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COMPOSITION CHANGE OF BINARY COMPOUNDS UNDER CONDITIONS  
OF EQUILIBRIUM AND VACUUM VAPORIZATION

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Composition Change of Binary Compounds Under Conditions  
of Equilibrium and Vacuum Vaporization

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ABSTRACT

The composition of binary compounds changes as a function of temperature when in equilibrium with the vapor. This change, for the IIB-VIA and IA-VIIA compounds is small, within the limits of solubility. The equilibrium vacancy concentrations are controlled by their free energies of formation. The composition changes in a different manner when the solid is heated in vacuum. Vacuum evaporation rates are controlled by the activation free energy of a surface reaction which, under proper conditions, may also control the bulk concentration of vacancies. Experimental verification of this effect is proposed. It has been shown that closed system vapor pressure measurements are extremely sensitive to minute changes of the solid composition. The measured apparent vapor pressure is a function of the reaction chamber volume for composition changes  $\geq 2 \times 10^{-8}$  moles/cm<sup>3</sup>. In turn, the sensitivity of closed system vapor pressure measurements may be used for accurate determination of off-stoichiometry.

## Introduction

Most binary compounds exhibit off-stoichiometry when in equilibrium<sup>1</sup> with the vapor at temperature,  $T$ . This deviation is due to the difference in the free energy of anion and cation vacancy formation in the bulk of the solid.<sup>2</sup> For the IA-VIIA and the IIB-VIA compounds it is below the detection limit of most chemical analytical techniques.<sup>3,4</sup> ( $\leq 10^{-4}$  moles/cm<sup>3</sup>) However, it is easily detectable by various electrical and optical measurements.<sup>5,6</sup> It will be shown that the solid composition also shows temperature dependence under equilibrium conditions.<sup>7,8</sup>

Partial vaporization of these compounds into vacuum at the same temperature,  $T$ , will result in a residue of composition other than the equilibrium composition. Vacuum evaporation<sup>9</sup> is controlled by the kinetics of a surface reaction<sup>10,11</sup> which is responsible for producing the vaporizing species. This surface reaction limitation manifests itself in a vacuum evaporation rate which is much lower than the maximum vaporization rate observed under equilibrium conditions.<sup>12</sup> The composition of the solid residue which has been subjected to the vacuum evaporation will depend on the energetics of the rate controlling surface step and not on the equilibrium vacancy concentration.

We shall show that the solid composition may also be temperature dependent under vacuum evaporation conditions provided that the crystal constituents vaporize independently and that the two surface reaction steps which control the vaporization of the binary compound have different activation free energies.

Vapor pressure measurements, in general, fall into two categories. Those which are carried out in a closed system such as dew point,<sup>13</sup>

bourdon gauge,<sup>14a,b</sup> optical-absorption,<sup>15</sup> and other static techniques<sup>16</sup> belong to the first class. Dynamic measurements which belong to the other class are performed in an open reaction chamber from which the vapor is allowed to escape at such a slow rate that equilibrium between the solid and the vapor remains virtually unperturbed. Effusion<sup>17</sup> and transpiration<sup>18</sup> type measurements belong to this group.

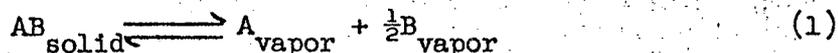
In this paper we would like to show that static vapor pressure measurements are very sensitive to small deviations from equilibrium composition. Hence, the heat treatment of binary compounds prior to carrying out such a measurement could greatly influence the results. In turn, the sensitivity of the closed system vapor pressure measurements to off-stoichiometry can be used to detect and measure accurately minute changes in the composition of the binary compounds.

For all of the binary compounds discussed in this paper we shall assume that all changes in the solid composition takes place within the solubility limit of the compound, thus, the precipitation of the compound constituents cannot take place. The off-stoichiometry is limited therefore to a small concentration range depending on the solubility of each component in the binary compound.

#### Composition of Binary Compound in Equilibrium with its Vapor

Deviations from stoichiometry has been studied in several binary compounds<sup>19,20</sup> via electrical<sup>21</sup> and optical measurements,<sup>15</sup> since the presence of lattice vacancies give rise to the formation of charged donor and acceptor states. The total vapor pressure is at a minimum<sup>18</sup> when equilibrium is established between the solid and the vapor at any

given temperature. Assume that vaporization is congruent<sup>10,11</sup> and that the binary compound undergoes dissociation upon evaporation according to the following reaction:\*



The partial pressures of the vapor species can be expressed<sup>2,22</sup> as

$$RT \ln \bar{p}_A = (E_f - E_a) - E_A + T\Delta S_A - \mu_A^\circ \quad (2)$$

$$\frac{1}{2}RT \ln \bar{p}_{B_2} = (E_d - E_f) - E_B + T\Delta S_B - \mu_B^\circ + \Delta F_{B_2} \quad (3)$$

where  $E_f$ ,  $E_a$  and  $E_d$  are, respectively, the energies associated with the Fermi level, the acceptor state which is due to cation vacancy (assuming that it can only be a singly ionized acceptor) and the donor state which is due to an anion vacancy (assuming it can only be a singly ionized donor).  $E_A$  and  $E_B$  are the energies to remove atoms A and B from the lattice to infinity, respectively. All of the energies are relative to the infinitely dispersed atoms in their lowest quantum state. Thus, the energies required to form the ionized acceptor and donor vacancies,  $V_a^-$  and  $V_d^+$ , are  $E_A - (E_f - E_a)$  and  $E_B - (E_d - E_f)$  respectively. R and T have their usual meaning. The entropy of the solid,  $\Delta S_s$ , is given by

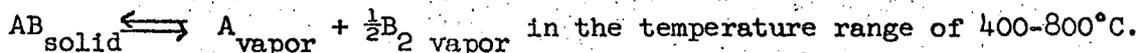
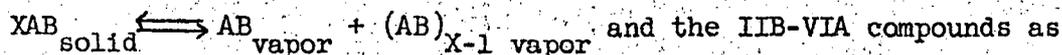
$$\Delta S_A = V_A^- \ln S/V_A^- + R \ln K_A \quad (4)$$

and

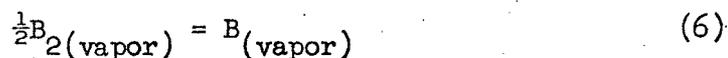
$$\Delta S_B = V_B^+ \ln S/V_B^+ + R \ln K_B \quad (5)$$

\*

IA-VIIA compounds evaporate according to the net reaction:



for the two sublattices, where  $V_A^- \ln S/V_A^-$  and  $V_B^+ \ln S/V_B^+$  are the entropies of mixing associated with the introduction of the ionized vacancies into the lattice and  $S$  is the concentration of lattice sites in each sublattice.  $R \ln K_A$  and  $R \ln K_B$  are the vibrational entropies of the sublattices including the change of lattice vibrations in the vicinity of the vacancies.<sup>2</sup>  $\bar{p}_A$  and  $\bar{p}_B$  are the partial pressures of the compound constituents;  $\mu_A^\circ$  and  $\mu_B^\circ$  are the chemical potentials of the ideal gases A and B, at one atmosphere, respectively.  $\Delta F_{B_2}$  is the standard free energy of the reaction



It is assumed that the concentration of vacancies in the lattice is so low that vacancy aggregation effects<sup>2</sup> can be neglected.

Equations (2) and (3) show that if the free energies of anion and cation vacancy formation are different, which is the usual case, then at any given temperature any binary compounds will exhibit off-stoichiometry. The equilibrium composition is determined by the solubility of these vacancies and the mass action equation for ionized vacancies:<sup>\*\*</sup>

$$(V_A^-)(V_B^+) = k \quad (7)$$

where  $k$  is the Schottky constant.<sup>23</sup>

<sup>\*\*</sup> It is assumed that all donor and acceptor vacancies are ionized at the elevated temperatures for which vacuum vaporization rates and/or equilibrium vapor concentrations are experimentally significant. This is the temperature range which is considered by this paper. It is in the range of 400-800°C for both the IIB-VIA and IA-VIIA groups of binary compounds.

Typical concentrations of anion or cation vacancies in IIB-VIA and IA-VIIA compounds in the temperature range of interest fall between  $10^{-8}$  to  $10^{-4}$  moles/cm<sup>3</sup>.<sup>1,24</sup>

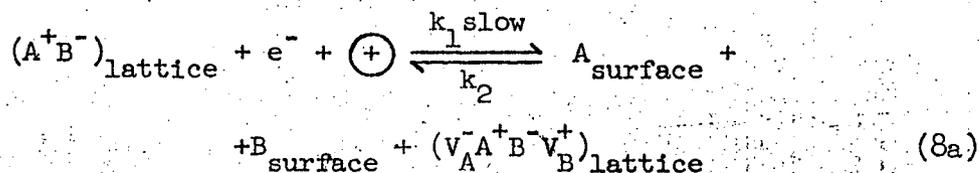
From Eqs. (2) and (3) one can calculate the temperature dependence of the deviation from stoichiometry of the equilibrium solid composition. However, calculations of this kind give rather ambiguous results due to the exponential energy dependence of the partial pressures. A few percent error in any of the energy terms gives rise to large errors in the calculated values of the partial pressures. The accuracy of values of  $E_A$ ,  $E_B$  calculated for the IIB-VIA<sup>25</sup> and IA-VIIA compounds<sup>26</sup> are not better than 10%. Estimates of the entropy contribution are even poorer.<sup>25,27</sup> Also,  $E_f$ , the Fermi level, varies with the change of the crystal composition which must be taken into account and the temperature dependence of  $E_f - E_a$  and  $E_d - E_f$  cannot be neglected.<sup>6</sup> Therefore, we shall give only a schematic representation of the temperature dependence of the equilibrium solid composition in Fig. 1, which is apparent already from Eqs. (2) and (3). We have plotted the logarithm of the ionized vacancy concentrations as a function of reciprocal temperature. It is not unreasonable to assume that for some of the binary compounds due to the difference in the free energies of anion and cation vacancy formation the vacancy concentration curves may cross over as a function of temperature. This case is shown in Fig. 1. The crossover point would correspond to stoichiometry. At even higher temperature those vacancies will dominate which were in the minority at temperatures below the crossover point temperature. Thus, the solid can change from n to p type as a function of temperature assuming electronic conductivity and that the donor anion vacancies were dominant at low temperatures.

Composition of Binary Compounds Under  
Vacuum Evaporation Conditions

Vacuum evaporation is a kinetic experiment, as opposed to evaporation from an equilibrium source such as an effusion cell. The rate of vaporization in vacuum is proportional to the surface area of the solid<sup>28</sup> while evaporation from an equilibrium source is surface area independent.

It was found<sup>10</sup> that the vacuum evaporation of many solids including the IIB-VIA and IA-VIIA compounds is limited by a slow surface reaction step rather than by the desorption of the mobile surface atoms.<sup>9</sup> The evaporation of IIB-VIA compounds is controlled by a surface reaction<sup>10,11</sup> which involves charge transfer. Electrons and holes must be captured by the ions at the surface before vaporizing as neutral species. This mechanism was determined in studies of the effect of light<sup>29</sup> and impurities<sup>11,30</sup> on the evaporation rate of one face of a cadmium sulfide single crystal.<sup>28</sup>

Assume the following simple sequence of surface reactions:

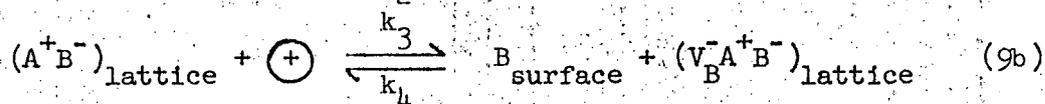
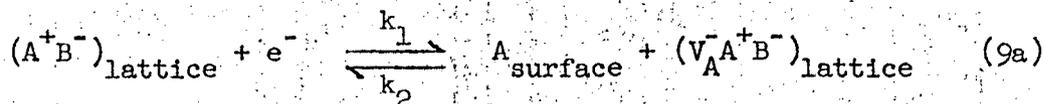


The vacancy concentration at the surface is determined by the activation free energy of vaporization,  $\Delta F_V^*$ . In general all compounds which undergo rearrangement, i.e., association or dissociation upon evaporation will have a  $\Delta F_V^*$  different from the equilibrium free energy of vaporization  $\Delta F_V^\circ$ .<sup>9,12,31</sup> Thus, if bulk diffusion rates of vacancies are fast at the evaporation temperature, as is the case for the IIB-VIA compounds,<sup>11,24</sup> (vacancies from the surface could diffuse into the bulk faster than they are removed via the vaporization process), the "steady state composition" of the binary compound crystal<sup>\*\*\*</sup> which is subjected to vacuum evaporation at a given temperature can be different from that of the equilibrium crystal composition at the same temperature.

If the evaporation mechanism which is given in Eqs. (8a-8d) is operative, the vacancy concentration is controlled by the rates of simultaneous trapping of electrons and holes by the cation and the anion at the surface, Eq. (8a). When evaporation takes place according to this mechanism the composition of the freely vaporizing crystal should show little or no temperature dependence since both anion and cation vacancies are produced by the same rate determining reaction step. Hence, their ratio  $V_A^+/V_B^- = \text{constant}$  at any temperature. If there is a temperature dependence of the crystal composition under vacuum evaporation conditions, the formation of anion and cation vacancies must take place in two parallel reaction steps. An example to this type of evaporation mechanism is:

\*\*\*

The use of single crystals is necessary for the vacuum evaporation experiment in order to observe the change of composition.<sup>9</sup> Powders have large inner surface and channel structure in which the vaporizing atoms may undergo many collisions.<sup>32</sup>



Since  $k_5, k_6, k_7 \gg k_1, k_3$  for surface reaction limited vaporization the temperature dependence and the relative magnitudes of  $k_1$  and  $k_3$ , thus the rate of electron or hole trapping by the ions at the surface will determine the crystal composition as well as the vapor composition in this case.<sup>33</sup>

The difference between the "steady state composition" and equilibrium composition of a binary compound crystal could be measured experimentally. For this purpose one crystal should be allowed to vaporize in vacuum until a steady state vaporization rate is obtained.<sup>10</sup> Another crystal should be allowed to vaporize in an effusion cell at the same temperature employed for the vacuum evaporation until again, steady state rate is obtained for the vapor flux through the orifice of the equilibrium source. Electrical measurements<sup>21</sup> could be used to measure the composition difference between the crystals which were subjected to vaporization by these two different methods.

It must be emphasized that bulk diffusion rates of vacancies which are formed at the surface on account of the evaporation surface reaction must be fast, in order to observe a different composition for crystals subjected to vacuum evaporation from that of the equilibrium composition.

If diffusion rates are slow relative to the evaporation rate, there could be no communication between the surface and the bulk of the crystal throughout the evaporation, hence the variation in the vacancy concentration is limited to a small surface layer which vaporizes rapidly.

Effect of Small Changes of the Crystal Composition  
on Closed System Vapor Pressure Measurements

The composition of binary compounds, as it was described above, is a function of the heat treatment it is subjected to when prepared, prior to the vapor pressure measurement. The heat treatment may be carried out at different temperatures in a closed (equilibrium) or an open reaction vessel (in vacuum or under transpiration conditions). The change in composition is small since the only case we are considering here is when off-stoichiometry is within the solubility limit of both compound constituents. We would like to show the effect of such a small change in composition on the vapor pressure as measured in a closed reaction chamber.

Assume that the compound, AB, has a composition corresponding to  $10^{16}$ - $10^{18}$  atom/cm<sup>3</sup> excess A as prepared for the vapor pressure experiment. This data could be obtained by conductivity measurements assuming that all of the anion vacancies which are due to the presence of excess A, are ionized. In equilibrium at a given temperature  $T = 1000^\circ\text{K}$ , the binary compound should only contain  $10^{14}$  atom/cm<sup>3</sup> excess A. The composition of the solid therefore, will change by removal of excess A into the vapor phase. The extent to which the equilibrium composition will be approached depends, however, on the volume of the reaction vessel. Figure 2 shows the total pressure,  $P_{\text{total}}$ , over the solid, AB, as a function of the volume of the reaction chamber for different concentrations of excess A.

It is assumed that the vapor behaves as an ideal gas and that the volume of the solid in equilibrium with the vapor is  $V_{\text{solid}} = 1 \text{ cm}^3$ . The partial pressure,  $p_A$ , was calculated assuming that Henry's law ( $\bar{p}_A = k(V_B^-)$ ) holds for such dilute solid solutions. In order to calculate the constant,  $k$ , the value,  $\bar{p}_A = 3.7 \times 10^{-5} \text{ atm}$  was used for the partial pressure over the binary compound of equilibrium composition. This is the partial pressure of cadmium vapor over cadmium sulfide at  $T = 1000^\circ\text{K}$ , as measured by effusion methods. The expressions,  $P V_{\text{vapor}} = (N - n_{\text{solid}}) k'T$  and  $V_{\text{vessel}} = V_{\text{vapor}} + V_{\text{solid}}$  were used in the calculations, where  $N$  is the total number of excess A atoms over that of the equilibrium value and  $n_{\text{solid}}$  is the number of excess atoms in the solid as calculated using Henry's law.  $k'$  is the Boltzmann constant,  $V_{\text{vessel}}$  and  $V_{\text{vapor}}$  are the volume of the reaction vessel and the vapor, respectively. The total pressure of CdS at  $1000^\circ\text{K}$  over the equilibrium solid composition is  $P_{\text{total}} = 5.5 \times 10^{-5} \text{ atm}$ . At small volumes, the partial pressure of A due to the excess of A in the solid, is much larger than its equilibrium partial pressure. As the volume increases the contribution of excess A over that of its equilibrium value to the total pressure decreases and the true value of  $P_{\text{eq}}$  is approached. It is clear from Fig. 2 that small changes of the solid composition could result in large errors in the experimental data. Setting the sensitivity of closed system vapor pressure measurements arbitrarily at 0.1 torr, a composition change of  $10^{16} \text{ atom/cm}^3$  ( $1.7 \times 10^{-8} \text{ moles/cm}^3$ ) could produce a measurable error in the measurements using a reaction chamber of volume  $V = 5 \text{ cm}^3$ . The interpretation of the results of the closed chamber vapor pressure experiments could be further obscured by measurement of the apparent equilibrium vapor pressure as a function of temperature in the same closed reaction vessel. The equilibrium solid composition changes as a function of temperature according to Eqs. (2) and (3).

The dependence of the apparent equilibrium vapor pressure on the volume of the reaction vessel could however, be used to measure small changes of the solid composition accurately. Since it is an absolute method, it should lead to more accurate determination of the off-stoichiometry within the sensitivity of the technique than electrical measurements in which an assumption has to be made as to the charge state of the vacancy. It could also be used to test the validity of Henry's law for dilute solid solutions.

Closed systems which are used for spectroscopic determination of the vapor composition are also subjected to the analysis given above as it has been well demonstrated recently.<sup>15,34</sup> These results may also explain some of the discrepancies between the vapor pressure data obtained by static and dynamic vapor pressure measurements for several binary compounds.<sup>35</sup>

Inaccuracies in vapor pressure measurements due to variation of the solid composition can be avoided by using open reaction chamber techniques such as effusion or transpiration. While the vapor is slowly removed from the vicinity of the solid, the composition of the binary compound will adjust itself to the conditions of the experiment provided that bulk diffusion rates of vacancies are greater than the removal rate of the vaporizing surface species. There will be, however, a transient evaporation rate before steady state is attained, the extent of which will depend on the magnitude of the solid composition variation and the bulk vacancy diffusion rates.

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Figure Captions

- Fig. 1 Schematic representation of the change in the equilibrium composition as a function of temperature for a binary compound, AB, with transition from  $V_A^- \ll V_B^+$  to  $V_A^- \gg V_B^+$ .
- Fig. 2 Variation of the total pressure,  $P_{\text{total}}$ , over the binary compound, AB, at 1000°K as a function of the volume of the reaction vessel for small excesses of A. ( $10^{16}$  atom/cm<sup>3</sup>,  $10^{17}$  atom/cm<sup>3</sup>,  $10^{18}$  atom/cm<sup>3</sup>). In equilibrium, the concentration of excess A is  $10^{14}$  atom/cm<sup>3</sup>.

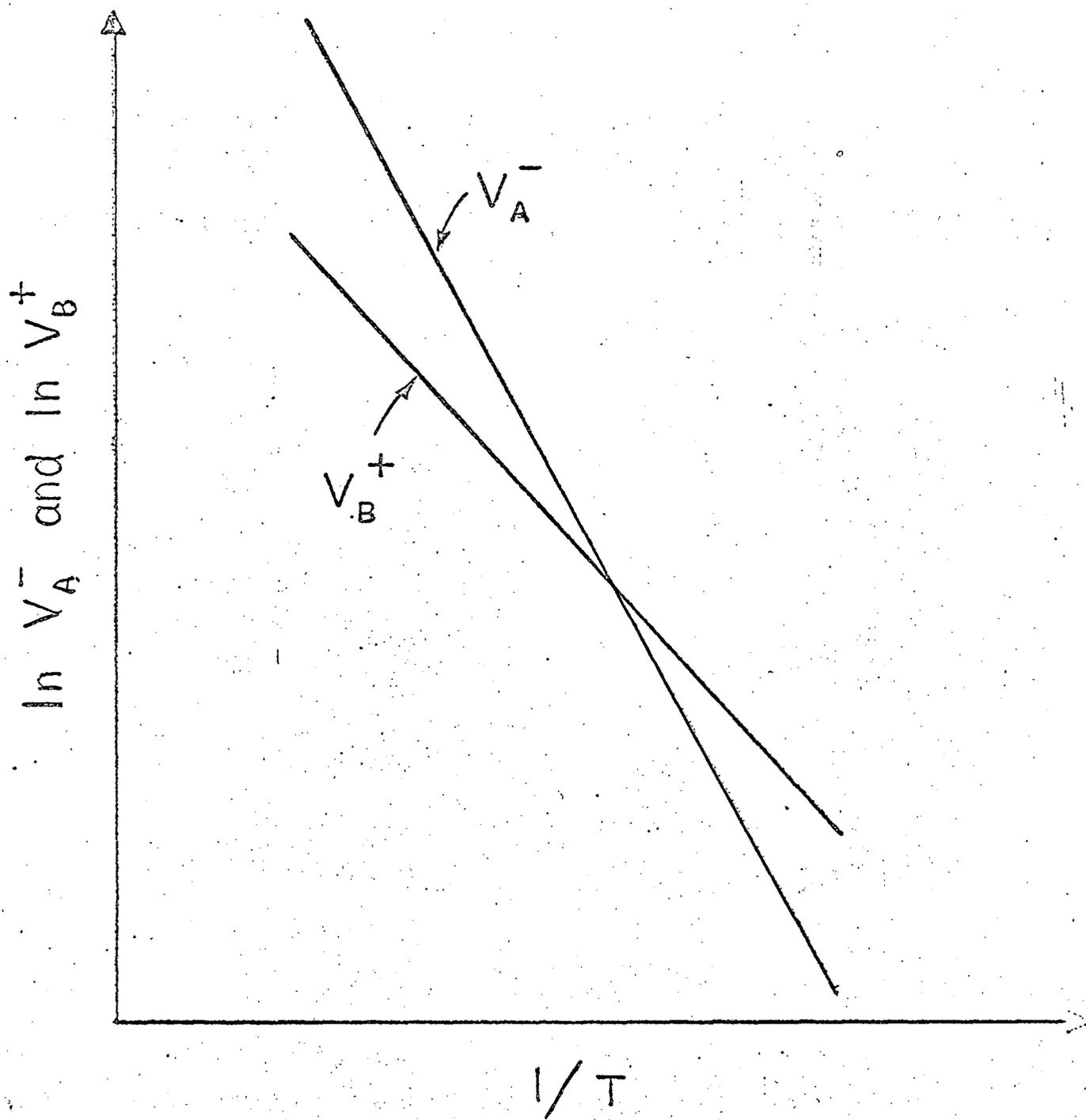


Fig. 1.

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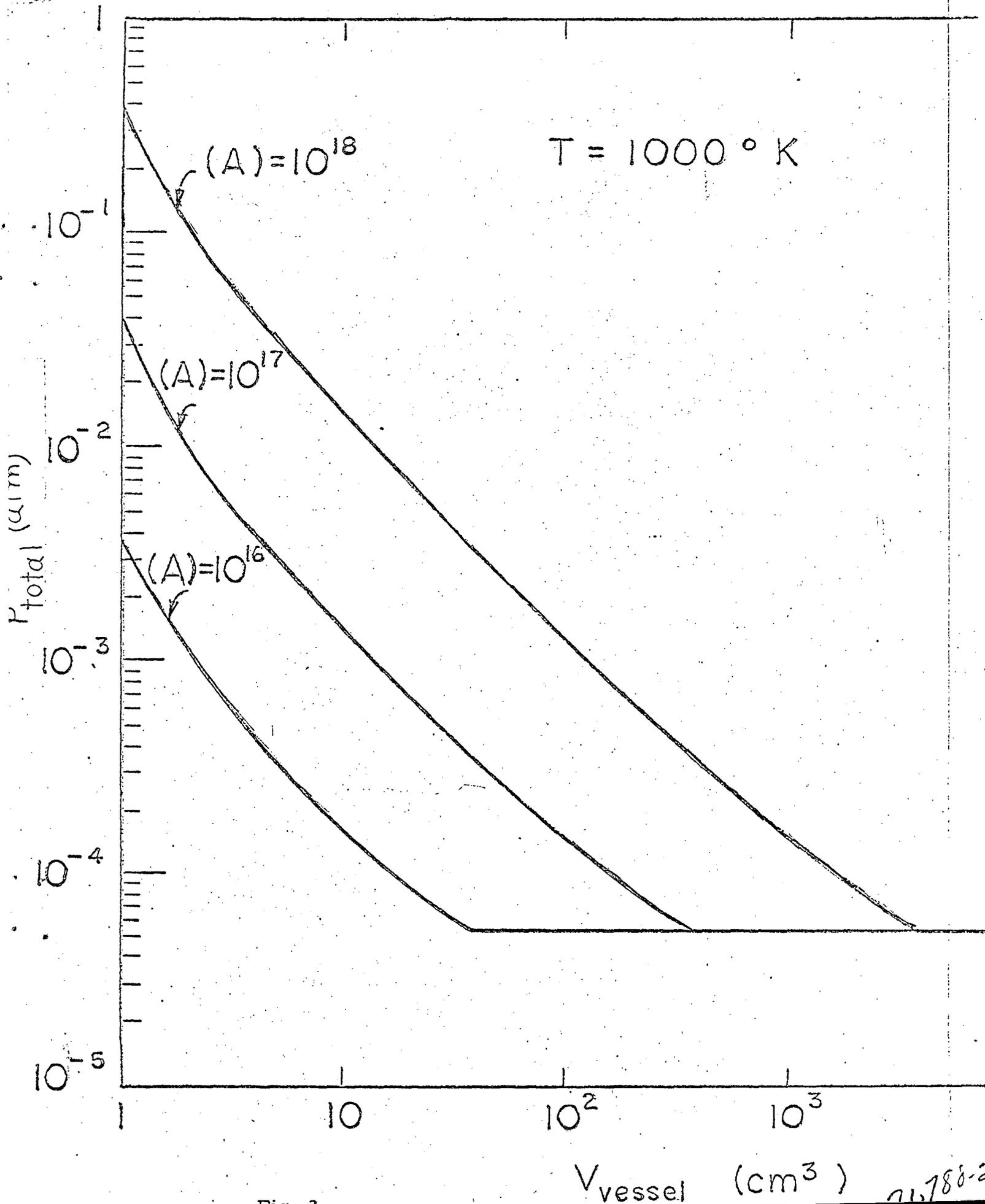


Fig. 2.

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