

VAPORIZATION PROCESSES FAR FROM EQUILIBRIUM AT HIGH TEMPERATURES

J. DROWART

Laboratorium voor Fysische Chemie, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels, Belgium

Abstract - Mass spectrometric investigation of steady-state effusion taking place far from equilibrium instead of close thereto, as is more commonly the case, is described for various compounds in the As-O system. Part of the vaporization processes are nevertheless observed to obey the mass action law; they are thus characterized by a zero net rate of reaction and hence allow calculation of meaningful reaction enthalpies and of thermochemical properties for the gaseous molecules involved in the corresponding processes. $Sb_{2-x}As_xO_3$ solutions with $x = 0.5, 1.0, 1.5,$ and 1.9 are characterized by extremely low vaporization coefficients. For $x \geq 1.0$, the solutions exhibit oscillatory vaporization above a certain temperature.

INTRODUCTION

Knudsen effusion and Langmuir free surface vaporization are inherently nonequilibrium processes (1). Despite this, the evaporation, diffusion and reaction coefficients in most high temperature systems allow determination of accurate thermochemical data by conventional and mass spectrometric Knudsen cell methods operating under steady-state conditions close to equilibrium. Well-known exceptions are red phosphorus, arsenic, and monoclinic arsenic trioxide (claudetite). The present paper gives an account of a brief study of the latter substance and of an extended investigation of binary (As-O) and ternary (M-As-O) systems (2). In these only part of the components of the gas phase appear to be mutually in equilibrium but not with all the condensed phases present in the systems.

EXPERIMENTAL

Measurements were performed by the mass spectrometric Knudsen cell method using procedures (3,4) and instrumentation (5) described earlier. Quartz Knudsen cells with channel type effusion orifices with effective area $a_e = 1.6 \times 10^{-2}, 0.14,$ and 0.84 mm^2 were used in most experiments. Steady-state partial pressures were determined by quantitative vaporization of known initial amounts of the substance investigated and integration of the ion intensities as a function of time. Ionization was realized by electron impact with 21 eV electrons (30 μA). Due to transfer of thermally acquired internal energy during the ionization processes, a well-known phenomenon for polyatomic molecules (6), the observed ratio of fragment to parent ion intensity is a function of temperature. This was studied in most detail for $As_4O_6(g)$ (7). The temperature dependence of the dissociative ionization, as well as superposition of identical parent and fragment ions, were taken into account for all gaseous species when calculating their relative or absolute partial pressures. Further particulars and detailed primary data are given in Ref. 2.

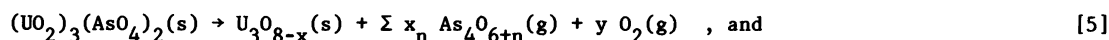
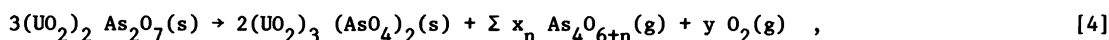
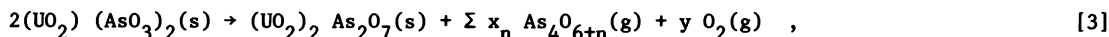
For the calculation of thermochemical data, thermodynamic functions given in the literature were used for As_2O_3 (arsenolite), $As_2O_5(s)$ and $As_4O_6(g)$. For $As_4O_{6+n}(g)$ with $n = 1$ to 4 , $AsO(g)$, $AsO_2(g)$, and $As_2O_3(g)$, they were calculated with the usual statistical mechanical formulae using experimental spectroscopic or estimated molecular constants.

RESULTS AND DISCUSSION

It is generally accepted (8,9) that As_2O_3 (arsenolite) sublimates to form the gaseous molecule $As_4O_6(g)$ with unit evaporation coefficient in the temperature interval 375-550 K, where this compound is actually metastable relative to claudetite (8,10,11). Claudetite on the contrary is characterized by a low evaporation coefficient in the same temperature interval (8). Mass spectrometric analysis for arsenolite (2,7,12) and claudetite (2) confirmed that $As_4O_6(g)$ is by far the most predominant, if not the only gaseous molecule to be formed during the vaporization of both these substances. For claudetite, this result is, despite the much lower pressure, in agreement with the thermodynamic properties of $As_4O_6(g)$, derived from the sublimation of arsenolite and of the other gaseous molecules in the (As-O) system discussed below. During the experiments, the Knudsen cell was heated up well above the melting point of claudetite, $587.6 \pm 1.4 \text{ K}$ (13). At 600 K, $p(As_4O_6) = 1.3 \times 10^{-3} \text{ atm}$ (14)

was measured with $a = 1.6 \times 10^{-2} \text{ mm}^2$ and $p = 4.8 \times 10^{-4} \text{ atm}$ with $a_e = 0.14 \text{ mm}^2$. A pressure $p^\circ(\text{As}_4\text{O}_6) = 0.127 \text{ atm}$ is normally expected for $\text{As}_2\text{O}_3(1)$ (13).

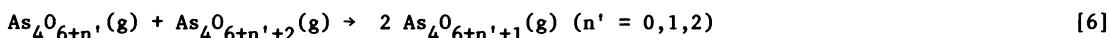
Mass spectrometric analysis of the vapor phase produced from $\text{As}_2\text{O}_5(\text{s})$ (2,7,15), $\text{As}_2\text{O}_4(\text{s})$ (2,7) and meta-, pyro-, and ortho-uranylarsenate (2,7) shows that the vaporization processes are quite complex. The molecules present in the gas phase are $\text{As}_4\text{O}_{6+n}(\text{g})$ with $n = 0$ to 4 and $\text{O}_2(\text{g})$ (2,7,15), in proportions that depend on the temperature, on the area of the effusion orifice and on the chemical composition of the system. The overall vaporization behavior can be described by



$n = 0$ to 4. x_n is a function of temperature, orifice area and to some extent, previous thermal history of the sample during its study since in reactions [3] to [5] the system is not necessarily monovariant. The vaporization processes [1] through [5] were studied in the overall temperature range 600-1000 K. The effective total pressures are about 10^{-6} to 10^{-5} atm at 700 K for [1], 10^{-5} to 10^{-4} atm at 980 K for [2] through [4], depending upon a_e , and 10^{-5} atm for [5], irrespective of a_e .

The composition of the vapor is markedly different for the various values of a_e . Approximate average values $\langle 6+n \rangle$ are 7.65 for process [1] at 700 K and 8.43 for process [2] at 980 K, when $a_e = 0.84 \text{ mm}^2$; they become 7.38 and 7.79, respectively when $a_e = 1.5 \times 10^{-2} \text{ mm}^2$. For processes [2], [3], and [4], all at 980 K, with $a_e = 1.5 \times 10^{-2} \text{ mm}^2$, $\langle 6+n \rangle = 7.08$, 6.63, and 6.01. For process [4], the same value for $\langle 6+n \rangle$ is found when $a_e = 0.84 \text{ mm}^2$.

During the evaporation of all systems in [1] through [5], $\prod p_i^{v_i}$, the product of the partial pressure for each molecule i raised to a power equal to the stoichiometric coefficient v_i in the reactions [6]



is observed to be constant at constant temperature and to be reproducible irrespective of the system or the experimental circumstances. This means that equilibrium between the molecules desorbing from the vaporizing surfaces is established and that $\prod p_i^{v_i} = K_n^\circ$, where K_n° is the equilibrium constant for the reaction. Similar conclusions have been reached in other systems (16-19).

The second and third law reaction enthalpies for the metathesis reactions [6], in which oxygen atoms are transferred from one molecule to another, are respectively: $\Delta H^\circ(0 \text{ K})/\text{kJ mol}^{-1} = -14.9 \pm 0.6$ and -14.0 ± 1.0 for $n' = 0$; -15.0 ± 0.5 and -15.2 ± 0.8 for $n' = 1$; -19.0 ± 1.5 and -16.9 ± 0.8 for $n' = 2$. All uncertainties cited are standard deviations. These values may be compared with $\Delta H^\circ(900 \text{ K}) \cong \Delta H^\circ(0 \text{ K})/\text{kJ mol}^{-1} = +12.7 \pm 15$ for $n' = 0$, -19.1 ± 25 for $n' = 1$ and -9.7 ± 36 for $n' = 2$, calculated from the second law data in Ref. 15. In Ref. 15 the vaporization of $\text{As}_2\text{O}_5(\text{s})$ was studied without correcting for the superposition of common parent and fragment ions. Because this correction is especially important for $\text{As}_4\text{O}_6^\ddagger$ from $\text{As}_4\text{O}_6(\text{g})$ and from $\text{As}_4\text{O}_8(\text{g})$, the discordance between the present results and those in Ref. 15 is largest for $n' = 0$ in the above series.

In the experiments where the study of reactions [6] yielded the results just described, third law treatment of the data for the reactions



provided ΔH° (0 K) values that depend on experimental circumstances. For example, $\Delta H^\circ(0 \text{ K})/\text{kJ mol}^{-1} = 94.6 \pm 4$ above $(\text{UO}_2)_3(\text{AsO})_2(\text{s})$ and 130 ± 4 above $(\text{UO})_3(\text{AsO}_3)_2(\text{s})$ resulted for $\text{As}_4\text{O}_7(\text{g})$. The corresponding second law value in Ref. 15, measured above $\text{As}_2\text{O}_5(\text{s})$ with $a_e = 0.2 \text{ mm}^2$, is even higher: $\Delta H^\circ(900 \text{ K}) = 149.3 \pm 6 \text{ kJ mol}^{-1}$, or $\Delta H^\circ(0 \text{ K}) = 175.4 \pm 6 \text{ kJ mol}^{-1}$. Similar situations obtain for $\text{As}_4\text{O}_8(\text{g})$, $\text{As}_4\text{O}_9(\text{g})$, and $\text{As}_4\text{O}_{10}(\text{g})$ upon thermochemical treatment of reaction [7] for these species.

The lowest value for ΔH° (reaction [7], $n = 1$, 0 K) viz. $94.6 \pm 4 \text{ kJ mol}^{-1}$, together with $D^\circ(\text{O}_2, \text{g}, 0 \text{ K}) = 493.57 \text{ kJ mol}^{-1}$ leads to $D^\circ(\text{O-As}_4\text{O}_6, \text{g}, 0 \text{ K}) = 341.4 \pm 4 \text{ kJ mol}^{-1}$. Although it could have been assumed that this lowest value of ΔH° corresponds to equilibrium among all gaseous species, it was considered that this remained to be established. The reactions



with $\text{M}(\text{g}) = \text{Pb}(\text{g})$ or $\text{Bi}(\text{g})$ were therefore studied respectively around 1200 K and between 1000 and 1125 K in a stainless steel Knudsen cell in which ortho-uranylarsenate, $\text{Fe}_2\text{O}_3(\text{s})$ and $\text{PbO}(\text{s})$ (20) or $\text{Bi}_2\text{O}_3(\text{s})$ had been placed. With ΔH° (reaction [8], 0 K)/ $\text{kJ mol}^{-1} = -29.2 \pm 0.6$ when $\text{M}(\text{g}) = \text{Pb}(\text{g})$ and $+0.2 \pm 1.0$ when $\text{M}(\text{g}) = \text{Bi}(\text{g})$, $D^\circ(\text{PbO}, \text{g}, 0 \text{ K}) = 374.0 \pm 4.2$ (21,22) and $D^\circ(\text{BiO}, \text{g}, 0 \text{ K}) = 338.9 \pm 5.9$ (22), $D^\circ(\text{O-As}_4\text{O}_6, \text{g}, 0 \text{ K}) = 344.8 \pm 6.7$ and $339.1 \pm 7.5 \text{ kJ mol}^{-1}$ respectively, were obtained, in agreement with the result cited above. As will be shown below, this value can be obtained in yet another way.

By combination with the third law values for the oxygen metathesis reactions [6], $D^\circ(\text{O-As}_4\text{O}_6, \text{g}, 0 \text{ K}) = 341.8 \pm 5$ leads to $D^\circ(\text{O-As}_4\text{O}_7, \text{g}, 0 \text{ K}) = 327.8 \pm 6$, $D^\circ(\text{O-As}_4\text{O}_8, \text{g}, 0 \text{ K}) = 312.6 \pm 6$ and $D^\circ(\text{O-As}_4\text{O}_9, \text{g}, 0 \text{ K}) = 295.7 \pm 6$, all in kJ mol^{-1} . $D^\circ(\text{O-As}_4\text{O}_{6+n'}, \text{g})$ represents the energy required to remove one oxygen atom from $\text{As}_4\text{O}_7(\text{g})$ to form $\text{As}_4\text{O}_6(\text{g})$ when $n' = 0$. Similarly it represents energy required, to remove one oxygen atom from $\text{As}_4\text{O}_8(\text{g})$ when $n' = 1$, from $\text{As}_4\text{O}_9(\text{g})$ when $n' = 2$, and from $\text{As}_4\text{O}_{10}(\text{g})$ when $n' = 3$. $D^\circ(\text{O-As}_4\text{O}_{6+n'})$ is thus in sequence, the bond energy of the first, second, third, and fourth apical oxygen atom removed from the supposedly tetrahedral $\text{As}_4\text{O}_{10}(\text{g})$ molecule to stepwise form the tetrahedral $\text{As}_4\text{O}_6(\text{g})$ molecule.

For the reaction



it is observed that the partial pressures are independent of the area of the effusion orifice. They lead to ΔH° (reaction [9], 0 K) = $353.5 \pm 5 \text{ kcal mol}^{-1}$. Appropriate combination of this result with $\Delta H^\circ(\text{f}, 298)/\text{kJ mol}^{-1} = -924.9$ for $\text{As}_2\text{O}_5(\text{s})$ (23), $+1196.2$ for $\text{As}_4\text{O}_6(\text{g})$, 246.75 for $\text{O}(\text{g})$ and $\Delta H^\circ(298 \text{ K}) = \Delta H^\circ(0 \text{ K})$ for the metathesis reactions [7] yields: $D^\circ(\text{O-As}_4\text{O}_6, \text{g}, 298 \text{ K}) = 346.5$ or $D^\circ(\text{O-As}_4\text{O}_6, \text{g}, 0 \text{ K}) = 341 \pm 7 \text{ kJ mol}^{-1}$, essentially identical to the value cited above. This confirms that the evaporation coefficient $\alpha(\text{As}_4\text{O}_{10}) = 1$ above $\text{As}_2\text{O}_5(\text{s})$ and that the accepted standard enthalpies of formation of As_2O_3 (arsenolite), of $\text{As}_2\text{O}_5(\text{s})$, of $\text{As}_4\text{O}_6(\text{g})$, and the oxygen metathesis reaction enthalpies are all mutually consistent within experimental accuracy.

Further supporting evidence therefore is that the total static pressure above $\text{As}_2\text{O}_5(\text{s})$ determined (24) by the dew-point method can be reconstructed starting from the partial pressure measured for $\text{As}_4\text{O}_{10}(\text{g})$, and $\text{Pr}_i = \text{K}_i^n$, for the successive oxygen metathesis reactions [6] and $D^\circ(\text{O-As}_4\text{O}_6, \text{g}, 0 \text{ K})$ obtained as was explained.

Additional measurements in the (As-O) system, carried out between 1070 and 1245 K, made possible the study of the reactions



Third law treatment yields ΔH° (reaction, 0 K) = 5.9 ± 0.7 and $15.5 \pm 5 \text{ kJ mol}^{-1}$ for processes [10] and [11] respectively. Second and third law treatment respectively lead to

ΔH° (reaction [12], 0 K) = 356.1 ± 11 and 367.9 ± 0.9 and ΔH° (reaction [13], 0 K) = 457.0 ± 1.6 and 457.9 ± 0.6 kJ mol⁻¹. For the latter two reactions, a trans (C_s) structure has been assumed for As₂O₃(g) (25).

Together with $D^\circ(\text{O-As}_4\text{O}_6, \text{g}, 0 \text{ K}) = 341.8 \pm 5$ kJ mol⁻¹, reaction [10] provides $D^\circ(\text{O-AsO}, \text{g}, 0 \text{ K}) = 347.7 \pm 5$ and $\Delta H^\circ(\text{atomization}, \text{AsO}_2, \text{g}, 0 \text{ K}) = 828.0 \pm 7$ kJ mol⁻¹. These results are consistent with those derived from ΔH° (reaction [11], 0 K), that yields $D^\circ(\text{O-AsO}, \text{g}, 0 \text{ K}) = 354.4 \pm 7$ kJ mol⁻¹. By combination with ΔH° (reaction [12], 0 K) and $D^\circ(\text{AsO}, \text{g}, 0 \text{ K}) = 480.3 \pm 4$ kJ mol⁻¹ (26-28), ΔH° (atomization, As₂O₃, g, 0 K) = 1676.2 ± 8 kJ mol⁻¹ is obtained. This result confirms ΔH° (reaction [13], 0 K) = 457.9 ± 0.6 kJ mol⁻¹, which by combination with ΔH° (atomization, As₄O₆, g, 0 K) = 3802.4 ± 6.7 kJ mol⁻¹ (9,29) yields ΔH° (atomization, As₂O₃, g, 0 K) = 1672.3 ± 5 kJ mol⁻¹. In the thermochemical cycles used to calculate these results, preference has systematically been given to the data obtained by third law treatment of the experimental data.

Independent investigation of the (As-O) system (12) at other oxygen potentials and temperatures than those established in the experiments summarized here, has led to the characterization of additional gaseous species, such as As₄O₅(g), As₄O₄(g), As₄O₃(g) and perhaps As₃O₄(g). An upper bound for the partial pressure of the As₄O₅(g) molecule determined in the present study leads to a limiting value for $D^\circ(\text{O-As}_4\text{O}_5, \text{g}, 0 \text{ K})$ which indicates that there is consistency between the investigations 2 and 12 of the gaseous molecules in the (As-O) system. These molecules appear to be as numerous as in the (P-O) (30) and the (Bi-O) (31) systems as chemical analogy leads one to expect.

The observation of reproducible and constant values for $\Pi_i^{\nu_i}$ in equations [6], studied above As₂O₄(s), As₂O₅(s), meta-, pyro-, and ortho-uranylarsenate, is at first sight startling in systems where the reactions described by equations [1] to [5] or [7] appear not to correspond to steady-state conditions close to equilibrium. The explanation is as follows.

The systems studied involve ρ distinct chemical species. Thermodynamic treatment of irreversible processes (1,32) shows that it should be possible to describe the total rate of entropy production in a system that is out of equilibrium in terms of $\leq(\rho-1)$ processes. Other processes among the total of $\rho(\rho-1)/2$ processes that conceivably take place in the system then jointly lead to a zero rate of entropy production. Among the redundant processes, reactions that obey the mass action law do not contribute to the entropy production. This is equivalent to the net reaction rate for the latter processes being zero and equilibrium being established between the molecules involved in these particular processes.

The $(\rho-2)$ processes that provide a description of the vaporization of the present systems may be taken to be the reactions with $n = 0$ to 4 in Eqs. [1] to [5]. The processes represented by Eq. [6] with $n' = 0, 1$ or 2 then belong to the category of reactions that do not contribute to the rate of entropy production. These conclusions would not be modified if $(\rho-\xi-2)$ processes among those in Eq. [1] to [5] and ξ among those in Eq. [6] were retained to describe the vaporization. A number of appropriate linear combinations of these $(\rho-\xi-2)$ processes and ξ reactions, e.g. processes such as [7], would then indeed have to be taken into account in the evaluation of the total rate of entropy production in the alternate, but equivalent (1,32), description of the system vaporizing under nonequilibrium conditions.

In kinetic terms, a zero rate of entropy production corresponds to the direct and the reverse reactions in processes such as those in Eq. [6] balancing one another under steady-state conditions where $Z_{ev}(n = 0 \text{ to } 4) = Z_{eff}(n = 0 \text{ to } 4)$, $Z_{ev}(\text{O}_2) = Z_{eff}(\text{O}_2)$, $4\sum p(\text{As}_4\text{O}_{6+n})/M^{0.5}(\text{As}_4\text{O}_{6+n}) = \sum [(6+n)p(\text{As}_4\text{O}_{6+n})/M^{0.5}(\text{As}_4\text{O}_{6+n}) + 2p(\text{O}_2)/M^{0.5}(\text{O}_2)]$. In these relations, Z_{ev} and Z_{eff} respectively stand for the net number of molecules leaving the solid per unit time and for that effusing out of the Knudsen cell per unit time.

For the processes in Eq. [6], one can write

$$\vec{k}_n N(\text{As}_4\text{O}_{6+n'}) \cdot N(\text{As}_4\text{O}_{6+n'+2}) = \overleftarrow{k}_n N^2(\text{As}_4\text{O}_{6+n'+1}) \quad (14)$$

where $N = p/kT$ represents the number density in the gas phase, \vec{k}_n , the rate constant for the forward and \overleftarrow{k}_n , for the reverse reaction.

Since $\vec{k}_n/\overleftarrow{k}_n = K_n^\circ$, there follows that

$$N^2(\text{As}_4\text{O}_{6+n'+1})/N(\text{As}_4\text{O}_{6+n'}) \cdot N(\text{As}_4\text{O}_{6+n'+2}) = K_n^\circ \quad (15)$$

as well under steady state as under equilibrium conditions.

A corollary of the foregoing is that replacement of the pressure equivalent of the flux measured for the freely vaporizing solid in Eq. [15] by $\alpha_n p_{n'}$, where $p_{n'}$ is now the equilibrium pressure and α_n , the evaporation coefficient, should lead to:

$$\alpha^2(\text{As}_4\text{O}_{6+n'+1}) = \alpha(\text{As}_4\text{O}_{6+n'}) \cdot \alpha(\text{As}_4\text{O}_{6+n'+2}) \quad [16]$$

Replacing $(6+n')$ by explicit numbers, there follows $\alpha(7) = \alpha^3 / ^4(6)\alpha^{1/4}(10)$, $\alpha(8) = \alpha^{1/2}(6)\alpha^{1/2}(10)$, $\alpha(9) = \alpha^{1/4}\alpha^{3/4}(10)$, with obvious simplifications when $\alpha(10) = 1$, as was shown to be the case for $\text{As}_2\text{O}_5(\text{s})$. It may be mentioned that the presently described experiments could actually only be carried out in the temperature intervals given earlier because for $\text{As}_2\text{O}_4(\text{s})$, $\text{As}_2\text{O}_5(\text{s})$, meta- and pyro-uranylarsenate, $\alpha(6) \ll 1$. The partial pressures would indeed have been much higher than compatible with Knudsen effusive flow had this not been the case. It is also interesting to note that the individual steady-state partial pressures of the molecules $\text{As}_4\text{O}_{6+n}(\text{g})$ are interrelated at each temperature in much the same way that the partial pressures for polymeric molecules $A_m(\text{g})$ are related to their reference-state partial pressures in a system at equilibrium where element A is present at activity $a(\text{A})$: $p(A)_m = a^m(\text{A}) p^0(A)_m$.

At the pressures prevailing in the experiments described, the number of collisions in the gas phase is small. As in the case of $\text{As}_2(\text{g})$ and $\text{As}_4(\text{g})$ it is suggested that the equilibria between the $\text{As}_4\text{O}_{6+n}(\text{g})$ molecules are established in a surface layer of adsorbed species with high lateral mobility and collision frequency. The adsorbed species may be visualized as a two-dimensional gas that is a precursor to desorption to form the three dimensional gas. The relatively long residence times in the surface layer implied in this hypothesis are consistent with relations between enthalpies of sublimation and residence times discussed in Ref. 33.

The low vaporization coefficients in the systems considered are attributed to the marked structural differences between the condensed phases and the gaseous molecules, which make necessary extensive molecular rearrangement prior to vaporization. For similar reasons melting can be retarded, as was observed here for claudetite and previously for arsenolite (8), as well as for other compounds, such as cristobalite, quartz, the feldspar albite and others (34). It is noteworthy that several of these substances also give rise to glass formation upon cooling of the liquid phase, another indication of kinetic barriers in the phase transitions.

Difficulty in preparing $\text{As}_2\text{O}_5(\text{s})$ from $\text{As}_2\text{O}_3(\text{s})$, even under high oxygen pressures (35) again illustrates the very low rate of reaction of molecular oxygen in the As-O system.

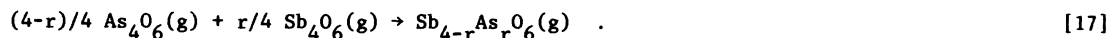
During the study of the vaporization of $(\text{UO}_2)_3(\text{AsO}_4)_2$, it was observed, however, that equilibration between molecular oxygen and the $\text{As}_4\text{O}_{6+n}(\text{g})$ molecules with $n = 0$ to 4 gradually became established after some time. The interpretation given is that a sufficient amount of $\text{U}_3\text{O}_8(\text{s})$ must first be formed and that this substance, possibly because of its non-stoichiometric nature, has a catalytic effect upon the establishment of equilibrium between all chemical species present in the system in the condensed and in the gas phases. This interpretation is in agreement with general conclusions of the thermodynamic treatment of irreversible processes with respect to the time dependence of the rate of entropy production (1, 36) during the evolution of a system towards equilibrium or better here, towards steady-state behavior close to equilibrium. The observations are further consistent with the conclusions in thermodynamics of irreversible processes concerning the role of reaction products with catalytic activity in open systems and their concentration therein.

During the investigation of the vaporization of meta- and pyro-uranylarsenate, it was noted that the pressures of $\text{O}_2(\text{g})$ and of the various $\text{As}_4\text{O}_{6+n}(\text{g})$ molecules increased at the melting points of the solid phase under study. At higher temperatures, vaporization became very irregular, pressure bursts being observed both by conventional methods (37) and mass spectrometrically (2). A macroscopic description would be that gas bubbles are formed in the melt and migrate to the surface to explode there.

That the presence of liquids may enhance the rate of vaporization of other substances has been noted in various systems, examples being given in Ref. 19. That liquids themselves may have higher rates of vaporization than the corresponding solid is illustrated by the observation of a discontinuity in the condensation coefficient of mercury at the melting point (38), or in the rate of vaporization of the oxides Al_2O_3 , Ga_2O_3 , and In_2O_3 upon fusion (39). For Al_2O_3 , the discontinuity in the rate of vaporization (39), for which an alternate interpretation had been given (40), has been confirmed (41), but shown to be less pronounced than was initially (39) reported. Simultaneously, it was demonstrated that the evaporation of this substance is suppressed by hydrogen more for the solid than for the liquid phase (41).

For systems closely related to those considered here, more or less regular pressure oscillations have recently (42) been observed while mass spectrometrically studying the vaporization of $(\text{Sb}_{2-x}\text{As}_x)\text{O}_3$ solutions prepared from the pure oxides in evacuated quartz ampoules. The pressure oscillations set in around 650, 780, and 800 K, respectively, for $x = 1.9$, 1.5, and 1.0 and persisted during vaporization of the major part of the samples. These oscillations had frequencies varying from ten of seconds at their onset temperatures to the order

of seconds at higher temperatures; they had apparent amplitudes varying from 0.5 to at least 10 times the base line pressures. Solutions with $x = 0.5$, however, vaporized in a steady-state fashion between 675 and 800 K. For the different compositions, the measured effective $\text{As}_4\text{O}_6(\text{g})$ pressures are several orders of magnitude lower than would be expected for nearly ideal solutions of the oxides, at least as long as either $\text{As}_2\text{O}_3(\text{l})$ or arsenolite are used as reference states. The various compositions further gave rise to little evolution in composition by preferential vaporization of e.g. $\text{As}_4\text{O}_6(\text{g})$ and $\text{SbAs}_3\text{O}_6(\text{g})$ before the instability set in for $x = 1.9, 1.5$ and 1.0 . Under those circumstances, the partial pressures for the $\text{Sb}_{4-r}\text{As}_r\text{O}_6(\text{g})$ molecules with $r = 0$ to 4 were such that $\text{p}_i = K_i^0$, where K_i^0 represents the equilibrium constants reported earlier (29) for the metal metathesis reactions



Although uptake of SiO_2 during preparation of the samples and formation of a quartz or quartzlike film which impaired vaporization can not be excluded, it is believed that an interpretation may be proposed in terms of chemical oscillations (1,36,43) or to phenomena closely related to, caused by the physical properties of the system (44). A Knudsen effusion cell is indeed an open container, while the observed pressures indicate that the system contained therein is far from equilibrium. The pressure oscillations are observed in the vicinity of the solidus-liquidus coexistence domain calculated for ideal solutions, tentatively used as a zero order approximation. If then the transformation of the glass or the claudetite-like solutions to the liquid is slow, the rate of vaporization of the glass phase low and that of the liquid phase much higher, the conditions which can lead to oscillatory behavior far from equilibrium (36,43) seem satisfied. This hypothesis takes into account that formation of a new phase is inherently a nonequilibrium process (38), which may require substantial superheating or undercooling relative to the expected transition point in order to occur. Growing of a newly forming phase and in particular of bubbles from nuclei are auto-catalytic phenomena (38). The oscillations observed in the $(\text{Sb}_{2-x}\text{As}_x)\text{O}_3$ solutions could therefore be associated not with the glass to normal liquid transition near the expected solidus-liquidus coexistence domain, but with transport properties in the liquid or viscous phase reaching appropriate values. Reference is made to detailed experimental investigation and computational treatment of the oscillatory evolution of carbon monoxide during the dehydration of formic acid (45,46).

Pronounced single and decaying pressure peaks for the vaporizing species have been mass spectrometrically recorded upon the first melting of incongruently melting substances such as Ta_2O_5 , contained in tantalum (18) or K_2CrO_4 (47). These substances could thus be heated above their equilibrium melting point upon first crossing this temperature. The pressure peaks rapidly grew smaller upon cycling the temperature around the melting point and eventually were no longer observed. The explanation proposed is that either a sufficient number of nuclei or large enough amounts of the co-existing solid and liquid phases had been formed. Thereby the diffusion length for their accretion decreased, in such fashion that a noticeable affinity (driving force or difference in free energy) was no longer required to cause the transition to occur by leaving a metastable or the unstable point on the extrapolated free energy versus temperature curve of the solid phase. Many cases of similar or of closely related observations are given in Ref. 38. It is suggested that further examples of oscillatory behavior are provided in the report on high temperature vapor pressures of metals from metals and laser evaporation, presented at this conference (48).

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