

## OPTIMUM TEMPERATURE PROGRAMS TO ACHIEVE THERMOGRAVIMETRY WITH EQUILIBRIUM VAPOR PRESSURE AS A PROBE \*

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### ABSTRACT

Precise constant-temperature control of a computer-automated, simultaneous-Knudsen-torsion-effusion machine for measuring vapor pressures renders it capable of thermogravimetry with the rates of momentum loss and mass loss as probes. The former rate is proportional to the vapor pressure within the effusion cell. Virtual thermogravimetry is accomplished with temperature programs other than constant programs. Chemical transitions and new compounds are discovered from functional dependencies of vapor pressure and its differential on time and chemical composition. The technique is illustrated with examples from studies of a variety of vaporizing systems. The efficacies of various temperature programs are discussed. Unusual cases of increasing rate of mass loss at constant temperature and of increasing vapor pressure when the temperature is lowered have been discovered by this method and are presented.

### INTRODUCTION

A plot of vapor pressure versus temperature as  $\log p$  vs.  $1/T$  constitutes a phase diagram, with the condensed phase in the region above the line and the vapor phase below. In a system with complicated chemistry in the vaporization process, a complicated plot of  $\log p$  vs.  $1/T$  can be obtained. Translation of such plots into a description of the chemical reactions occurring depends upon careful experimental design as well as upon the usual careful measurements. In this paper, we present and discuss some known experimental designs and some which we have developed to deal with processes of varying complexity in the vaporization of binary and ternary metal chalcogenides.

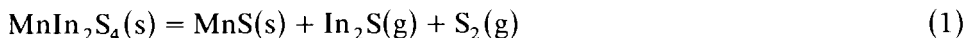
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## EXPERIMENTAL BASIS

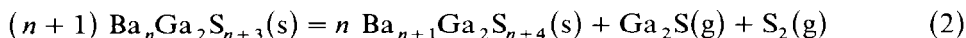
We have developed a computer-automated data-acquisition system for a high-temperature simultaneous torsion-effusion Knudsen-effusion vapor-pressure machine [1,2]. The system includes automatic setting and control of the temperature of the furnace within which vapor pressures are measured. This equipment allows continuous measurement of the vapor pressure by the Knudsen method [3–5] and by the torsion (or Volmer) method [4–6], continuous measurement of the molecular weight of the effusing vapor by combining the two measurements of the vapor pressure [4,5], and continuous measurement of the mass of the substance remaining in the effusion cell. The latter ability in combination with the knowledge of the nature of the effusing vapor and the initial mass and composition of the sample allows continuous monitoring of the sample composition to be made. Hence, thermogravimetric traces of equilibrium vapor pressure versus sample composition can be obtained [7].

We have conducted a series of studies of the vaporization chemistry of binary and ternary sulfides, selenides, and tellurides in temperature ranges from 600°C up to 2100°C [8–11]. These systems ranged in complexity from the relatively simple vaporization of  $\text{MnIn}_2\text{S}_4(\text{s})$  [12,13], through the vaporization of  $\text{BaGa}_2\text{S}_4(\text{s})$  [14] in which a multitude of solid phases were found, to the very complex vaporization of  $\text{CdIn}_2\text{Se}_4(\text{s})$  [11]. For illustrative purposes, the corresponding vaporization reactions are given here



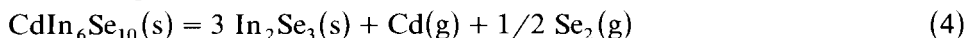
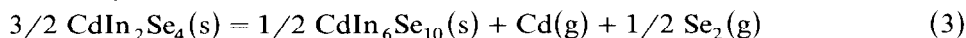
Reaction (1) produces vapor pressures in the normally useful range of our machine (0.1–10 Pa) in the temperature range 1050–1250 K; the vapor pressure of  $\text{MnS}(\text{s})$  is unimportant in this temperature range and was not observed in the study of  $\text{MnIn}_2\text{S}_4(\text{s})$ . Hence, only a single line of points on a  $\log p$  vs.  $1/T$  scale was observed, this line separating the region of stability of  $\text{MnIn}_2\text{S}_4(\text{s})$  from the region of stability of  $\text{MnS}(\text{s}) + \text{In}_2\text{S}(\text{g}) + \text{S}_2(\text{g})$ .

The vaporization of  $\text{BaGa}_2\text{S}_4(\text{s})$  occurred via the sequential reactions



with  $n = 1-4$ . The ultimate loss of  $\text{Ga}_2\text{S}_3$  to produce  $\text{BaS}(\text{s})$  was not observed as the last reaction in the sequence. Five sequential lines of points on a  $\log p$  vs.  $1/T$  scale were observed, each lower than the previous one at a given temperature. Each separated two regions on the phase diagram.

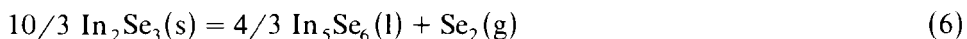
Vaporization of  $\text{CdIn}_2\text{Se}_4(\text{s})$  was complete, with measurable vapor pressures, until exhaustion of the sample. In this complicated system, some reactions were sequential with changing sample composition, some were dependent on the temperature at a given composition, and the final reaction was congruent



The initial vaporization of  $\text{In}_2\text{Se}_3(\text{s})$  was temperature dependent since two liquids could be in equilibrium simultaneously with the vapor. Above 1042 K the reaction was



and below 1042 K



When enough Se was lost, so that no solid remained,



Finally,  $\text{In}_5\text{Se}_6(\text{l})$  vaporized congruently



Since each reaction, (3)–(8), is represented by a line of points on the  $\log p$  vs.  $1/T$  diagram, since the change in mass of the sample in the course of reactions (5)–(7) is relatively small, and because of the importance of temperature in this system, some of the changes may be missed unless the program by which the data are collected is selected carefully.

#### TEMPERATURE PROGRAMS

Typically, one has no control over the order in which data are collected; the second must follow the first, etc., and hence one has no control over the progress of the composition of the sample after the initial composition is set. Although control of sample composition is conceivable with special cell designs [15], such control is usually not practical. One does, however, have control over the order of selection of temperatures at which vapor pressures are measured. This order should be selected with the intention of simplifying the separation of the effects of temperature and of sample composition, and with the intention of maximizing the opportunities to detect all effects as a result of chemical changes in the system. Some of the more useful and/or commonly seen are given here. In each case it is presumed that temperatures are chosen so as to be approximately evenly distributed on the  $1/T$  axis over the temperature range of the experiments.

##### *Monotonic*

The order of temperatures increases or decreases strictly. This type of program is one of the worst to be used, except with a congruently vaporizing sample. Even then it offers no advantage. Important but subtle chemical changes in the sample [9,16,17] are likely to be missed. An example of this is provided by a study [18] of the vaporization of  $\text{Ga}_2\text{Se}_3$  in which the temperature was increased monotonically. The following facts were missed:

(1)  $\text{Ga}_2\text{Se}_3$  vaporized incongruently [9] and (2) the vapor pressure depended on the recent heating history of the sample [9]. The congruently vaporizing composition at high temperature is different than that at low temperature in the range of the experiment, and this is revealed only when one measurement follows another made in the other temperature zone.

### *Isothermal*

The temperature is constant as the sample effuses from the cell. Vapor pressures are monitored until the sample is exhausted or until the vapor pressure is too low to be measured. This method is common in thermogravimetry. In most cases, phase changes are revealed through discontinuous decreases in vapor pressure, and regions of solution through continuous decreases.

Many advantages of simple interpretation are gained. However, to obtain vapor pressure as a function of temperature, an experiment with a separate sample is required at each temperature. Unusual phenomena, such as an increase in vapor pressure with decreasing temperature [16,17], will be missed. If the rate of mass loss is the probe, then in an extreme case, an increase in the rate of mass loss occurring with a decrease in vapor pressure can cause a phase change to be missed [10].

### *Random*

From a set of temperatures at which a sample is to be studied, temperatures are selected randomly. Each temperature can be written on a separate piece of paper, the pieces placed in a hat, and the pieces drawn out one at a time; other randomization procedures are available, many of them faster and more convenient than that described. In a case involving a very large sample and a very large number of measurements, this program is best. Every variation is likely to be tested. However, no guarantee of any particular variation will exist; in experiments with small samples and a limited number of measurements, the likelihood of missing important variations becomes significant. Hence, one seeks designed programs in which the likelihood of observing all chemical phenomena is maximized.

### *Dispersed*

$N$  temperatures are selected and ordered monotonically. This set of  $N$  temperatures is divided into  $n$  groups such that  $n^2 \approx N$  and such that the lowest  $\approx n$  temperatures are in the first group, the next lowest  $\approx n$  temperatures are in the second group, etc. The  $n$  groups are then ordered randomly and one temperature is selected from each group in that order until all temperatures are used. This procedure can be repeated until the sample is

exhausted or the desired information has been obtained. This program is most likely to reveal all chemical phenomena during vaporization of a sample of largely unknown properties. It is the best method, along with a small number of isothermal experiments, to apply to a new system.

### *Designed*

A temperature program can be designed to maximize the amount of information obtained from a given set of measurements after the characteristics of a vaporizing system have been determined from experiments using programs of the types already discussed. A random or dispersed program can be followed while the vaporization is univariant and an isothermal program followed shortly before, during, and shortly after, each phase change. Point-by-point selections can be made to establish dependence of vapor pressure on the heating history of the sample.

### *Separating temperature effects*

Vapor-pressure data from a program involving elements of randomization will be scattered by effects caused by changes in sample composition, temperature variation, and normally distributed errors. The latter can be kept small with care and/or dealt with by statistical methods. Separating the effects caused by temperature variation is important if the effects due to changes in sample composition are to be deduced. Also important is a record and display of the order in which measurements are taken.

When the chemical reactions are known, temperature effects can be largely filtered out by a third-law treatment [19]. The treatment requires knowledge of the Gibbs energy function,  $\phi^\ominus$  of each substance in the reactions;  $\Delta H^\ominus$  (298 K) of each reaction is obtained.

$$\Delta H^\ominus(298\text{ K}) = -T \left[ R \ln K_p + \Delta\phi^\ominus(T) \right] \quad (9)$$

For a given vaporization reaction, eqn. (9) should give the same value of  $\Delta H^\ominus$  (298 K) from every measurement. Variations in  $\Delta H^\ominus$  (298 K) reveal random errors, incorrect Gibbs energy functions (e.g. owing to incorrect assignment of vaporization reaction), phase changes, extraneous temperature effects (e.g. incorrect temperatures), etc.

A computer program in FORTRAN which analyzes and displays data in a variety of useful forms is available [20]. Sequences in the plots are displayed by use of sequential symbols. Effects caused by the factors listed above are revealed. By displaying the data properly, virtual thermogravimetric traces can be deduced from measurements of vapor pressures as functions of temperature; the effect of many isothermal experiments can be gained from one experiment with a dispersed program.

In an experiment using an effusion cell with two chambers [21], amounts of sample must be loaded into the two chambers in proportion to the effective area of the effusion orifices in the chambers [7], otherwise phase changes as a result of composition changes will not occur simultaneously in the two chambers, and an analysis of the results will be doubly complicated.

## THERMOGRAVIMETRIC CURVES

An experiment conducted under an isothermal temperature program would be similar to a classical thermogravimetry experiment. Such experiments have been reported [10,11]. A simulated experiment with several pertinent features is shown in Fig. 1. The amount of mass lost from the sample is represented in arbitrary units on the abscissa. The vapor pressure over the sample as measured by the Knudsen effusion method is represented in arbitrary units on the left ordinate. The derivative of the plot of vapor pressure vs. mass lost is represented on the right ordinate.

Each phase change of the sample, occurring as mass is lost by effusion, is revealed by a decrease in vapor pressure. The plot of the derivative reaches a peak at each phase change; the derivative plot is particularly useful because it can reveal vapor-pressure decreases which are obscured by other features in the plot [11]. In Fig. 1, phase changes appear at points A, B, C, and D.

The feature in the plots at point D is particularly worthy of note because it appears to contradict the requirement of a vapor pressure decrease as

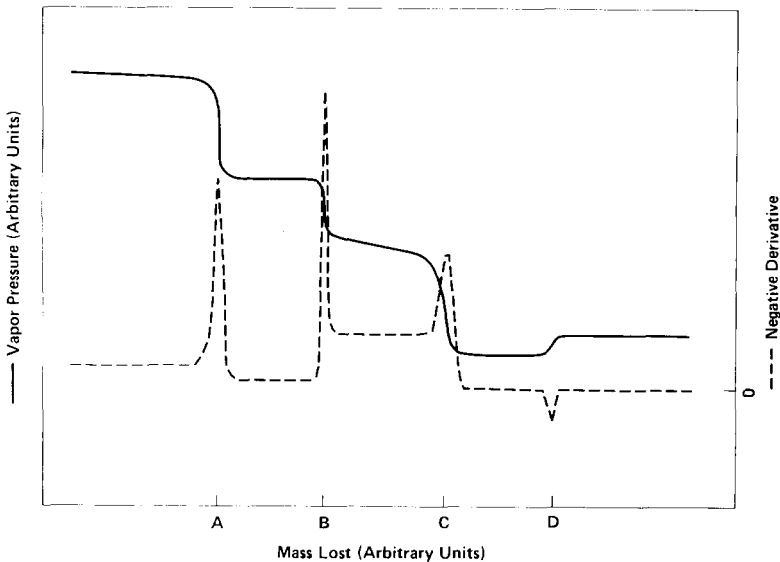


Fig. 1. Simulated thermogravimetric curve with equilibrium vapor pressure as the probe.

mass is lost across a phase change. Such a feature has in fact been observed [11]. The apparent increase in vapor pressure arose because the measurement was made by using the Knudsen-effusion method. The calculated vapor pressure is proportional to the rate of mass loss. The rate of mass loss is proportional to the actual vapor pressure and to the square root of the molecular weight of the effusing vapor as expressed by the Knudsen equation [3,4]

$$dg/dt = Pa(M/2\pi RT)^{1/2} \quad (10)$$

in which  $a$  is the effective area of the orifice through which vapor effuses,  $M$  is the molecular weight and  $P$  is the actual pressure of the vapor.

The feature at D in Fig. 1 occurred when, owing to a phase change, the vaporization reaction changed to produce a vapor with higher molecular weight, an effect which was large enough to overcome the necessary decrease in vapor pressure. Such an effect is seen on going from vaporization by reaction (7) to vaporization by reaction (8). The molecular weight of  $\text{Se}_2(\text{g})$  is 158; that of the mixture of  $\text{In}_2\text{Se}(\text{g})$  and  $\text{Se}_2(\text{g})$  from reaction (8) is 253.

If the vapor pressure in Fig. 1 is measured by the torsion effusion method, then the vapor pressure decreases at point D. This was observed [11].

It should be noted that any thermogravimetric method which uses mass as probe could fail to detect a change in the condensed phase when the molecular weight of the vapor increases as the vapor pressure decreases. A simultaneous, independent probe should be used when possible.

A technical question is whether the methods described herein are properly called thermogravimetry; certainly they do not conform strictly to the internationally accepted definition of that term [22]. However, mass is monitored by a planned program, possibly isothermal, as the sample undergoes composition changes due to heating; and chemical changes are revealed by changes in the probe, equilibrium vapor pressure. Perhaps the definition of thermogravimetry should be extended to include these methods.

## SUMMARY

A single vaporization experiment with the proper experimental design can yield results equivalent to those accumulated from many isothermal thermograms. Careful preparation, optimum design of the temperature program, and efficient analysis of the data are required. Factors to be taken into account, the most common experimental designs, and types of analysis have been described.

## ACKNOWLEDGMENT

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