and there is no apparent explanation

The experimental ratios of total ion currents $I_{d,t}/I_{m,t}$ (Eqn 9) are also presented in Figure 6. Comparison of these ratios to the ratio of partial pressures p_d/p_m gives the ratio of cross sections σ_d/σ_m (Eqn 8). Comparison with the solution, ML(III-2), one derives a value of about one for the ratio of σ_d/σ_m from most of the mass spectrometer data, and the ratio depends rather noticeably on temperature. Both the magnitude of the ratio, and the temperature dependence is in disagreement with what is generally accepted in high temperature mass spectrometry [23]. On the other hand, the ML(III-1) solution gives about 1.4 for the ratio of σ_d/σ_m and essentially no temperature dependence. This result is in full accordance with the expected behavior of the cross section ratios for high temperature mass spectrometry. At higher temperatures, using transpiration mass spectrometry to observe vapor species above the liquid, some temperature dependence of cross sections has been reported [12], but those studies indicate that the lower temperature MS work should show no effect.

All the above discussion supports increasing the recommended value for the entropy of K_2Cl_2 , compared with the currently accepted tabulated data [69, 70]. To increase the entropy of K_2Cl_2 by $10 \text{ J mol}^{-1} \text{ K}^{-1}$ only requires decreasing the three unmeasured frequencies of the dimer by about 30 percent from the values of the ion models (*e.g. from* 212, 111, & 145 cm^{-1} [70] *to* 170, 89, & 116 cm^{-1}). Such a reduction may seem to yield unreasonably low frequencies, but may be considered more likely if the dimer molecule is not rigid, *i.e.* the rigid-rotator-harmonic oscillator approximation is not a reasonable hypothesis in this case. There have been suggestions that relatively free rotation (the "polytopic" model) is a possibility in this system, which would strongly support lower fundamental vibrational frequencies. Clearly, more experiments and calculations on the K_2Cl_2 structure are necessary to obtain a more reliable answer.

Our conclusion regarding the lack of information on molecular constants for K_2Cl_2 affects the ML(III-2) and ML(III-1) solutions also. These solutions required values of the heat capacity for K_2Cl_2 taken from Ref. [70] to make the temperature corrections of the enthalpy and entropy of Reaction (7) (Eqns 18 and 19). Fortunately, the effect of low vibrational frequency uncertainties on the heat capacity differs from that for the entropy. While changing low frequencies influences the entropy strongly, the vibrational partition function contribution to the heat capacity is essentially constant and equal to the classical limit - the gas constant R .

As the recommended values, the set of parameters from the solution, ML(III-1), has been chosen. This solution was obtained by the Maximum Likelihood method, with the entropy of Reaction (5) calculated from the absolute entropies. The ML(III-1) solution does not differ significantly from the Second Law treatment ML(II), but the deviation of ΔS_m° from the absolute entropies is significantly smaller. As a result, the estimated uncertainties of the parameters are considerably smaller than in ML(II).

The total and partial pressures over potassium chloride, as calculated according to the recommended parameters ML(III-1), are presented in Table 7.

Recalculating the enthalpies and entropies at 298 K gives $\Delta H_m^\circ = 221.54 \pm 0.5 \text{ kJ mol}^{-1}$, $\Delta H_{dm}^\circ = 47.25 \pm 5.4 \text{ kJ mol}^{-1}$ and $\Delta S_{dm} = 39.15 \pm 3.8 \text{ J mol}^{-1} \text{ K}^{-1}$. As the Third Law treatment of Reaction (5) was accepted, ΔS_m° at 298 K is the same as in Ref. [70] ($156.41 \pm 0.2 \text{ J mol}^{-1} \text{ K}^{-1}$). These values, together with the enthalpy of formation $\Delta_f H^\circ(KCl, s, 298.15 \text{ K}) = -436.49 \pm 0.1 \text{ kJ mol}^{-1}$, and the entropies, $S^\circ(KCl, s, 298.15 \text{ K}) = 82.57 \pm 0.15 \text{ J mol}^{-1} \text{ K}^{-1}$ and $S^\circ(KCl, g, 298.15 \text{ K}) = 238.98 \pm 0.02 \text{ J mol}^{-1} \text{ K}^{-1}$ from [70] lead to $\Delta_f H^\circ(KCl, g, 298.15 \text{ K}) = -214.95 \pm 0.5 \text{ kJ mol}^{-1}$, $\Delta_f H^\circ(K_2Cl_2, g, 298.15 \text{ K}) = -604.19 \pm 5.4 \text{ kJ mol}^{-1}$ and $S^\circ(K_2Cl_2, g, 298.15 \text{ K}) = 360.70 \pm 3.8 \text{ J mol}^{-1} \text{ K}^{-1}$. Recalculation to 0 K gives $\Delta_f H^\circ(KCl, g) = -213.16 \pm 0.5 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(K_2Cl_2, g) = -600.80 \pm 5.4 \text{ kJ mol}^{-1}$.

SYMBOLS

(the number of the applicable equation is given in parentheses)

- $\Delta H_m^\circ, \Delta S_m^\circ$ - the enthalpy and entropy of Reaction (5)
 $\Delta H_d^\circ, \Delta S_d^\circ$ - the enthalpy and entropy of Reaction (6)
 $\Delta H_{dm}^\circ, \Delta S_{dm}^\circ$ - the enthalpy and entropy of Reaction (7)
 M - molecular mass of KCl
 ρ - the molecular flow through unit area in unit time
 p_m, p_d - the partial pressures of KCl and K_2Cl_2 {all pressures in Pa units}
 p_c - the partial pressure of carrier gas in the transpiration method
 p_{sys} - the total system pressure inside the transpiration apparatus
 $I_{m,t}, I_{d,t}$ - the total ion currents formed from KCl and K_2Cl_2 , (8)
 σ_m, σ_d - the total ionization cross sections KCl and K_2Cl_2 , (9)
 p_{tot} - the total vapor pressure, (2)
 p_{KE} - the apparent pressure of Knudsen effusion, (10)
 p_{TR} - the apparent pressure of transpiration method, (11)
 y_i - an experimental value
 \vec{y} - a vector of experimental values
 h_i - a value, calculated according to a fitting equation
 \vec{h} - a vector of fitting values
 Q_i - an unknown parameter
 $\ln p_{ij}$ - an experimental pressure {i.e., $\ln p_{tot}$, $\ln p_{KE}$, or $\ln p_{TR}$ }
 $\ln p_{ij}^{calc}$ - the pressure, calculated according to fitting equations (13)-(15)
 $i = 1, \dots, M$ - the experiment number
 M - number of all experiments
 $j = 1, \dots, N_i$ - the point number in the i -th experiment
 N_i - number of points in the i -th experiment
 SS - the sum of squared deviations (12) or the general sum of squared deviations (27)
 L - the function whose maximum coincides with the maximum of the likelihood function
 σ_f - the standard deviation of the fitting equation
 e_{ij} - the difference between the experimental and calculated pressure, (20)
 \vec{e} - a vector of all differences e_{ij} , of length $\sum_i N_i$
 \vec{e}_i - a vector of differences e_{ij} for the i -th experiment, of length N_i
 $e_{r,ij}$ - the "true" reproducibility error for $\ln p_{ij}$, (21)
 $e_{a,i}$ - the systematic shift error in the i -th experiment, (21)
 $e_{b,i}$ - the systematic tilt error in the i -th experiment, (21)
 Q - the set of experiments {WA, FR, BB1, PB, NP, SC1, BV1, BV2, BV3, BB2, SC2, MM, BD, MW, NS, D1, D2, MK, KK2, KK3}
 Q_a - the set of experiments {WA, FR, BB1, PB, NP, SC1, BV1, BV2, BV3, BB2, SC2, MM, BD, MW, NS}

- Q_b - the set of experiments {WA, FR, BB1, PB, NP, SC1, BV1, BV2, BV3, BB2, SC2, MM, D1, D2, MK, KK2, KK3}
- $\sigma_{r,i}^2$ - the variance of the "true" reproducibility errors in the i -th experiment
- $\sigma_{a,i}^2$ - the variance of the systematic shift error in the i -th experiment
- $\sigma_{b,i}^2$ - the variance of the systematic tilt error in the i -th experiment
- σ_r^2 - the variance of the "true" reproducibility errors for experiments in the set Q
- σ_a^2 - the variance of the systematic shift error for experiments in the set Q_a
- σ_b^2 - the variance of the systematic tilt error for experiments in the set Q
- D - a dispersion matrix
- I - the unity matrix
- V_i - the dispersion matrix for the i -th experiment, (26)
- 1_i - a vector of length N_i , composed of ones
- $x_{ij} = 10^3 (1/T_{ij} - 1/T_i)$
- \bar{x}_i - the i -th experiment vector from x_{ij}

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TABLE 1. Temperature dependence of ions

Year	Author(s)	Temperature K	$\Delta H(K^+)^a$ kJ mol ⁻¹	$\Delta(KCl^+)^a$ kJ mol ⁻¹	$\Delta H(K_2Cl^+)^a$ kJ mol ⁻¹
1960	Milne & Klein	842-1011	209		254
		774- 999	205		239
		814-1016	209		241
		822- 953	220		267
1969	Grimley & Joyce	800- 880	207±3	209±3	243±4
1979	Wagner & Schafer	821- 882		213	243
1984	Hastie, <i>et al</i>	987-1289	170	150	213
		1085-1305	164	149	207

^a($\Delta H(K^+)$ is the slope of a line in coordinates $R \ln I(K^+)T$ vs. $10^3/T$, the other ions have been treated the same. From Eqn 1, this treatment gives the heat of vaporization from condensed KCl (data of Hastie, *et al* for vapors over liquid KCl, data of others over solid KCl, *i.e. sublimation*)

Table 2. Total vapor pressure experiments with KCl

Year	Author(s)	method	Temperature K	N	$\epsilon_{r,i}$	$\epsilon_{a,i}$	$\epsilon_{b,i}$ ×10 ³ K	Code
1921	Ruff & Mugdan	BP	1393-1688	7	0.04	0.08	1.5	RM
1921	Wartenberg & Albrecht	BP	1389-1691	16	0.06	0.00	-0.2	WA
1926	Fiock & Rodebush	RD	1179-1378	9	0.01	-0.01	-0.1	FR
1936	Deitz	M	847- 936	9	0.03	0.19	0.0	D1
1956	Barton & Bloom	BP	1275-1539	11 ^{eq}	- ^b	-0.01	0.1	BB1
1958	Pugh & Barrow	TE	819- 945	137 ^{eq}	- ^b	-0.02	0.2	PB
1961	Novikov & Polyachenok	BP	1170-1466	9	0.02	-0.01	0.2	NP
1963	Schrrier & Clark	BP	1189-1418	31 ^{eq}	- ^b	0.04	0.2	SC1
1967	Kushkin et al	BP	1173-1323	7 ^{eq}	- ^b	-0.06	-1.0	K
1973	Barchuk & Dubovoi	BP	1170-1466	6	0.01	-0.01	0.5	BD
1975	Burylev & Mironov	BP	1299-1557	7 ^{eq}	- ^b	-0.10	2.4	BM

^a(BP - boiling point; RD - Rodebush & Dixon; M - manometer; TE - torsion effusion)

^{eq}primary experimental data are not available, only an equation is given

^bnot available

Table 3. Knudsen effusion experiments with KCl

Year	Author(s)	Expt. type ^a	Temperature K	N	$e_{r,i}$	$e_{a,i}$	$e_{b,i}$ $\times 10^3$ K	Code
1936	Deitz	ML	913-932	4	0.04	0.25	-0.2	D2
1938	Mayer & Winter	ML	899-935	5	0.03	0.02	1.5	MW
1944	Zimm & Mayer	SI	624-945	21	0.09	-0.06	-0.3	ZM
1953	Bradley & Volans 1	ML	713-835	14	0.03	0.02	0.0	BV1
1953	Bradley & Volans 2	ML	771-863	7	0.01	0.00	0.0	BV2
1953	Bradley & Volans 3	ML	785-870	16	0.01	-0.03	0.1	BV3
1956	Muller & Kusch	SI	872-967	10	0.01	-0.40	-0.2	MK
1957	Nesmeyanov & Sazonov	RI	753-897	7	0.07	0.00	-0.5	NS
1974	Ewing & Stern	ML	834-945	24	0.02	-0.11	0.5	ES
1984	Kawano & Kenpo 1	SI	687-877	11	0.04	0.35	-0.7	KK1
1984	Kawano & Kenpo 2	SI	692-874	11	0.04	0.32	-0.1	KK1
1984	Kawano & Kenpo 3	SI	696-866	10	0.03	0.27	-0.1	KK1
1981	van der Kemp	ML	842-952	170.16		0.05	2.1	vK

^a(ML - mass loss, SI - surface ionization, RI - radioactive indicator)

Table 4. Transpiration experiments with KCl

Year	Author(s)	Temperature K	N	$e_{r,i}$	$e_{a,i}$	$e_{b,i}$ $\times 10^3$ K	Code
1939	Naryshkin	1023-1188	3	0.05	-0.16	-1.0	N
1953	Treadwell & Werner	859-1024	13	0.02	0.17	-0.7	TW
1959	Barton & Bloom	1250-1473	7	0.02	-0.03	-0.3	BB2
1963	Schrier & Clark	1153-1352	10	0.01	0.01	-0.1	SC2
1965	Murgulescu & Marta	1373-1473	23	0.04	0.02	-0.4	MM

Table 5. Enthalpies and entropies of reactions (5) and (7)
(all quantities given are at 1044 K for the sublimation process)

Source	ΔH_m° kJ mol ⁻¹	ΔS_m° J mol ⁻¹ K ⁻¹	ΔH_{dm}° kJ mol ⁻¹	ΔS_{dm}° J mol ⁻¹	p_d/p_m	L K ⁻¹
JANAF	206.47±0.5	132.14	23.65±4.2	16.25	0.46	2450.96
Gurvich	207.15±3.0	133.03±0.5	26.26±7.6	14.48±6.3	0.28	2455.80
OLS	208.70±2.0	134.94±2.4	30.53±11	17.78±11	0.25	2484.62
ML(II)	206.77±1.3	133.03±1.6	37.84±6.6	24.92±6.0	0.26	2505.58
ML(III-1)	206.77±0.5	a	37.83±5.4	24.91±3.8	0.26	2505.58
ML(III-2)	206.82±0.6	b	25.74±8.9	b	0.29	2464.44

^a ΔS_m° was kept constant (133.03±0.5)

^b ΔS_m° and ΔS_{dm}° were kept constant (133.03±0.5 and 14.48±6.3)

Table 6. Estimations of variance components

Code	ML(III-1)			ML(III-2)		
	$\sigma_{r,i}$	$\sigma_{a,i}$	$\sigma_{b,i}$	$\sigma_{r,i}$	$\sigma_{a,i}$	$\sigma_{b,i}$
I	0.032	0.017	0.11	0.032	0.055	0.21
RM	0.035	0.084	1.50	0.036	0.009	1.75
D1	0.032	0.191	0.11	0.032	0.231	0.21
K	0.030	0.061	0.93	0.030	0.084	0.58
BD	0.032	0.017	0.47	0.032	0.055	0.80
BM	0.031	0.097	2.35	0.031	0.151	2.64
D2	0.032	0.256	0.11	0.032	0.311	0.21
MW	0.032	0.017	1.22	0.032	0.055	1.29
ZM	0.092	0.057	0.29	0.089	0.000	0.37
MK	0.032	0.399	0.11	0.032	0.344	0.21
NS	0.032	0.017	0.45	0.032	0.055	0.51
ES	0.021	0.107	0.51	0.022	0.051	0.53
KK1	0.040	0.353	0.71	0.041	0.401	0.80
KK2	0.032	0.318	0.11	0.032	0.367	0.21
KK3	0.032	0.272	0.11	0.032	0.320	0.21
vK	0.155	0.027	1.91	0.155	0.095	1.95
N	0.050	0.162	0.86	0.049	0.145	0.09
TW	0.018	0.173	0.72	0.018	0.243	0.57

Table 7. Total vapor pressure and partial pressures of KCl and K₂Cl₂

T K	p _{tot} Pa	p(KCl) Pa	p(K ₂ Cl ₂) Pa	p(K ₂ Cl ₂)/p(KCl)
500.	8.73×10 ⁻¹¹	8.72×10 ⁻¹¹	1.01×10 ⁻¹³	1.16×10 ⁻⁰³
550.	1.03×10 ⁻⁰⁸	1.02×10 ⁻⁰⁸	3.19×10 ⁻¹¹	3.11×10 ⁻⁰³
600.	5.38×10 ⁻⁰⁷	5.34×10 ⁻⁰⁷	3.76×10 ⁻⁰⁹	7.05×10 ⁻⁰³
650.	1.52×10 ⁻⁰⁵	1.50×10 ⁻⁰⁵	2.09×10 ⁻⁰⁷	1.40×10 ⁻⁰²
700.	2.63×10 ⁻⁰⁴	2.57×10 ⁻⁰⁴	6.39×10 ⁻⁰⁶	2.49×10 ⁻⁰²
750.	3.11×10 ⁻⁰³	2.99×10 ⁻⁰³	1.22×10 ⁻⁰⁴	4.07×10 ⁻⁰²
800.	2.69×10 ⁻⁰²	2.53×10 ⁻⁰²	1.58×10 ⁻⁰³	6.23×10 ⁻⁰²
850.	1.80×10 ⁻⁰¹	1.65×10 ⁻⁰¹	1.49×10 ⁻⁰²	9.00×10 ⁻⁰²
900.	9.75×10 ⁻⁰¹	8.67×10 ⁻⁰¹	1.08×10 ⁻⁰¹	1.24×10 ⁻⁰¹
950.	4.42×10 ⁺⁰⁰	3.79×10 ⁺⁰⁰	6.24×10 ⁻⁰¹	1.65×10 ⁻⁰¹
1000.	1.72×10 ⁺⁰¹	1.42×10 ⁺⁰¹	3.00×10 ⁺⁰⁰	2.11×10 ⁻⁰¹
1050.	5.76×10 ⁺⁰¹	4.58×10 ⁺⁰¹	1.18×10 ⁺⁰¹	2.58×10 ⁻⁰¹
1100.	1.48×10 ⁺⁰²	1.16×10 ⁺⁰²	3.18×10 ⁺⁰¹	2.73×10 ⁻⁰¹
1150.	3.48×10 ⁺⁰²	2.71×10 ⁺⁰²	7.73×10 ⁺⁰¹	2.85×10 ⁻⁰¹
1200.	7.56×10 ⁺⁰²	5.84×10 ⁺⁰²	1.72×10 ⁺⁰²	2.95×10 ⁻⁰¹
1250.	1.53×10 ⁺⁰³	1.17×10 ⁺⁰³	3.56×10 ⁺⁰²	3.03×10 ⁻⁰¹
1300.	2.91×10 ⁺⁰³	2.23×10 ⁺⁰³	6.88×10 ⁺⁰²	3.09×10 ⁻⁰¹
1350.	5.25×10 ⁺⁰³	4.00×10 ⁺⁰³	1.25×10 ⁺⁰³	3.13×10 ⁻⁰¹
1400.	9.02×10 ⁺⁰³	6.85×10 ⁺⁰³	2.16×10 ⁺⁰³	3.15×10 ⁻⁰¹
1450.	1.48×10 ⁺⁰⁴	1.13×10 ⁺⁰⁴	3.56×10 ⁺⁰³	3.16×10 ⁻⁰¹
1500.	2.35×10 ⁺⁰⁴	1.78×10 ⁺⁰⁴	5.64×10 ⁺⁰³	3.16×10 ⁻⁰¹
1550.	3.59×10 ⁺⁰⁴	2.73×10 ⁺⁰⁴	8.58×10 ⁺⁰³	3.15×10 ⁻⁰¹
1600.	5.31×10 ⁺⁰⁴	4.05×10 ⁺⁰⁴	1.26×10 ⁺⁰⁴	3.12×10 ⁻⁰¹
1650.	7.64×10 ⁺⁰⁴	5.84×10 ⁺⁰⁴	1.81×10 ⁺⁰⁴	3.09×10 ⁻⁰¹
1700.	1.07×10 ⁺⁰⁵	8.22×10 ⁺⁰⁴	2.51×10 ⁺⁰⁴	3.05×10 ⁻⁰¹
1750.	1.47×10 ⁺⁰⁵	1.13×10 ⁺⁰⁵	3.40×10 ⁺⁰⁴	3.01×10 ⁻⁰¹
1800.	1.97×10 ⁺⁰⁵	1.52×10 ⁺⁰⁵	4.51×10 ⁺⁰⁴	2.96×10 ⁻⁰¹

FIGURE CAPTIONS

Fig. 1. Residuals of the experimental total vapor pressures and the ML(III-2) curve from the recommended ML(III-1) solution.

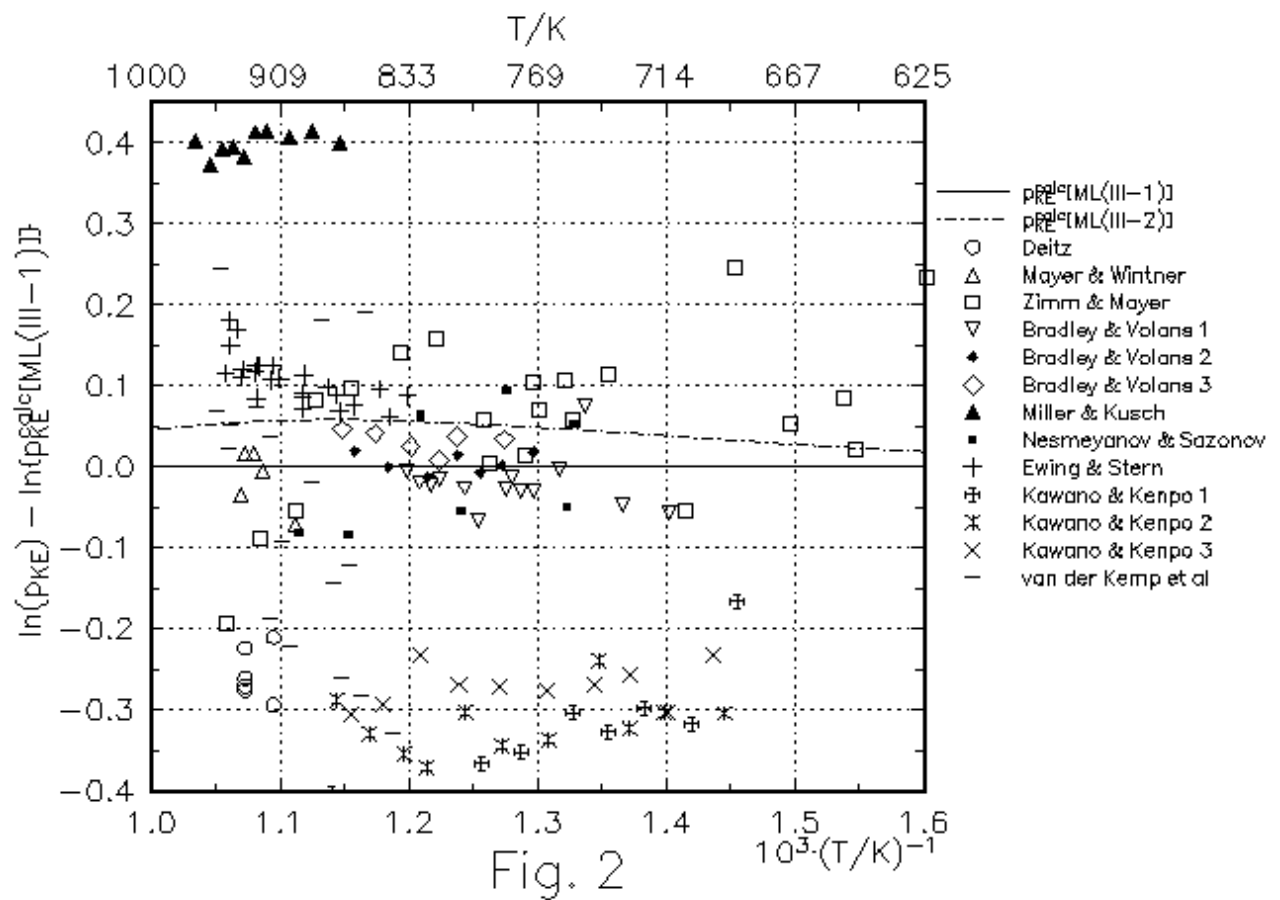
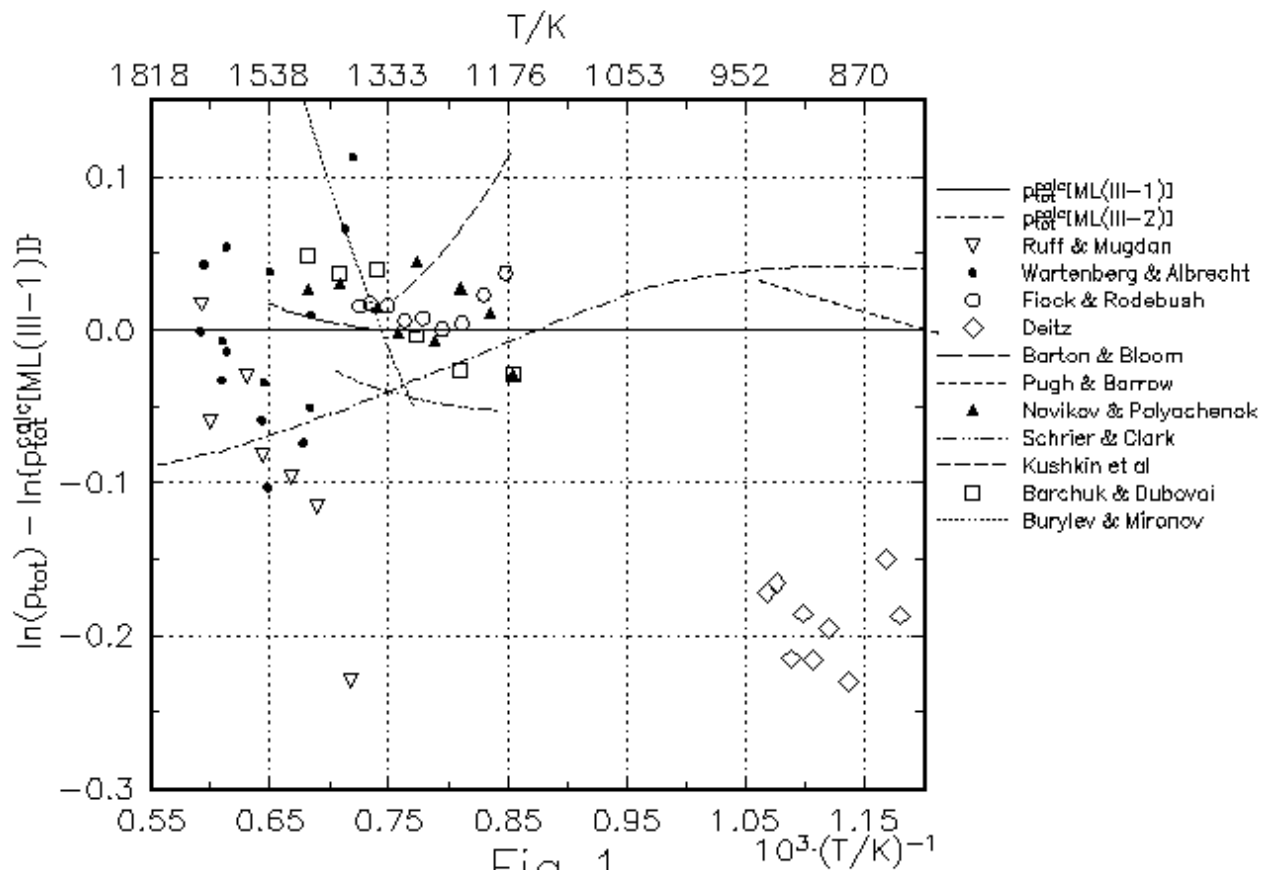
Fig. 2. Residuals of the experimental Knudsen effusion data and the ML(III-2) curve from the ML(III-1) recommended solution.

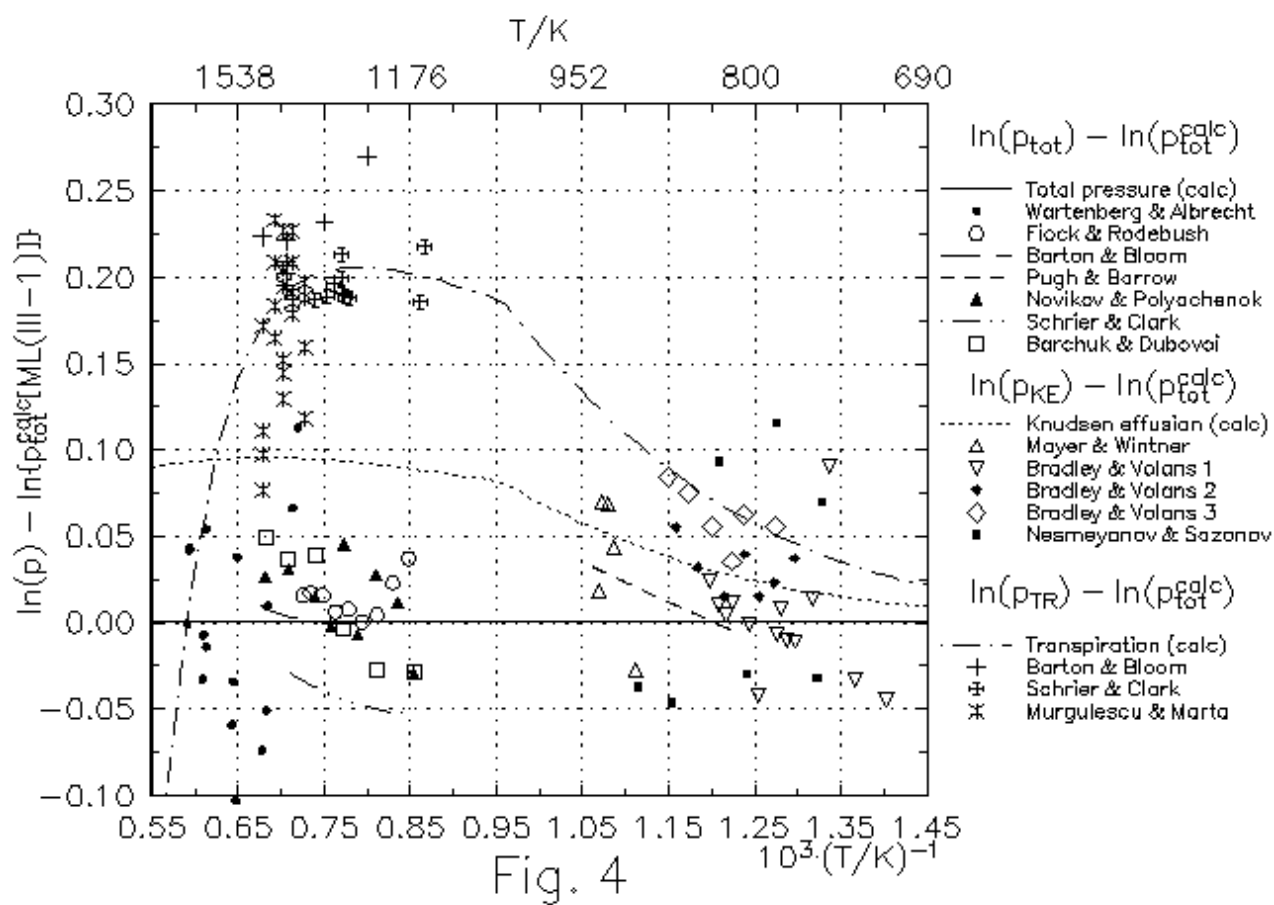
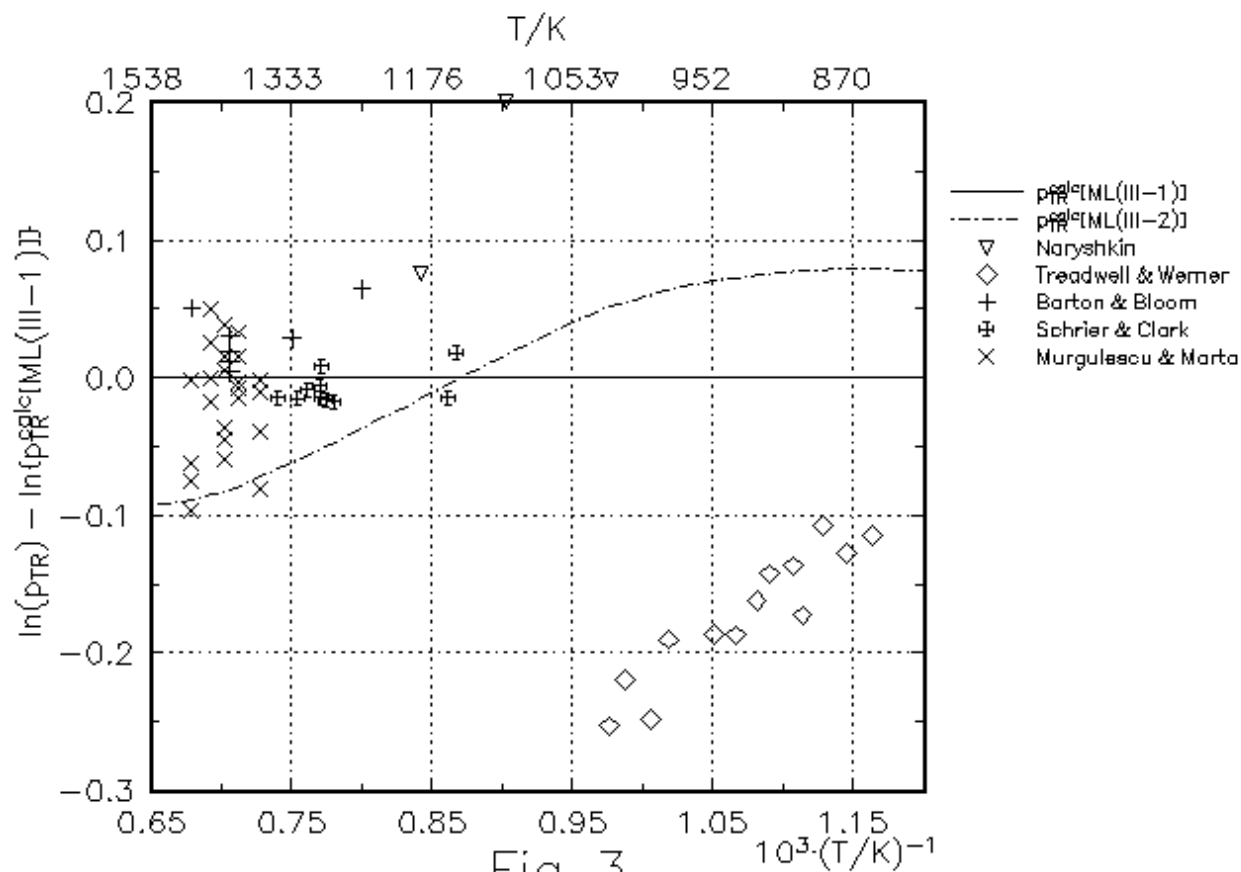
Fig. 3. Residuals of the experimental transpiration data and the ML(III-2) curve from the ML(III-1) recommended solution.

Fig. 4. Residuals of the experimental total vapor pressure, Knudsen effusion and transpiration data, and the OLS fits to each type of data from the ML(III-1) recommended solution.

Fig. 5. Shift and tilt errors from the ML(III-1) recommended solution for experiments. The points plotted with code symbols refer to codes in Tables 2-4. The large circle represents a tolerance limit for OLS fits (see text) and includes the twelve experiments with codes PB, NP, SC1, BB1, BV3, BV1, BV2, FR, SC2, SC2, MM, WA, BB2, listed in decreasing ordinate order.

Fig. 6. The ratio of partial pressures $p(\text{K}_2\text{Cl}_2)/p(\text{KCl})$ and total ion currents $I_{a,t}/I_{m,t}$ (Eqns. 8 and 9), including mass spectrometric data with estimated instrument constant corrections.





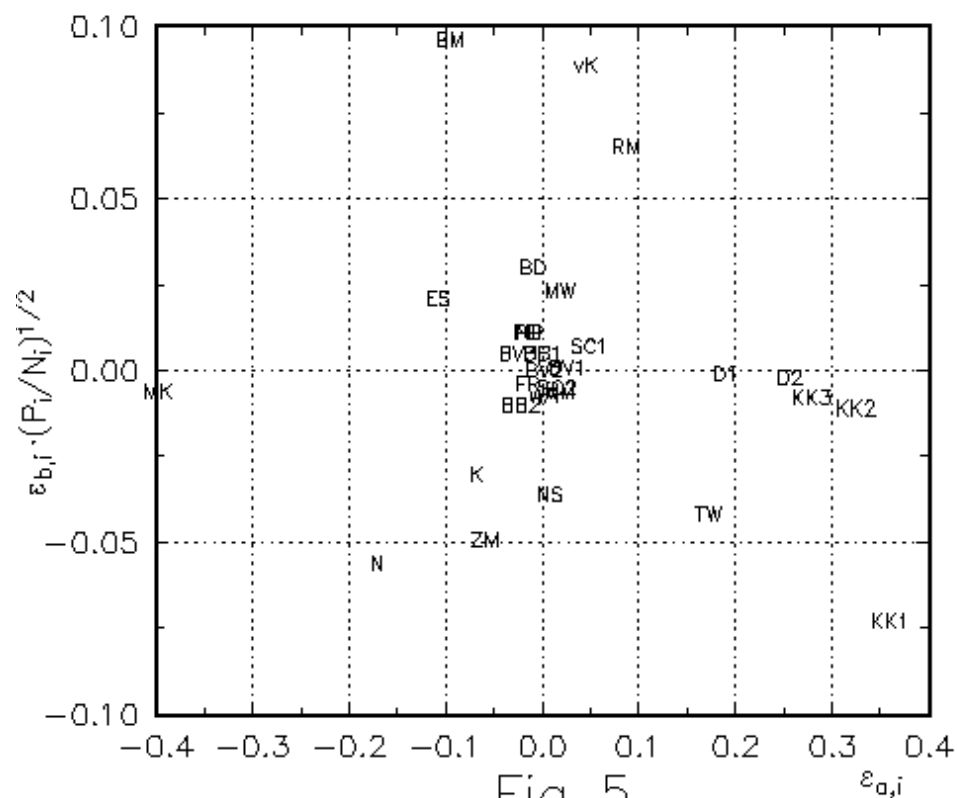


Fig. 5

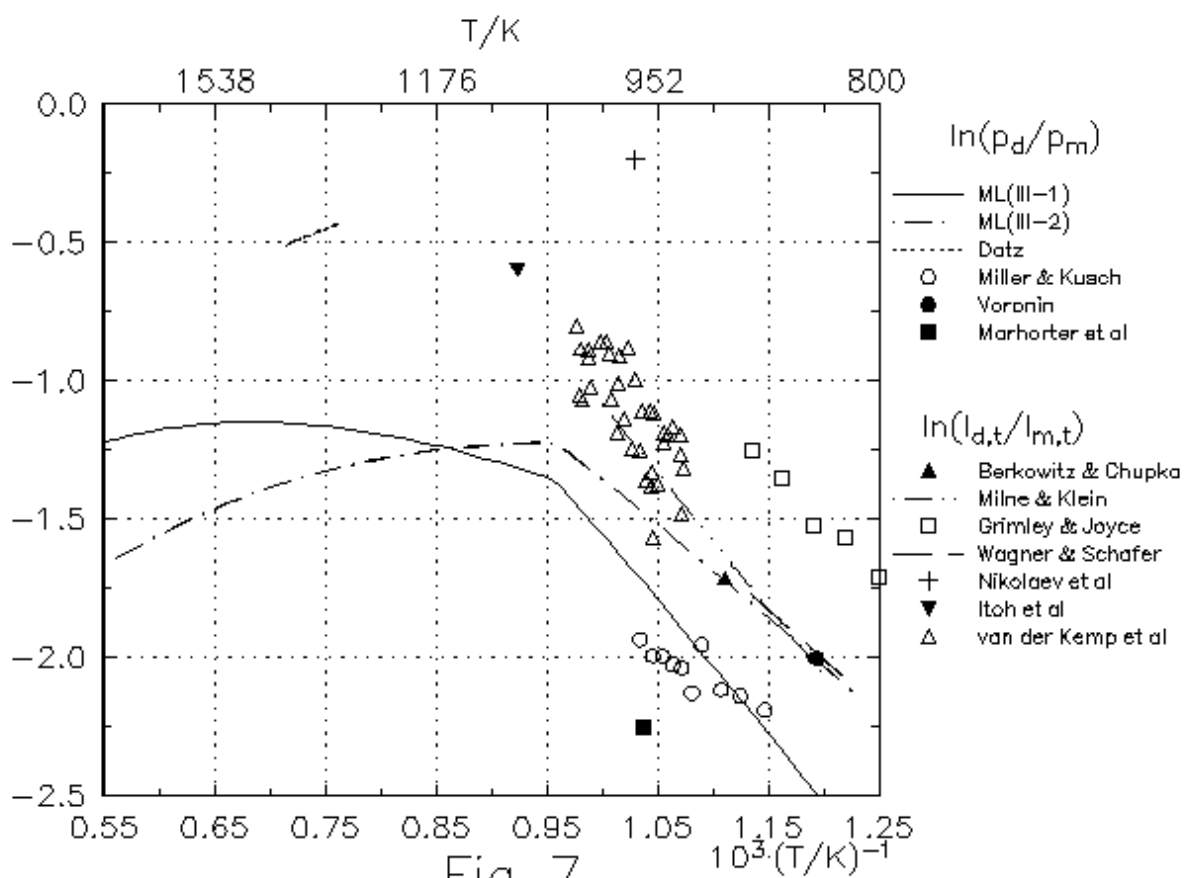


Fig. 7