

Dissociation energies of alkali antimonides as thin layers

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Abstract. Optical transmittance and Auger Electron Spectroscopy (AES) analyses are used to derive some thermodynamic data from alkali antimonide compounds deposited on glass substrates as thin layers. These measurements are performed in the course of the deposition of the layers as well as during their thermal dissociation (linear temperature–time dependence) under UHV conditions.

The optical and AES measurements recorded during the dissociation process are analysed in terms of dissociation energies and equilibrium alkali vapour pressures (P_{Cs} , P_{K} , P_{Na}) over the compounds.

The dissociation phenomenon is analysed and considered to be neither alkali-diffusion limited nor layer morphology limited.

Dissociation behaviours of alkali antimonides with respect to temperature and time are deduced and discussed from the above results. It is shown that $P_{\text{K}} = 5 \times 10^{-10}$ Torr and $P_{\text{Na}} = 1 \times 10^{-11}$ Torr at 200 °C over the Na_2KSb . Without alkali pressures, at 200 °C, 6% of a Na_2KSb layer is dissociated within 1 h whereas 50% of a NaK_2Sb one is dissociated. The dissociation energy, Φ , of a Cs monolayer deposited on the top of the Na_2KSb compound is also considered and is about $\Phi = 35 \pm 1$ kcal mol⁻¹. At room temperature, the corresponding value of P_{Cs} is 2×10^{-17} Torr.

Finally, optical transmittance measurements associated with the AES analysis are shown to be powerful tools for the measurement of dissociation energies and the assessment of related phenomena.

1. Introduction

Alkali antimonide compounds deposited on glass substrates as thin layers are well known photoemitters (Sommer 1968). Despite their large field of applications (Piétri 1973), their chemical behaviour, with respect to temperature and time, has not really been considered. Only a few papers have considered this subject in the past (Kansky 1972). For a relevant analysis, such studies need measurements combining both the physics of thin layers under ultra-high vacuum (UHV) conditions and the chemistry of these materials. The aim of this paper is to illustrate how such a complex situation can be studied by optical measurements allied with Auger Electron Spectroscopy (AES). An alkali antimonide compound heated under UHV is dissociated and converted into a new alkali antimonide compound. This transformation is observed by optical and AES measurements and analysed in terms of dissociation energies of the material considered.

Furthermore, the equilibrium vapour pressures of the alkalis over the compounds can be derived from these measurements. Finally, the results are applied to some concrete situations related to the growth of alkali antimonide layers and to their life time-temperature dependence.

2. Experimental technique

The experiments are performed in an ultra-high vacuum equipment at a total pressure of approximately 1×10^{-10} Torr, mainly composed of hydrogen. The experimental arrangement is shown schematically in figure 1. Deposition and thermal dissociation of

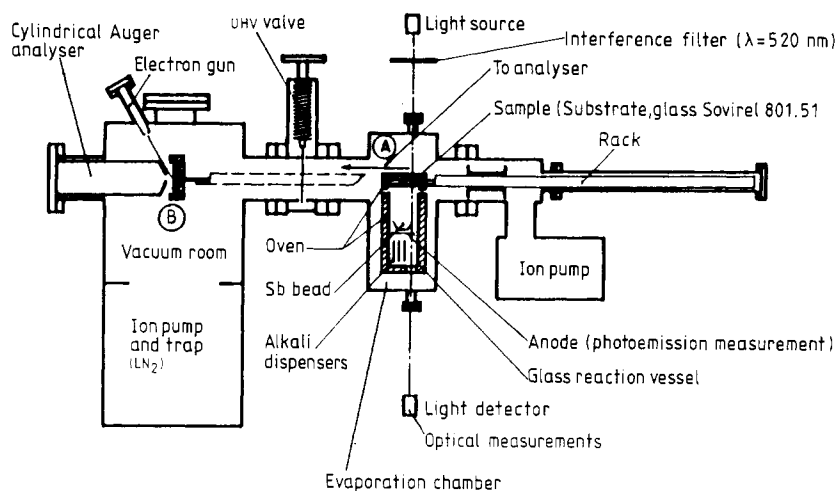


Figure 1. Experimental equipment.

antimonide layers were carried out in chamber A. Thermal dissociation of the layers was produced by raising the sample temperature linearly with time. The state of the layers was monitored continuously in chamber A by measuring the optical transmission at $\lambda = 520$ nm. The AES analyses were performed after moving the sample from chamber A to B, using measurement conditions identical to those described by Dolizy and Grolière (1983).

Alkalis are evaporated from sources made of small Ni pipes containing alkali chromates and aluminium powder (Simondet *et al* 1980). Antimony is evaporated from a Sb bead melted on a Ni wire.

3. Dissociation of the alkali antimonide compounds

3.1. Optical analyses and AES investigations

Consider the compound K_3Sb deposited on a glass substrate as a thin layer (450 \AA). The dissociation (figure 2) of K_3Sb into K_2Sb takes place according to:



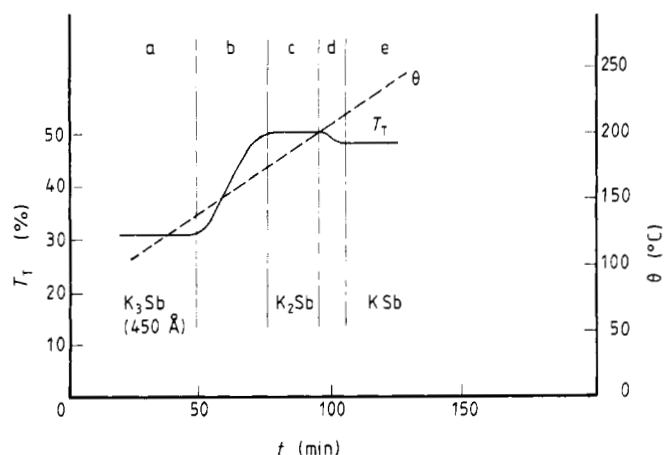


Figure 2. Experimental optical transmittance measured during dissociation of K_3Sb into KSb through K_2Sb . The slope $\Delta\theta/\Delta t = 0.023^\circ C s^{-1}$.

Beyond this stage, the dissociation of K_2Sb into KSb takes place, corresponding to:



The AES measurements performed at each stage of the dissociation process give the corresponding surface composition of the layer. Before dissociation (stage a, figure 2), the material is nearly K_3Sb (figure 3) and becomes close to KSb (stage c) through K_2Sb (stage e). During the dissociation process (stage b), AES measurements indicate that the surface of the layer corresponds to K_xSb with $2 < x < 3$, indicating that the surface

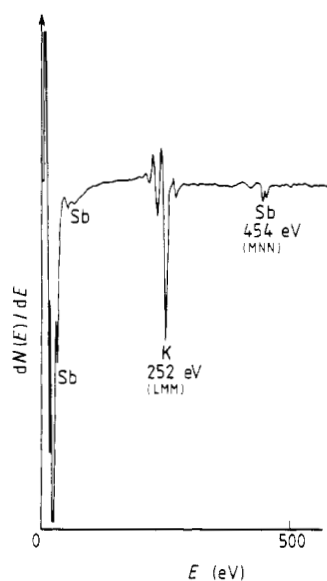


Figure 3. Auger spectrum of the compound K_3Sb recorded before dissociation (stage a, figure 2).

composition is probably a mixture of two phases K_3Sb and K_2Sb (Dolizy and Grolière 1983). In the course of the K_3Sb dissociation into K_2Sb , it can be assumed that the intermediate layer is composed of a homogeneous mixture of two phases ($K_3Sb + K_2Sb$) (figure 4). Figure 5 shows the theoretical optical transmission value T_T with respect to the amount of K_3Sb transformed into K_2Sb based on a homogeneous mixture (Apnes

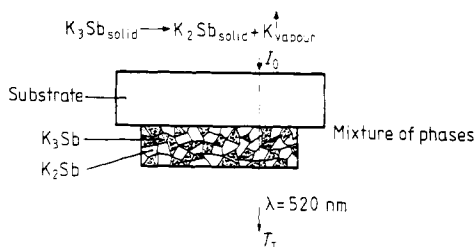


Figure 4. Model for the dissociation of K_3Sb . $n_{K_3Sb} = 1.9 - 0.9i$. $n_{K_2Sb} = 1.7 - 0.5i$.

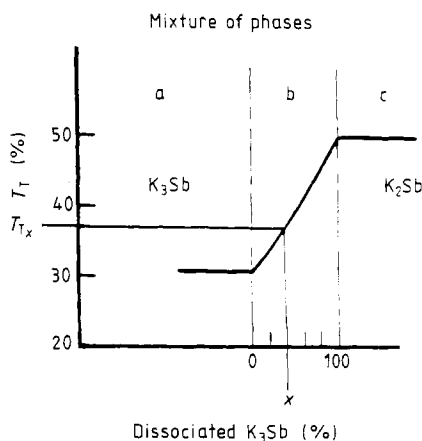


Figure 5. Theoretical optical transmission with respect to the amount of K_3Sb layer of thickness 450 \AA transformed into K_2Sb .

1982) of the two phases (effective medium theory). The optical transmission values, with respect to the amount of material transformed, are quasilinear from the initial phase to the final one.

The optical transmission curve $T_T = f(t)$ (figure 2, stage b) measured during dissociation using a linear temperature sweep, when combined with the computed function $T_T = f(a)$, where a is the amount of dissociation K_3Sb , allows the determination of an experimental relative dissociation rate of the layer, $\mathcal{R}_{opt} = da/dt$ plotted against time and temperature as shown in figure 6. The dissociation rate reaches a sharp maximum at a characteristic temperature θ_m .

Finally, it appears clearly that the optical transmission is a useful and relevant tool for analysing the behaviour of an alkali antimonide compound under thermal dissociation. These measurements can be analysed in more detail, combining them with thermodynamic aspects as shall be developed in the next paragraph.

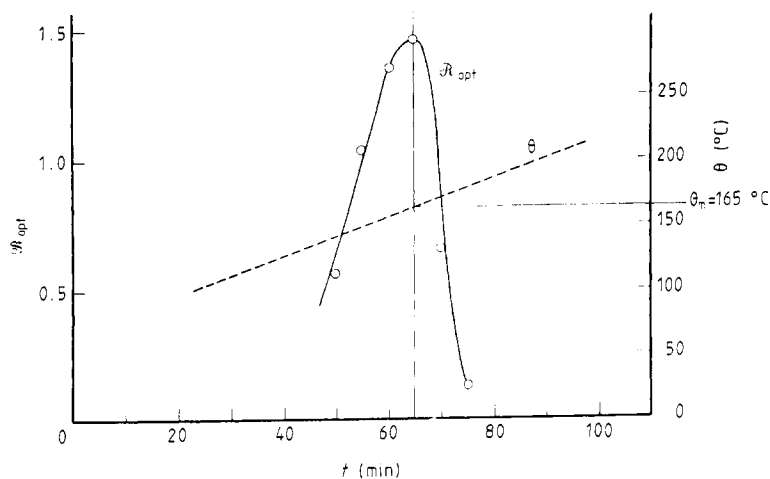


Figure 6. Relative dissociation rate deduced from optical transmittance measurements. $e_{K_3Sb} = 450 \text{ \AA}$. $\Delta\theta/\Delta t = 0.023 \text{ }^\circ\text{C s}^{-1}$.

3.2. Dissociation energies and related phenomena

In the course of the chemical dissociation of an alkali antimonide (relation (1)), the number of K_3Sb moles per surface unit (cm^2) in the layer at a time t after the beginning of the dissociation process is $N_m(t)$. It is assumed that the very thin layer behaves as a 'surface' when such a process is applied to it. Then, it can be supposed that the whole process including diffusion and evaporation of the alkali atoms is not dependent on thickness. The formula used to describe the experimental results is based on a first-order reaction process (Maissel 1970). The reciprocal period of thermal vibration of the alkali atoms leaving the surface of the layer is assumed to be constant and taken as $1 \times 10^{14} \text{ s}^{-1}$.

During dissociation, $N_m/N_m(t=0)$ can be deduced from optical transmission measurements (figure 2, stage b). As an example, this ratio takes the values 0.95 and 0.05 at temperatures $T_1 = 143 \text{ }^\circ\text{C}$ and $T_2 = 178 \text{ }^\circ\text{C}$ respectively. These two values give two different values (Φ_1 and Φ_2 differ from each other by less than 3%) corresponding to the energy of the atoms inside the compound which is assumed here to determine the activation energy for dissociation. In this paper, it has been assumed that the average value $\Phi = (\Phi_1 + \Phi_2)/2$ is the dissociation energy of the alkali atoms considered from the compound under investigation.

Table 1 summarises the results obtained on K_3Sb layers which have different thicknesses $e(K_3Sb)$ (note that θ_m is calculated from a model based on a first-order reaction process). It appears, from table 1, that Φ increases slowly with layer thickness. Never-

Table 1. Results for K_3Sb .

| $e(K_3Sb)$ (\AA) | 200 | 450 | 1000 |
|---|------------------|------------------|------------------|
| θ_1 ($^\circ\text{C}$); θ_2 ($^\circ\text{C}$) | 137; 180 | 143; 178 | 141; 185 |
| Φ (kcal mol^{-1}) | 33.500 ± 0.5 | 33.688 ± 0.5 | 33.938 ± 0.5 |
| θ_m ($^\circ\text{C}$) ($\Delta\theta/\Delta t = 0.023$) | 167 | 170 | 173 |

Table 2. The dissociation energies of various antimonides.

| Compound | Cs ₃ Sb | Cs ₅ Sb ₂ | K ₃ Sb | K ₂ Sb | Na ₂ KSb | Na ₃ Sb |
|--|--------------------|---------------------------------|-------------------|-------------------|---------------------|--------------------|
| Φ (kcal mol ⁻¹) | 29.6 ± 0.5 | 31.5 ± 0.5 | 33.7 ± 0.5 | 35.6 ± 0.5 | 40.5 ± 0.5 | 44.6 ± 0.5 |
| θ_m (°C)($\Delta\theta/\Delta t = 0.023$) | 117 | 141 | 170 | 194 | 257 | 309 |

theless, it is noted that this Φ -variation is of the same order as the experimental accuracy. Therefore, it is concluded that Φ does not depend on the thickness of the layer as far as it does not exceed 1000 Å. This supports the assumption made in the previous section.

It is also important to mention that (due to a strong nucleation process) a thin K₃Sb layer, deposited on a glass substrate, may have a discontinuous structure especially for layer thicknesses thinner than 750 Å (Dolizy 1980). Therefore, the values of Φ measured here are not dependent on morphology.

The decomposition of thin films of complex antimonide materials is difficult to study and, without a complete understanding of the chemical mechanisms, the dissociation energy deduced from this work has to be considered as the apparent activation energy characterising the dissociation.

The compounds Cs₃Sb, Cs₅Sb₂, Na₃Sb and Na₂KSb have been investigated as described before. The dissociation energies of these compounds are summarised in table 2.

The experimental function $N_m/N_m(t=0)$ of a K₃Sb layer, as well as its dissociation rate, are shown as examples in figure 7 plotted against temperature. The curve giving the dissociation rate against θ is very comparable with the one shown in figure 6 which was deduced from optical measurements.

Table 2 suggests that the smaller the alkali atoms the higher the corresponding dissociation energy Φ of the compound. Figure 8 shows the relationship between Φ and the atom size of the alkali. The Φ -values of saturated monoalkali compounds can be

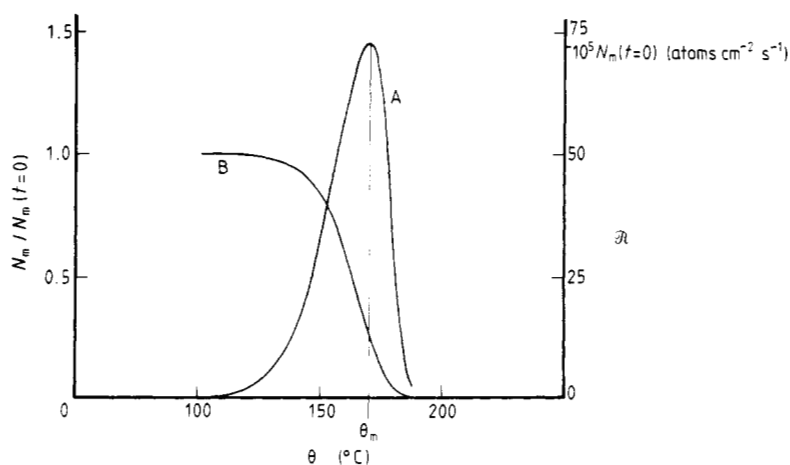


Figure 7. Dissociation rate (\mathcal{R} , curve A) and variation of the number of K₃Sb moles ($N_m/N_m(t=0)$, curve B) plotted against a linear temperature increase. $\Delta\theta/\Delta t = 0.023$ °C s⁻¹, $\Phi = 33\,688$ cal mol⁻¹, $e_{K_3Sb} = 450$ Å.

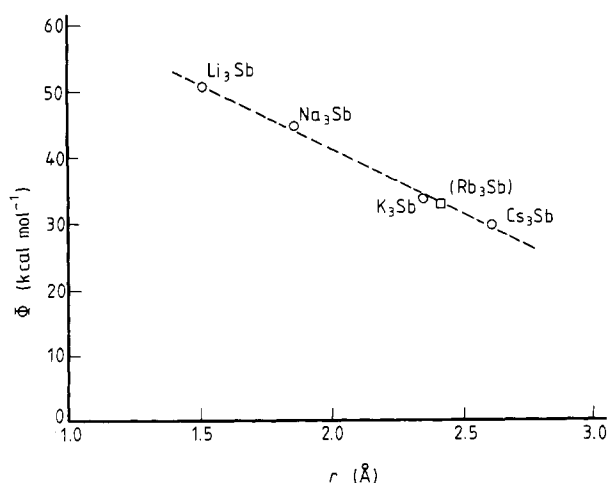


Figure 8. Dissociation energy of saturated antimony alkalis plotted against the atomic radius of the corresponding alkali. The line is Φ (kcal mol⁻¹) = 81 - 20 r (Å).

expressed as:

$$\Phi \text{ (kcal mol}^{-1}\text{)} = -20r(\text{Å}) + 81$$

where r is the atomic radius of the alkali.

The Φ -value of Li₃Sb has been determined (Riglet 1984) as $\Phi = 51$ kcal mol⁻¹ which fits our results very well. The dissociation energy of Rb₃Sb is not known though its value from figure 8 would be Φ (Rb₃Sb) = 33 kcal mol⁻¹.

It can also be observed that the Φ -values of alkali antimonide compounds containing (Sb, Na, K) increase linearly with the sodium content from K₃Sb up to Na₃Sb through Na₂KSb (figure 9). Therefore the Φ -value of an intermediate phase such as NaK₂Sb may be obtained to reasonable accuracy by interpolation: Φ (NaK₂Sb) = 37 kcal mol⁻¹. Extension of this rule to the K_xCs_{3-x}Sb system yields Φ (K₂CsSb) = 32.3 kcal mol⁻¹.

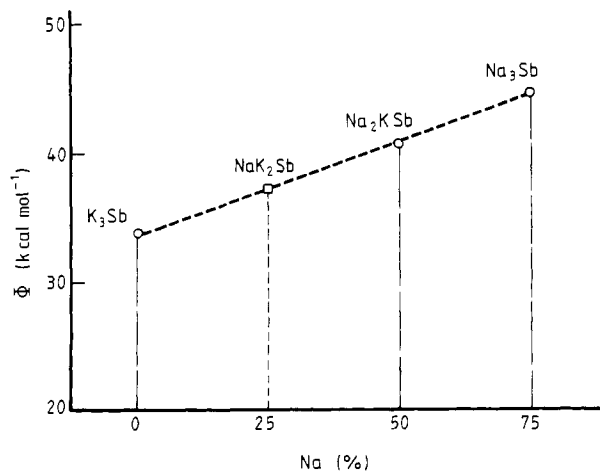


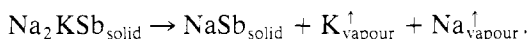
Figure 9. Dissociation energy as a function of Na content in the (Na, K, Sb) system.

4. Equilibrium alkali vapour pressures over the compounds

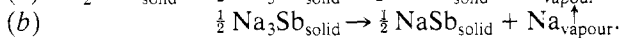
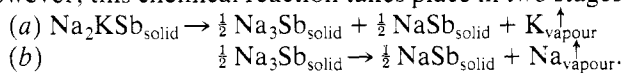
At a given temperature, the number of alkali atoms leaving the saturated alkali compound per unit area and per unit time can be compensated by alkali atoms coming from the vapour phase. The number of alkali atoms on the unit surface is defined as $N_{ad} = N_0 e_0$; e_0 is taken as the equivalent thickness equal to the lattice constant of the material (first neighbours to the vacuum) and N_0 the number of alkali atoms per unit thickness of the considered compound. The sticking coefficient, α , of alkalis on quasi-saturated monoalkali antimonide compounds has been determined experimentally. The value of α is of the order of 0.025–0.05 for temperatures ranging from 130 to 250 °C.

The values of the dissociation energies as determined in the previous section are used to evaluate the equilibrium alkali vapour pressures over the alkali antimonide compounds. The alkali equilibrium pressures over Na_3Sb , Cs_3Sb and K_3Sb are given in figure 10. The caesium vapour pressure P_{Cs} over Cs_3Sb is in good agreement with published results (Lagousov and Ioukhvidine 1967, Kiyoshi Miyake 1961). The sodium pressure P_{Na} over Na_3Sb is also in very good agreement with the results given by Voronine *et al* (1967).

As for the material Na_2KSb , the physical situation is more complicated. After the complete dissociation of Na_2KSb , the NaSb material is obtained as follows:



However, this chemical reaction takes place in two stages:



Therefore, the potassium partial pressure, P_{K} , for the thermodynamic equilibrium over the Na_2KSb is determined by using the dissociation energy $\Phi = 40.5 \text{ kcal mol}^{-1}$ which relates to the Na_2KSb material whereas the P_{Na} over this compound is the sodium pressure over Na_3Sb for obtaining the thermodynamic equilibrium conditions. The values of P_{K} and P_{Na} are shown in figure 11 as functions of temperature to obtain equilibrium conditions over Na_2KSb . It is of interest to outline that the ratio $P_{\text{K}}/P_{\text{Na}}$ has

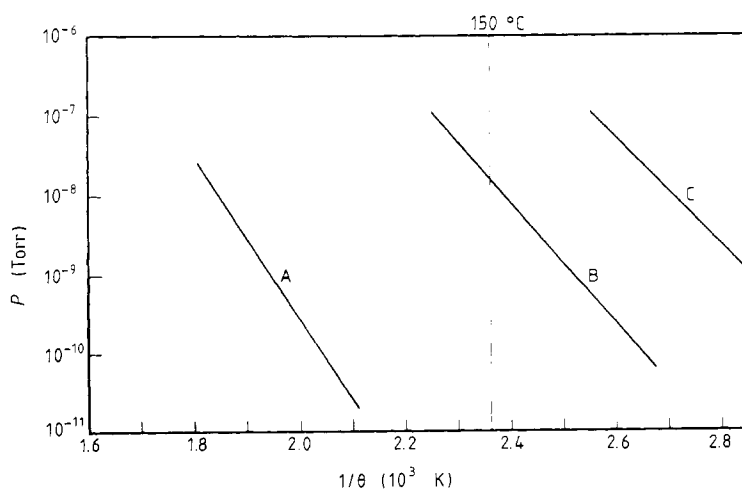


Figure 10. Equilibrium alkali vapour pressures over monoalkali antimonide layers: A. $P_{\text{Na}/\text{Na}_3\text{Sb}}$; B. $P_{\text{K}/\text{K}_3\text{Sb}}$; C. $P_{\text{Cs}/\text{Cs}_3\text{Sb}}$.

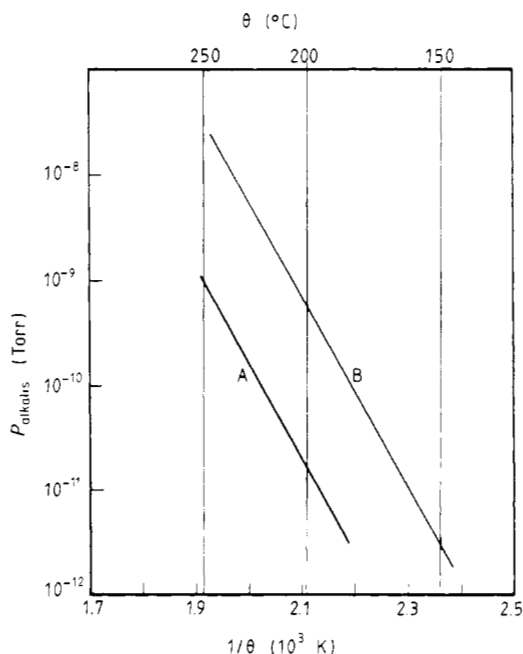


Figure 11. Equilibrium potassium and sodium vapour pressures over Na_2KSb : A. $P_{\text{Na Na}_2\text{KSb}}$; B. $P_{\text{K Na}_2\text{KSb}}$.

to be in the range 50 to 100 with regard to this equilibrium. This new result is important as will be outlined later on.

On the other hand, it is well known that the Na_2KSb compound deposited as a thin layer on a glass substrate becomes a very efficient photoemitter when it is covered with a monolayer of caesium (Sommer 1968, Dolizy *et al* 1982, Dolizy *et al* 1981) under UHV conditions. The caesium atoms deposited on the top of such a material are bound with an energy $\Phi = 35 \text{ kcal mol}^{-1}$. The corresponding value of P_{Cs} over Na_2KSb , Cs should be in the range of 10^{-17} Torr at 25°C . This result is also in very good agreement with the values published by Oliver (1971).

5. Applications to concrete situations

5.1. Growth of alkali antimonide compounds

The growth of an alkali antimonide compound generally takes place at high temperature inside a small glass envelope. First of all, the growth process temperature can be chosen within a range for which the growing material is not too much affected by the dissociation phenomena. Secondly, it is clear that the alkali vapour pressure has to be high enough to yield a saturated alkali compound. As an example, if the growth temperature of K_3Sb is chosen to be of the order of 150°C , then P_{K} has to be higher than 1.5×10^{-8} Torr to give a K_3Sb compound (see figure 10).

For a more complex material such as Na_2KSb , the ratio of vapour pressures $P_{\text{K}}/P_{\text{Na}}$ has to be as high as 50. At 200°C , the vapour/solid equilibrium is reached with $P_{\text{K}} \approx 5 \times 10^{-10}$ Torr and $P_{\text{Na}} \approx 1 \times 10^{-11}$ Torr.

5.2. Dissociation and related photoemissivity of alkali antimonide compounds under UHV

Assume that the alkali antimonide compounds are under an ultra-high vacuum (without any alkali pressure), the compound behaviour as a function of time at constant temperature can be derived from first-order reaction formula as long as the sample temperature is not too low compared with θ_m . Therefore, at 180 °C, Na₂KSb is rather stable whereas NaK₂Sb is much less so, as shown in figure 12. One characteristic of very high

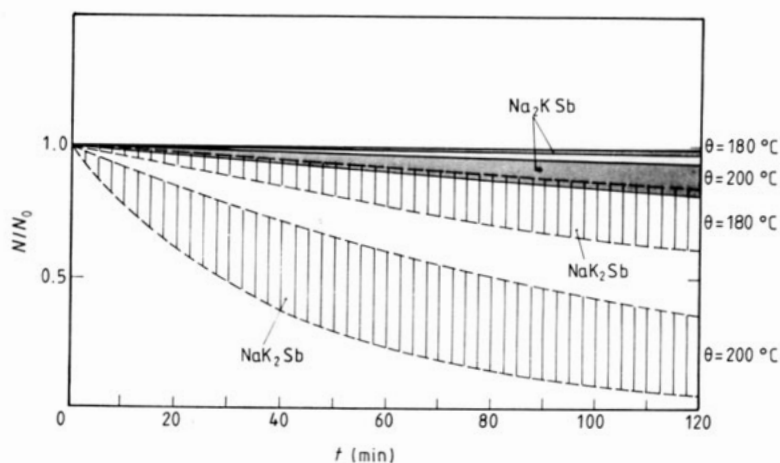


Figure 12. Variation of the number of moles of Na₂KSb and NaK₂Sb as a function of time.

importance about these materials is concerned with their photoemissivities (figure 13). At 200 °C, the Na₂KSb and NaK₂Sb compounds exhibit similar photoelectric quantum yields. Nevertheless, their composition behaviours plotted against time at 200 °C are quite different, Na₂KSb being rather stable whereas NaK₂Sb is not (figure 12). As a result, the photoemissivity stability of Na₂KSb is much better than that of NaK₂Sb, both taken at the same temperature. The ultimate upper-limit temperature for Na₂KSb use is therefore of the order of 200 °C.

Similar results can be obtained for other materials. For example, Cs₃Sb is a well known photoemitter (Sommer 1968) and the binding energy of caesium to antimony is rather low ($\Phi = 29.6 \text{ kcal mol}^{-1}$). As a result, even at room temperature, this material slowly dissociates in UHV.

5.3. Dissociation of Cs atoms deposited on the top of Na₂KSb

The photoemissivity of a pure and homogeneous Na₂KSb film can be considerably increased by applying a surface treatment in which caesium is evaporated onto the Na₂KSb film. At room temperature, the thermal stability of this photoemitter is very good as can also be predicted from the value Φ_{Cs} of the binding energy of caesium to the Na₂KSb material.

However, at higher temperature, the Cs atoms dissociate from the surface of the material. The use of such a complex material is therefore temperature limited. For temperatures higher than 100 °C, the surface composition becomes unstable and, conse-

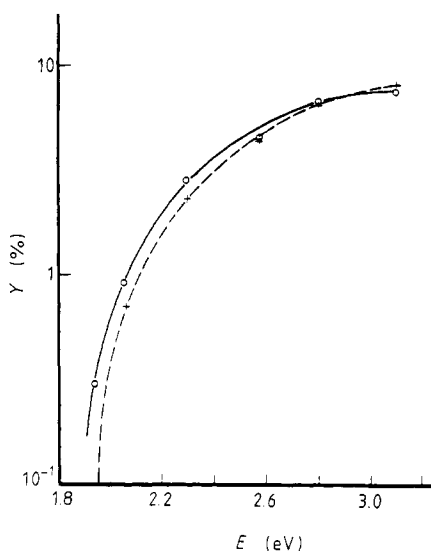


Figure 13. Photoelectric spectral response of Na_2KSb and NaK_2Sb layers in transmission mode (200 °C). Quantum yield, $Y(\%)$ (electron per incident photon) plotted against the energy of the incident radiation. Full curve, Na_2KSb (p type); broken curve, NaK_2Sb (n type).

quently, the photoemissivity is unstable as well. About 2% of one Cs monolayer disappear within one hour at 150 °C.

6. Conclusions

The optical measurements associated with AES analyses have been used for the determination of the apparent activation energies characterising the dissociation of the alkali antimonide compounds deposited on glass substrates under an ultra-high vacuum. The dissociation energies, Φ , of the alkali compounds as well as their equilibrium alkali partial vapour pressures have been determined.

The chemical and photoemissivity stabilities of these alkali compounds, with respect to temperature and time, have been considered. It is shown that the equilibrium partial vapour pressure ratio, $P_{\text{K}}/P_{\text{Na}}$, over Na_2KSb is in the range of 50 at 200 °C. The ultimate upper limit temperature for Na_2KSb used under UHV conditions is of the order of 200 °C. One monolayer of caesium deposited on the top of the Na_2KSb layer becomes unstable when the temperature reaches about 100 °C. At room temperature, the equilibrium partial pressure of caesium over Na_2KSb is about 2×10^{-17} Torr.

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