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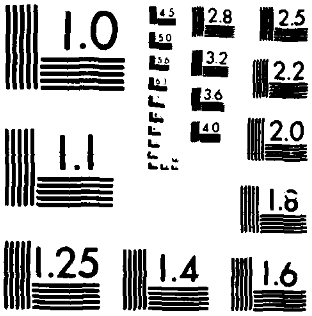
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ENTROPY-DRIVEN LOSS OF GAS-PHASE GROUP V SPECIES FROM GOLD/III-V COMPOUND SEMICONDUCTOR SYSTEMS

by

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ENTROPY DRIVEN LOSS OF GAS PHASE GROUP V SPECIES FROM GOLD/III-V COMPOUND SEMICONDUCTOR SYSTEMS

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ABSTRACT

Temperature-dependent chemical interactions between Au and nine III-V compound semiconductors (III=Al,Ga,In and V=P,As,Sb) have been calculated using bulk thermodynamic properties. Enthalpic considerations alone are insufficient to predict metal/compound semiconductor reactivities. The entropy of vaporization of the group V elements is shown to be an extremely important driving force for chemical reactions involving the III-V's, since it enables several endothermic reactions to occur spontaneously under certain temperature and pressure conditions. Plots of either Gibbs' Free Energies of reaction or equilibrium vapor pressure of the group V element versus temperature are used to predict critical reaction temperatures for each of the systems studied. These plots agree extremely well with previous experimental observations of thin film reactions of Au on GaAs.

I. INTRODUCTION

Chemical reactions that occur at the interface between a metal film and a compound semiconductor have been the subject of active academic and technical interest for many years. Brillson[1] has proposed that the relative chemical reactivity of the constituents at a metal/compound semiconductor interface controls the Schottky barrier height of the system. When reactions proceed, they consume a portion of the semiconductor material and may induce defects or even etch deep pits in the substrate.[2] Thus, it is extremely important to have a basic understanding of the chemistry of metal/semiconductor systems in order to be able to control the electronic properties and reliability of devices.

In the absence of sufficient information about reactivity in thin films and at interfaces, many investigators have used bulk thermodynamic properties of metals and semiconductors to model and predict thin film reactivities.[1,3,4] Deviations between calculations and observed behavior were often attributed to interfacial effects.[3,4] These investigators calculated enthalpies of reaction (ΔH_R) for various metal/semiconductor combinations to determine the feasibility of interaction. The true measure of reaction spontaneity, however, is the change in the Gibbs Free Energy of the system (ΔG_R), which takes into account the entropy change of the reaction (ΔS_R) of a system as well as ΔH_R.[5] Based on the assumption that metal/semiconductor reactions involve only solid phase products, the contribution of entropy was considered insignificant.[3] However, loss of gas phase species of the group V element from III-V compound semiconductors has been observed during reactions of thin metal films with substrates.[6] The formation of gas phase products requires the inclusion of the entropy change, which is positive and very large for a vaporization process, in reaction feasibility calculations.

The determination of ΔG_R as a function of temperature indicates the temperatures at which a reaction may occur spontaneously. However, thermodynamics cannot predict the rate at which it does take place; hence a reaction that is thermodynamically allowed may proceed at an immeasureably slow rate.[5] In this study, we have used bulk thermodynamic properties to predict, without considering surface, interface or mixing phenomena, conditions under which chemical reactions may occur between nine different III-V compound semiconductors and two metals, Au and the group III-Au intermetallic compound. Because systems with a positive entropy of reaction ($\Delta S_R > 0$) will eventually become thermodynamically spontaneous at high enough temperatures, the entropy of reaction is an important consideration, especially in systems that yield gas phase products. The purpose of this investigation was to ensure that the temperature dependence of the bulk chemistry of Au/III-V compound semiconductor systems is truly understood. The bulk thermodynamic calculations may be compared with experimental results for thin films on semiconductor substrates, thereby determining the relative importance of interfacial effects in metal/semiconductor reactions. Section II of this paper presents the theory and necessary thermodynamic data for the calculations, with results and discussion in sections III and IV, respectively.

II. CALCULATIONS AND THERMODYNAMIC DATA

When discussing relatively complex reactions involving many possible products, it is instructive to consider the phase rule derived by Gibbs in 1875:

$$f = c - p + 2, \qquad (1)$$

where c is the number of components, p is the number of phases and f is the number of degrees of freedom of the thermodynamic system under consideration.[7] In experiments where both the temperature and pressure are externally controlled, the number of degrees of freedom (f) is at least equal to two, giving

$$c >= p. \qquad (2)$$

This relation states that the number of phases present in a system may not exceed the number of components at equilibrium. For a system such as Au-III-V with three components, the maximum number of phases that may coexist is p=3. When a Au film is deposited onto a III-V substrate, the resulting system has a much larger amount of III-V than Au. If the reaction

$$Au + III\text{-}V \dashrightarrow Au\text{-}III + V \qquad (3)$$

(ie. the Au reacts with the III-V substrate to form the intermetallic compound Au-III and elemental V) is thermodynamically allowed, the system will not reach equilibrium until all the Au has been consumed. The three phases that comprise the system are then Au-III, V, and the unreacted III-V (the remaining substrate material). However, this implicitly assumes that the system is closed, ie. it is enclosed by some type of impermeable membrane, and that the external pressure chosen for the system is greater than the combined partial pressures of the products. In reality, such systems are almost always open, ie. they are in vacuum chambers or exposed to some ambient atmosphere during a heating cycle when the vapor pressure of the group V element becomes appreciable. When this is the case, one cannot control both the temperature and the pressure of the system independently; there are four phases present at equilibrium (III-V, Au-III, and both solid and gas phase element V), and fixing the temperature determines the partial pressure of V. If the gaseous species can expand into an infinitely large volume or is continuously pumped out of an enclosed vessel, the vaporization process will continue until all the solid elemental group V has escaped into the gas phase.

To determine the temperature at which a reaction is thermodynamically feasible, the ΔG_R of the system must be calculated:[5]

$$\Delta G_R = \Delta H_R - T\Delta S_R. \qquad (4)$$

A reaction will not occur spontaneously unless $\Delta G_R < 0$. It can be seen from Eq. 4 that if both ΔH_R and ΔS_R are positive, ΔG_R will be positive at low temperatures, but will decrease with increasing temperature until $\Delta G_R = 0$ at

$$T = \Delta H_R/\Delta S_R, \qquad (5)$$

when the reaction will first become thermodynamically feasible. For reactions in which a gas phase species is evolved as a product at a partial pressure other than one atmosphere,

$$\Delta G_R = \Delta G_R^o + nRT\ln(P), \qquad (6)$$

where ΔG_R^o is the Free Energy change of the reaction at one atmosphere, P is the partial pressure of the gaseous product in atmospheres (we will assume that the pressure is always low enough that the fugacity of the gas phase species is equal to the partial pressure), R is the gas constant, n is the number of moles of the product, and T is the temperature in Kelvins (K).[7] Substituting Eq. 4 at one atmosphere into Eq. 6,

$$\Delta G_R = \Delta H_R^o - T(\Delta S_R^o - nR\ln(P)). \qquad (7)$$

The temperature at which the reaction first becomes feasible ($\Delta G_R=0$) is

$$T = \Delta H_R^o/(\Delta S_R^o - nR\ln(P)). \qquad (8)$$

We thus see that this critical temperature is a function of the partial pressure of the gas phase product. Conversely, one may solve Eq. 7 for P to obtain

$$P = \exp(\Delta S_R^o/nR - \Delta H_R^o/nRT), \qquad (9)$$

which is the equilibrium vapor pressure of the reaction product as a function of the temperature of the system.

Values for the standard (1 atm.) enthalpy and entropy of reaction in the literature are usually given at 298K. At temperatures other than 298K, the enthalpy and entropy contents of the reactants and products must be considered.[7] One of the reactions of interest in this study is the arsenic loss from gallium arsenide:

$$GaAs(s) \dashrightarrow Ga(l) + (1/4)As_4(g). \qquad (10)$$

For this simple decomposition reaction,

$$\Delta H_R^o(T) = \Delta H_R^o(298) - (H_T - H_{298})_{GaAs} + (H_T - H_{298})_{Ga} + (1/4)(H_T - H_{298})_{As_4} \qquad (11)$$

and

$$\Delta S_R^o(T) = \Delta S_R^o(298) - (S_T - S_{298})_{GaAs} + (S_T - S_{298})_{Ga} + (1/4)(S_T - S_{298})_{As_4}, \quad (12)$$

where H_T and S_T are the standard enthalpy and entropy contents of the specified material at temperature T. Equations 11 and 12 are a result of ΔH_R and ΔS_R being state functions and independent of reaction path.

When no phase transitions occur between 298K and T, the quantities $(H_T - H_{298})$ and $(S_T - S_{298})$ are easily evaluated from the heat capacities of each of the materials. However, enthalpies and entropies of fusion must be considered when the melting point of one or more of the reactants or products occurs in this temperature range. For the GaAs reaction (Eq. 10), Ga melts at T_m=302K with an enthalpy of fusion $(\Delta H_f)^8$ of 1.336 kcal mole^{-1} and an entropy of fusion (ΔS_f) of 4.42 cal mole^{-1} K^{-1} calculated from

$$\Delta S_f = \Delta H_f/T_m. \quad (13)$$

When calculating the enthalpy and entropy for the reaction (Eq. 10), ΔH_f and ΔS_f are added to Eq. 11 and Eq. 12, respectively, at temperatures above 302K.

If the assumption is made that the heat capacity of each substance is independent of temperature, the difference between the enthalpy and entropy content at 298K and temperature T of a particular phase can be approximated by

$$(H_T - H_{298}) = Cp_{298}(T-298) \text{ and} \quad (14)$$

$$(S_T - S_{298}) = Cp_{298}\ln(T/298), \quad (15)$$

where Cp_{298} is the heat capacity at constant pressure and 298K.[7] The heat capacity change for a reaction (ΔCp_R) is usually very small (less than +/-2 cal K^{-1}), so any error in this approximation has a minimal effect on the calculation of ΔH_R or ΔS_R.

The data used for the present calculations were taken from various sources (see Table I). Not all of the thermodynamic data necessary for the calculations was available, requiring the estimation of certain values. The heat capacities (Cp) of solid substances for which there are no published values were assigned to be 3NR, where N in this case is the number of atoms in the molecular formula of a particular solid (e.g. N=2 for GaAs).[9] Values for the entropy of formation (ΔS^o_{298}) for various compounds were estimated, when not found in the literature, using standard entropies (S^o_{298}) in conjunction with third law principles,[5,10] which determine that the entropy of formation of a compound is equal to the standard entropy (S^o_{298}) of the compound minus the standard entropies of the elements from which it is formed.[11] For $AuIn_2$,

$$\Delta S^o_{298} = S^o_{298}(AuIn_2) - S^o_{298}(Au) - 2S^o_{298}(In). \qquad (16)$$

Standard entropies of the solid compounds were estimated from Debye theory[5,10] when Debye Temperatures were known, or were estimated using known values of similar compounds. It must be noted that there is some experimental uncertainty in all the bulk thermodynamic properties tabulated here, and some ambiguity as well since some authors failed to define the reference states for the compounds for which they reported thermodynamic properties. This is important, since some compounds are formed from elements that have more than one stable state (e.g. $P_{red}, P_{white}, P_{black}$), making comparison of data from among different sources less reliable. In spite of these limitations, the significant trends observed in the calculations are valid in the context of each compound semiconductor, but there may be a considerable error in any of the numbers calculated.

It is interesting to note some of the patterns and peculiarities in Table I. The heat capacities (Cp) of the solid phase compounds are all roughly 3NR (R=1.987 cal mole^{-1} K^{-1}). The enthalpies of formation of the Ga-V and In-V (V=P,As,Sb) compound semiconductors differ among themselves by approximately 7 kcal mole^{-1}, e.g. $\Delta H(GaP)$ = -24 kcal mole^{-1}, $\Delta H(GaAs)$ = -17 kcal mole^{-1}, and $\Delta H(GaSb)$ = -10 kcal mole^{-1}, while the Al-V compound semiconductors have vastly different enthalpies of formation. The entropies of formation of the III-P compound semiconductors have values more negative than the III-As and III-Sb compound semiconductors, which have roughly equal values. Although the enthalpies of formation and heat capacities of $AuGa_2$ and $AuIn_2$ are very similar, their entropies of formation are very different. The S^o_{298} values for $AuGa_2$ and $AuIn_2$ were estimated from Debye Temperatures[26] to be 31.9 and 32.4 cal mole^{-1} K^{-1}, respectively. These values agree very well with the value tabulated for $AuSn_2$, 32.4 cal mole^{-1} K^{-1}.[12] The large difference in the values for the entropies of formation is a result of the different values for the standard entropy of elemental Ga and In, 9.8 and 13.8 cal mole^{-1} K^{-1}, respectively (see Eq. 16). In some cases, when more than one value existed for a particular property, they differed from one another substantially (see the ΔH_f values for InP). However, in general the experimentally determined values for ΔH_f agreed well with each other, but they often differed greatly from theoretically calculated enthalpies of formation.[27]

III. RESULTS

Nine III-V compound semiconductors were considered, and values of $\Delta G_R(T)$ were calculated in a temperature range of 300-1000K. For each semiconductor, three types of reactions were considered:

a) III-V --> III + V

b) Au + III-V --> Au-III + V or Au-V

c) Au-III + III-V --> Au-$(III)_2$ + V or Au-V.

The form of the group V product could be the elemental solid, an intermetallic compound with gold, or a gas phase species (V_2 or V_4). The ΔG_R's for reactions a, b and c are plotted in Figs. 1 and 2 for the Au-AlSb and Au-GaAs systems to illustrate the various types of behavior that may be observed. In Fig. 3, the equilibrium vapor pressure of As_2 or As_4 as a function of temperature (Eq. 9) are plotted for the same reactions as shown in Fig. 2. Reaction (a) is the decomposition of the compound semiconductor into its elemental components. The vaporization of the group III element is not considered since the group V elements are much more volatile. The equilibrium vapor pressures over seven of the nine compound semiconductors are plotted as a function of temperature in Fig. 4. Reaction (b) is the reaction of Au with the compound semiconductor to give the intermetallic compound with a 1:1 atomic composition of Au and the group III element, as well as releasing the group V element or forming a compound of Au with Sb or P (As forms no intermetallic compounds with Au). Equilibrium P versus T curves of the six compound semiconductors that yield gas phase species as the most stable products are plotted in Fig. 5. Reaction (c) is the reaction of the Au-III intermetallic compound with the compound semiconductor (see Fig. 6). This reaction is of interest since the critical temperature of reaction for each semiconductor at any particular partial pressure of the group V element is much higher than the reaction temperature of (b).

Chemical reactions may proceed spontaneously when ΔG_R is less than zero. For each compound semiconductor, reactions that consume the semiconductor at the lowest temperatures are considered. Figure 1 shows a variety of antimony products for reactions of aluminum antimonide. The decomposition of AlSb occurs at a temperature greater than 850K if the Sb_2 partial pressure is held at 10^{-8}torr. The products of the decomposition are solid Al and gaseous Sb_2. When Au is deposited on AlSb, a solid phase reaction may occur spontaneously at room temperature yielding the intermetallic compounds $AuSb_2$ and AuAl as products. This reaction can proceed until one of the reactants has been completely consumed. However, if there is an excess of AlSb in the reaction mixture, both AuAl and $AuSb_2$ can react with the semiconductor to yield $AuAl_2$ and Sb(s) as products. All other compound semiconductor reactions with the appropriate Au-group III compound occur at temperatures greater than 500K, with some occurring as high as 1000K (AuAl and AlP, for instance). Figure 2 is a plot of the most frequently studied compound, GaAs, at 10^{-8}torr background As_2 or As_4. All three reactions (a,b,c) produce gas phase products; the thermal decomposition reaction yields As_2 while the reactions with Au and AuGa yield As_4. When Au is deposited on GaAs, a reaction can occur at a temperature as low as 520K, which is 350K less than the normal decomposition temperature. When AuGa is in contact with GaAs, however, the reaction temperature is 800K. It should be noted that the ΔG_R plots for the thermal decomposition and the reaction of GaAs with Au have roughly the same slopes, but the exothermic formation of AuGa in the latter causes the ΔG_R to be shifted toward more negative values with respect to the GaAs decomposition. Figure 3 contains the same reactions as Fig. 2, but the equilibrium vapor pressure of the appropriate As species is plotted as a function of temperature (Ellingham diagram).

Figure 4 shows the equilibrium vapor pressures of the appropriate group V species as a function of temperature for seven compound semiconductors. The other two semiconductors studied (AlP and AlAs) decompose at temperatures greater than 1000K for the pressure range given (10^{-5} to 10^{-10}torr). The logarithm of the pressure was plotted as a function of the temperature instead of the usual inverse of temperature (which gives a nearly straight line) as a convenience for quick reference with respect to laboratory experience. Six of the seven compound semiconductors yield diatomic group V molecules as the dominant gas phase products; however, at the temperatures plotted Sb_4 is present at a slightly higher vapor pressure than Sb_2 over InSb. Figure 5 shows reactions of Au with compound semiconductors that do not proceed unless a gas phase species is evolved. All systems studied involving antimony react to form solid phase products when combined with Au. It is interesting to note that the thermal decomposition reactions for the clean compound semiconductors (GaP,GaAs,InP,InAs) occur in a narrow temperature range compared to the chemical reactions with Au, which occur over a broad temperature range. A common feature of both figures is that AlP and AlAs require higher temperatures than GaP and GaAs to form gas phase products, which in turn, require higher temperatures than InP and InAs. In Fig. 5, the arsenide always reacts before the phosphide, in Fig. 4 the phosphide reacts before the arsenide. In Fig. 4, the antimonide always reacts before either the arsenide or the phosphide. In Fig. 5, only reactions of Au with AlP and GaP produce a diatomic gas; the other four reactions give a tetraatomic product.

Figure 6 shows reaction of the Au-III intermetallic compounds with compound semiconductors that yield gas phase products. These reactions all proceed in a temperature range higher than the reactions of Au with the corresponding compound semiconductor, yet lower than the decomposition reactions. Thus, the Au-III compounds are all more thermodynamically stable with respect to the compound semiconductor than is Au. Only the reaction of AuAl and AlSb yields no gaseous product, while the other eight Au-III reactions yield V_2 or V_4. The presence of discontinuities in the curves in Fig. 6 are the result of melting of the Au-III and Au-$(III)_2$ intermetallic compounds. AuGa, $AuGa_2$, AuIn and $AuIn_2$ melt in the temperature range of 700-800K,[13] while AuAl and $AuAl_2$ have very high melting points[14] and, as a result, do not display fusion effects in the AlAs and AlP vapor pressure curves.

IV. DISCUSSION

Though many authors have discussed the interface reactivity of metal/compound semiconductor contacts, entropic effects have not been explicitly considered. Our work shows that the entropy of formation of gas phase group V elements is a major driving force in the metal/semiconductor reactions. In an open system, the metal/semiconductor interface becomes unstable at temperatures high enough to cause the entropy of vaporization to dominate the enthalpy change of a reaction. Increasing the ambient group V pressure in the preparation chamber during thermal processing has been studied in an effort to minimize this effect.[15] Other methods include forming films by codeposition of the group III element with Au,[16] which may react to form an intermetallic compound that is more stable than elemental Au with respect to the compound semiconductor.

Ellingham diagrams (Figs. 3-6) have a special significance in this work; they reveal the temperature at which the semiconductor will decompose given a particular vapor pressure of the gas phase species. These figures do not reveal kinetic or quantitative vapor loss considerations that other investigators have studied.[6,15-17] We do not know how fast the reactions respond to changes in temperature or vacuum pressure. If the reactions respond slower than the vacuum pumping speed, a vacuum chamber may be maintained at a pressure less than the equilibrium vapor pressure of the group V species over the compound semiconductor. However, as a rough approximation, it may be assumed that the vacuum pressure (P_{vac}) is equal to the partial pressure of the group V element ($P_{vac}=P_V$). At pressures greater than the vapor pressure of V over III-V, it is assumed that an over pressure of V is present in the vacuum chamber, and the compound semiconductor is stable with respect to group V sublimation.

Various authors have observed the arsenic loss from GaAs with and without the presence of gold thin films. Sebestyen, et al., observed arsenic losses from GaAs at 890K with a total chamber pressure of 10^{-8}torr.[18] Our calculations indicate that GaAs should decompose at 870K at this pressure (see Figs. 2 and 3). Kinsbron, et al., found that for pressures less than 10^{-8}torr, GaAs in contact with Au starts to decompose at a temperature as low as 520K,[19] which is within 5K of the temperature calculated by us (see Figs. 2 and 3). Leung, et al., discovered arsenic losses under an ambient pressure of $5*10^{-6}$torr at 580K,[20] which also agrees with our calculations (note that a higher temperature is required to drive the reaction when the background pressure is higher). For the decomposition of InP, Gallagher and Chu[29] detected phosphorus losses (under a vacuum pressure of $5*10^{-8}$torr) at roughly 780-790K. Figure 4 yields a temperature of 780K for InP decomposition at this pressure ($\log(P) = -7.3$).

This excellent agreement between bulk thermodynamic calculations and experimental observations for reactions involving GaAs is contrary to the conclusions of Petro, et al.,[30] and indicates that interfacial thermodynamic effects are not required to explain the observed reactivity of Au on GaAs at temperatures as low as 500K. In fact, if discrepancies are found between predictions made by using the thermodynamic data in Table I and experimental measurements on any thin film systems, it would probably be necessary to remeasure the bulk thermodynamic data before concluding that surface ~~of~~ or interface effects are important, since the data in Table I may contain some significant errors.

V. CONCLUSIONS

We have calculated temperatures at which group V gaseous species evolve from III-V compound semiconductors with and without Au films using bulk thermodynamic considerations, and have observed that they agree closely with experimentally determined values. We have shown that under open-system conditions, entropy is a strong driving force in reactions between the III-V compound semiconductors and Au. The temperature at which gas phase species will be lost from the metal/compound semiconductor interface can be raised if the metal used increases ΔH_R in forming products with the semiconductor, ie. makes the reaction more endothermic. The effect of entropy in open systems invalidates the conclusion of McGilp[3] that the solid-state reaction equilibrium is temperature invariant. Bulk thermodynamics can be used to predict a great deal of the observed reactivity of thin metal films with compound semiconductors.

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Table I: Thermodynamic Properties at 298K and 1atm.[a]

Compound	$\widetilde{\Delta H}_f$ (kcal/mole)	$\widetilde{\Delta S}_f$ (cal/mole-K)	$\widetilde{Cp}$ (cal/mole-K)
Al(s)	0.0	0.00	5.8
Ga(s)	0.0	0.00	6.2
In(s)	0.0	0.00	6.4
Au(s)	0.0	0.00	6.1
P_{white}(s)	0.0	0.00	5.7
P_{red}(s)	-4.2	-4.36	5.1
P_2(g)	34.5	32.55	7.7
P_4(g)	14.1	27.62	16.0
As(s)	0.0	0.00	5.9
As_2(g)	53.1	40.27	8.4
As_4(g)	34.4	41.28	18.5[b]
Sb(s)	0.0	0.00	6.0
Sb_2(g)	56.3	38.93	8.7
Sb_4(g)	49.0	40.27	19.4[b]
AlP(s)	-39.8,-34.8[c]	-5.29[f]	10.0[c]
AlAs(s)	-27.8,-28.9[c]	-3.23[f]	10.3[c]
AlSb(s)	-11.9[c]	-2.16[f]	11.1[c]
GaP(s)	-24.8[d],-25.0[c]	-5.37[d]	10.4[e]
GaAs(s)	-17,-19.5[c]	-2.68	11.0
GaSb(s)	-10.0,-9.9[c]	-2.35	11.6
InP(s)	-21.2,-13.5[c]	-9.40	10.9
InAs(s)	-14.0,-14.8[c]	-4.03	11.4
InSb(s)	-7.3,-6.9[c]	-4.03	11.8

AuAl(s)	-15.6[g]	0.08[g]	12[h]
$AuAl_2$(s)	-28.1[g]	-0.87[g]	18[h]
AuGa(s)	-11.5[i]	1.9[j]	12.1[k]
$AuGa_2$(s)	-17.8[i]	1.0[l]	18.1[k]
AuIn(s)	-10.8	-1.9[j]	12.3[k]
$AuIn_2$(s)	-18.0	-6.6[l]	18.3[k]
Au_2P_3(s)	-23.3[m]	-16.1[n]	28.6[o]
$AuSb_2$(s)	-4.6[m]	-4.67[n]	18.5[o]

a. Unless otherwise noted, the values in this table were taken from Wagman, et al. (Ref.12).

b. Ref. 21

c. Ref. 22

d. Ref. 23

e. Ref. 24

f. Estimated from S^o_{298} values in Landolt-Bornstein (Ref.22 and text).

g. Ref. 14

h. Estimated by 3NR (Ref. 9 and text).

i. Ref. 25

j. Estimated from the S^o_{298} value of AuSn: based on the observation that the S^o_{298} value of $AuSn_2$ (Ref. 12) is nearly equal to S^o_{298} values of $AuGa_2$ and $AuIn_2$, which were estimated from Debye Temperatures (Ref. 26).

k. Ref. 13

l. Estimated from Debye Temperatures (Ref. 26 and text).

m. Ref. 9

n. Estimated from S^o_{298} values in Kubaschewski and Evans (Ref. 9).

o. Ref. 28

Figure Captions

Figure 1: ΔG_R as a function of temperature for reactions involving AlSb with a background pressure of Sb_2 of 10^{-8}torr. The reactions with Au and AuAl form solid state products even at room temperature.

Figure 2: ΔG_R as a function of temperature for reactions involving GaAs with a background pressure of 10^{-8}torr of As_2 or As_4. In each case, the gas phase product that yields the lower ΔG_R is shown.

Figure 3: The equilibrium vapor pressure in the range 10^{-5} to 10^{-10}torr for the same reactions shown in Fig. 2 as a function of temperature. The states at 10^{-8}torr are the same as those for $\Delta G_R=0$ in Fig. 2.

Figure 4: Equilibrium vapor pressures of the lowest Gibbs' Free Energy group V species over III-V compound semiconductors. AlP and AlAs decompose at temperatures greater than 1000K in the pressure range shown. Eight of the nine III-V compound semiconductors yield diatomic group V molecules as the dominant gas phase products; only for InSb does the tetraatomic group V species (Sb_4) have a slightly higher vapor pressure than Sb_2 in this pressure range.

Figure 5: Reactions of six compound semiconductors with gold that do not occur unless gas-phase group V products are evolved. The equilibrium vapor pressure of the gas phase species is shown as a

function of temperature. If the actual partial pressure is maintained below that indicated, the reaction

$$Au + III\text{-}V \longrightarrow Au\text{-}III + (1/n)V_n$$

may proceed spontaneously. The group V product released is given in parenthesis for each vapor pressure curve.

Figure 6: Reactions of eight III-V compound semiconductors with Au-III that yield gas phase group V products (AuAl reacts with AlSb to form solid-phase products as shown in Fig. 1). The reactions

$$Au\text{-}III + III\text{-}V \longrightarrow Au\text{-}(III)_2 + (1/n)V_n$$

may proceed spontaneously for vapor pressures of V_n lower than the equilibrium vapor pressure. The group V product released is given in parenthesis.

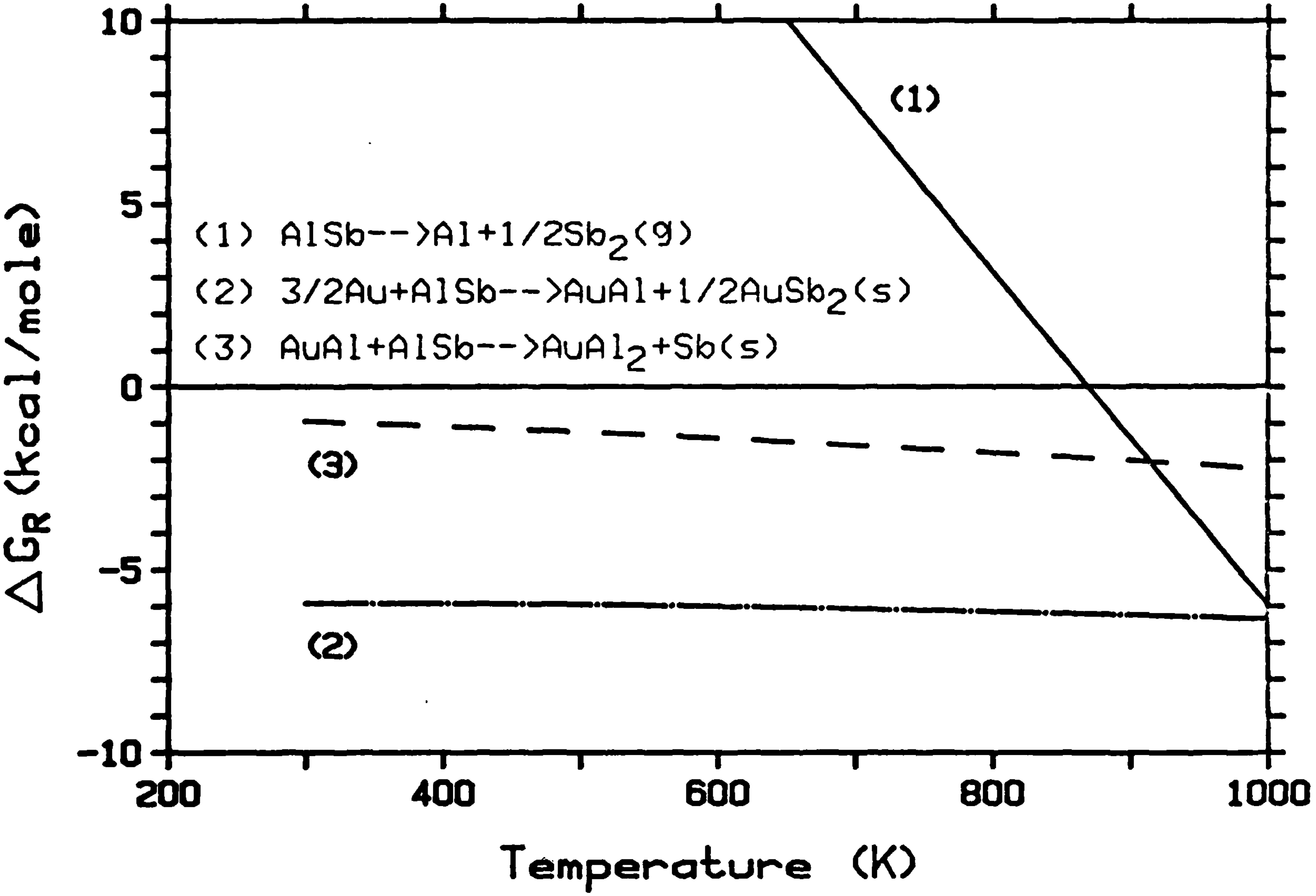
10
5
0
-5
-10
200
400
600
800
1000
ΔG_R (kcal/mole)
Temperature (K)
(1) AlSb-->Al+1/2Sb2(g)
(2) 3/2Au+AlSb-->AuAl+1/2AuSb2(s)
(3) AuAl+AlSb-->AuAl2+Sb(s)
(1)
(2)
(3)

Fig. 1

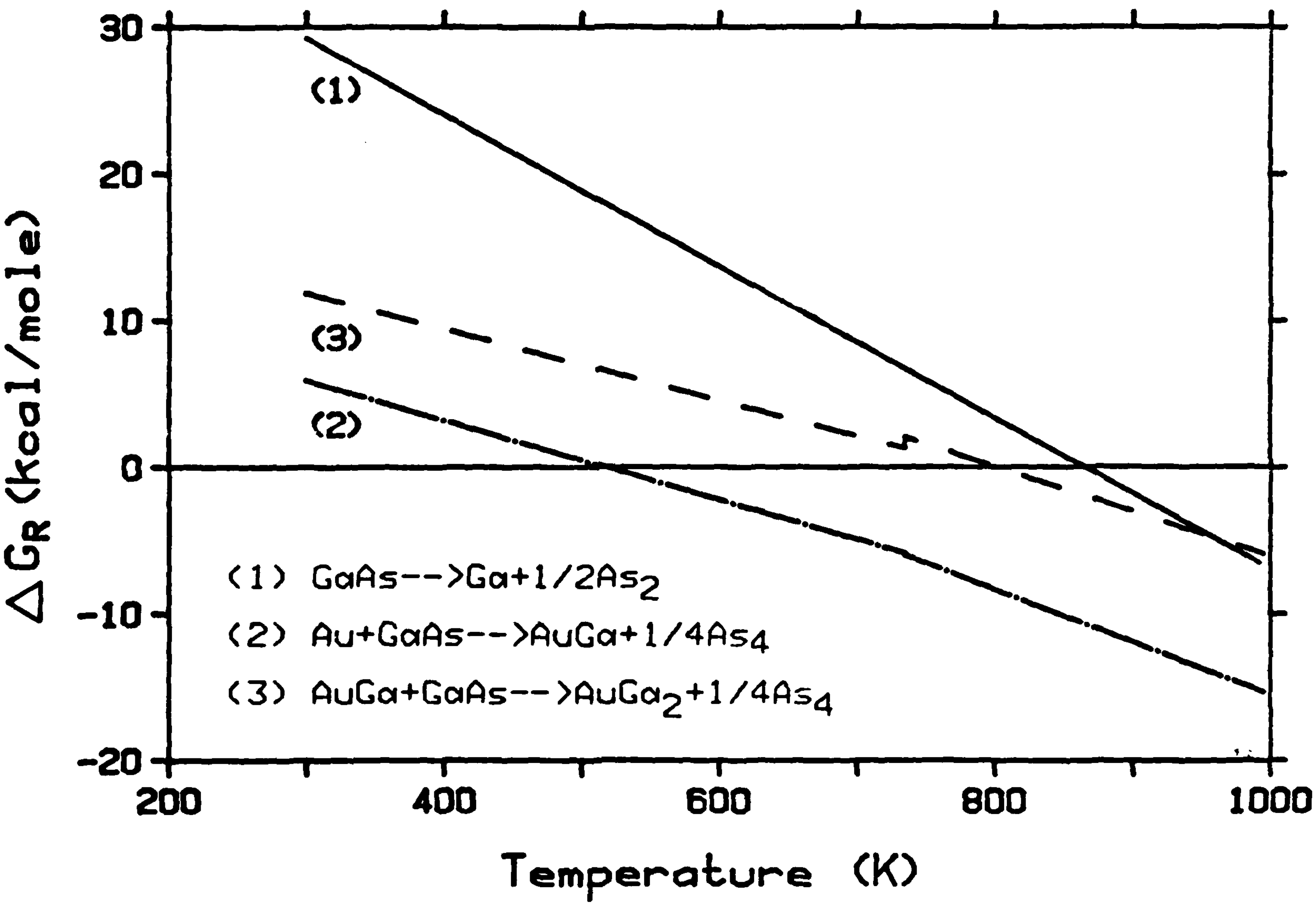
30
20
10
0
-10
-20
200
400
600
800
1000
(1)
(3)
(2)
(1) GaAs-->Ga+1/2As$_2$
(2) Au+GaAs-->AuGa+1/4As$_4$
(3) AuGa+GaAs-->AuGa$_2$+1/4As$_4$
ΔG_R (kcal/mole)
Temperature (K)

Fig. 2

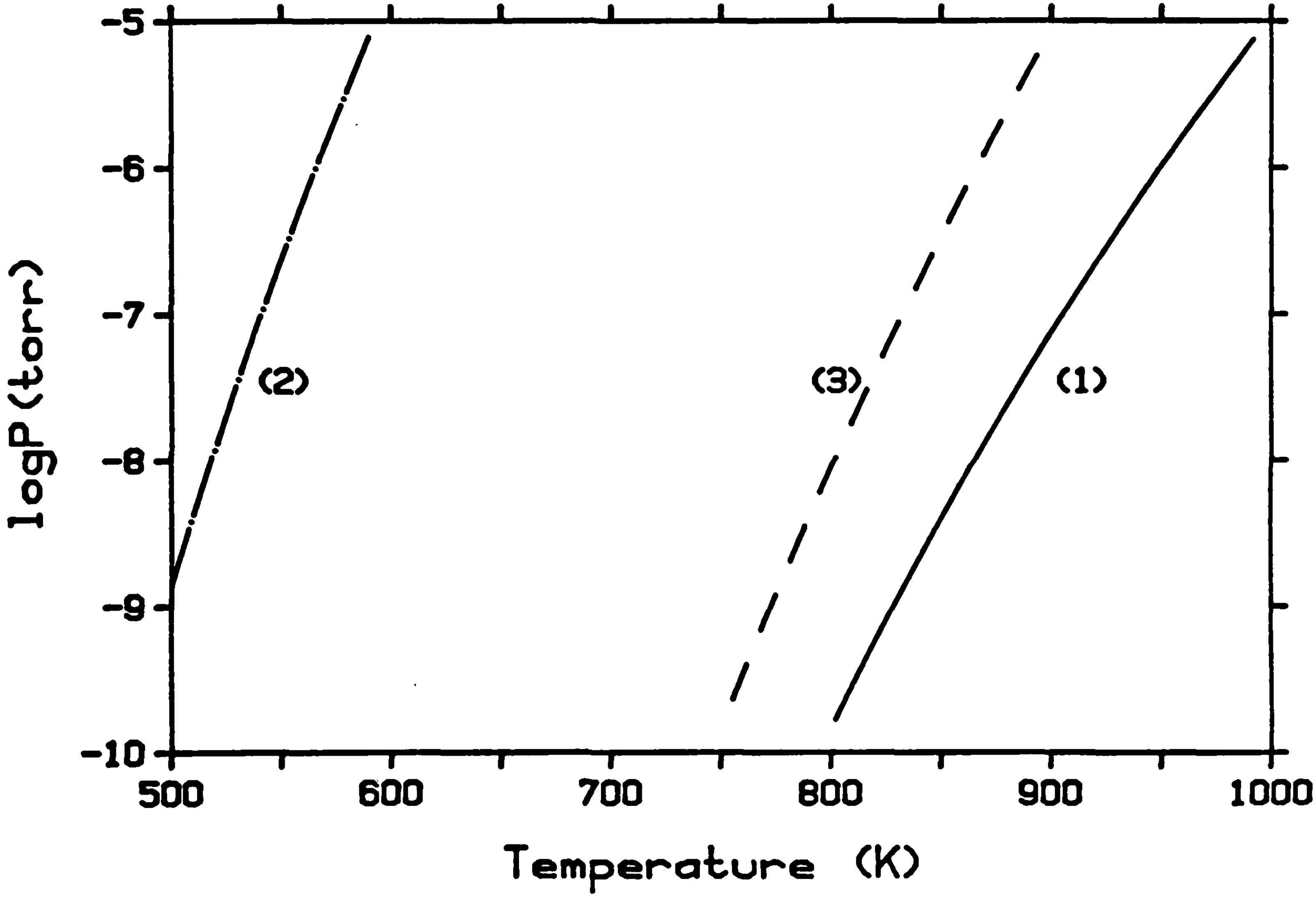

Fig. 3

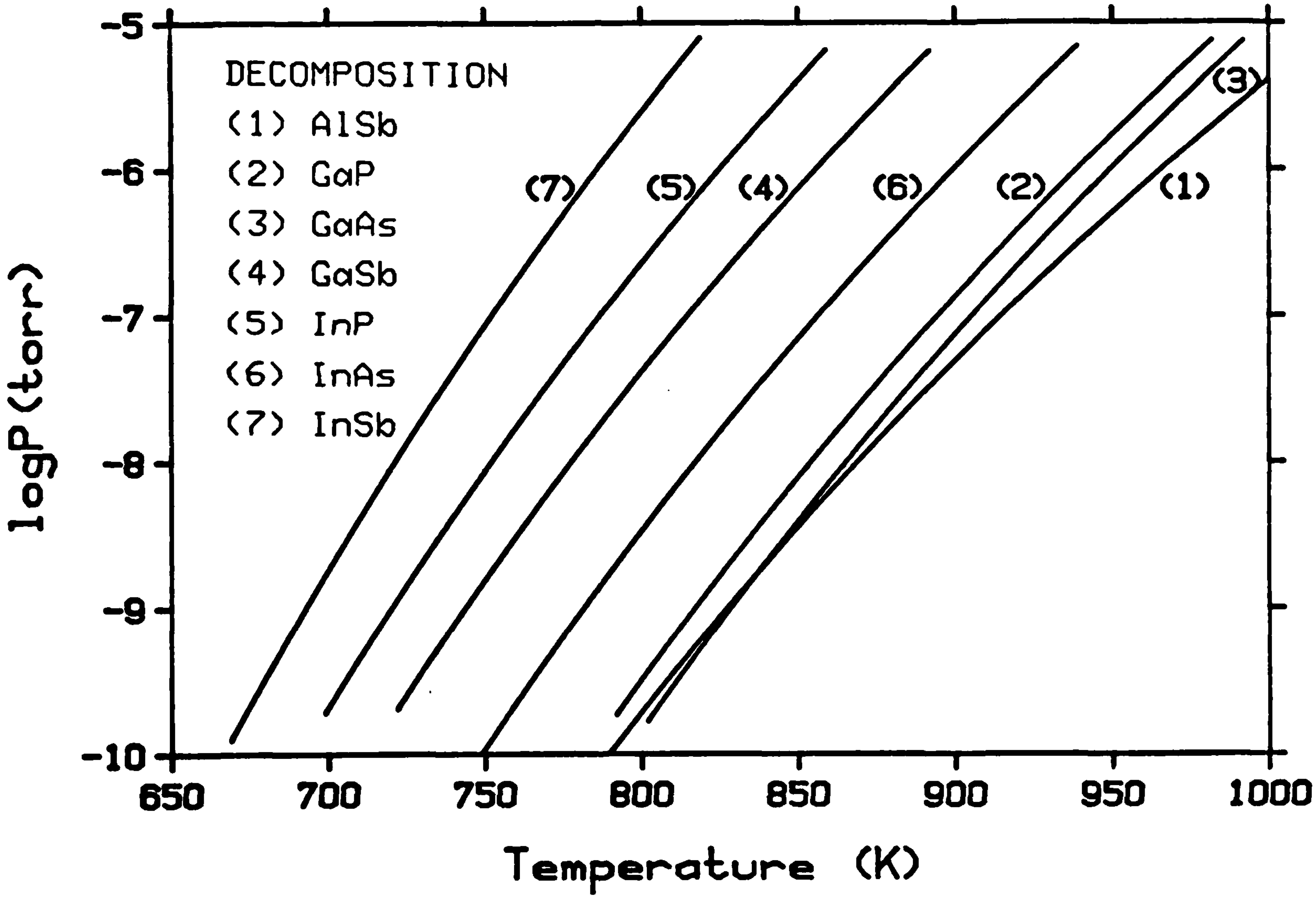
DECOMPOSITION
(1) AlSb
(2) GaP
(3) GaAs
(4) GaSb
(5) InP
(6) InAs
(7) InSb
(7)
(5)
(4)
(6)
(2)
(1)
(3)
-5
-6
-7
-8
-9
-10
650
700
750
800
850
900
950
1000
logP (torr)
Temperature (K)

Fig. 4

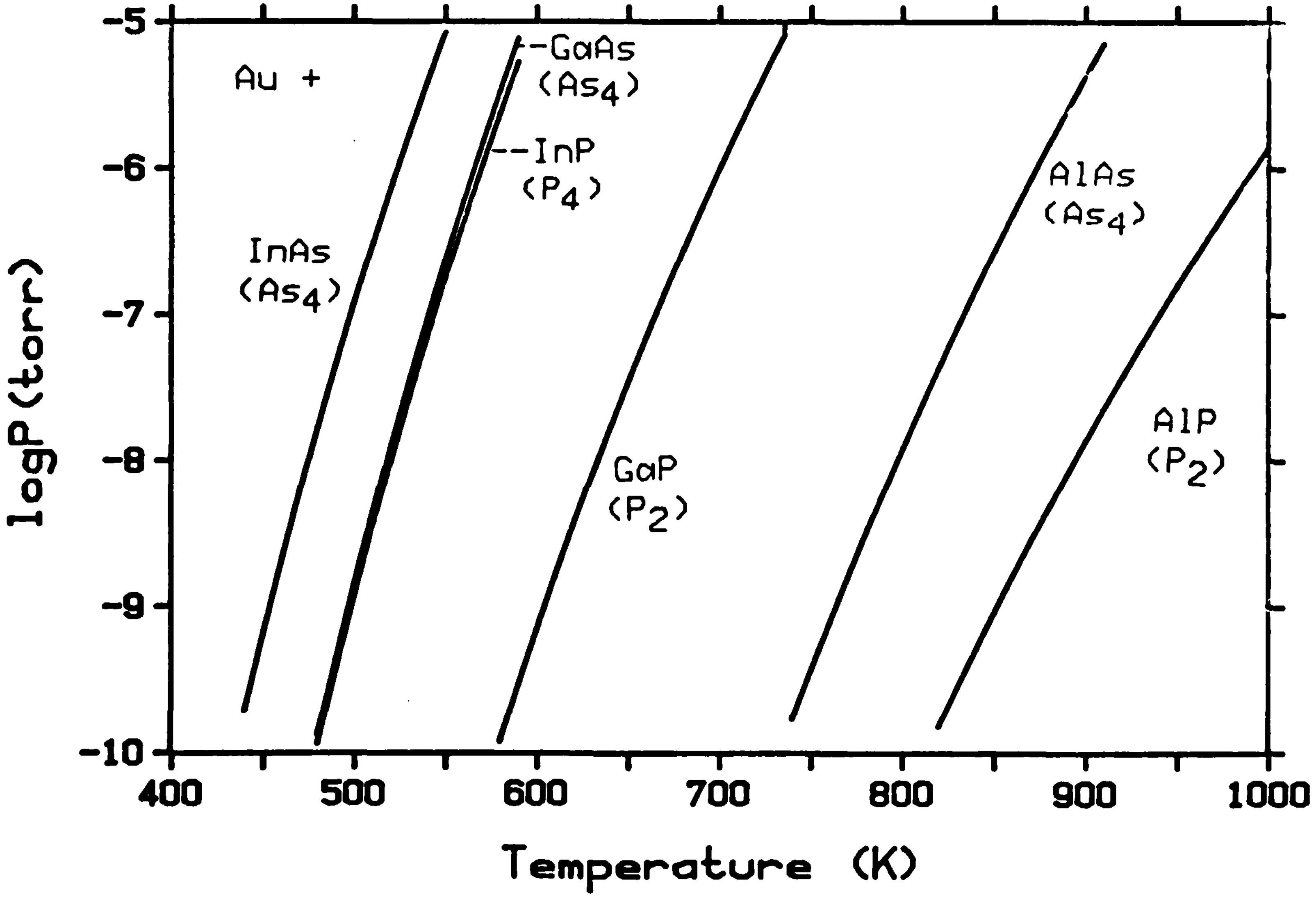
Au +
InAs
(As$_4$)
-GaAs
(As$_4$)
--InP
(P$_4$)
GaP
(P$_2$)
AlAs
(As$_4$)
AlP
(P$_2$)
-5
-6
-7
-8
-9
-10
logP (torr)
400
500
600
700
800
900
1000
Temperature (K)

Fig. 5

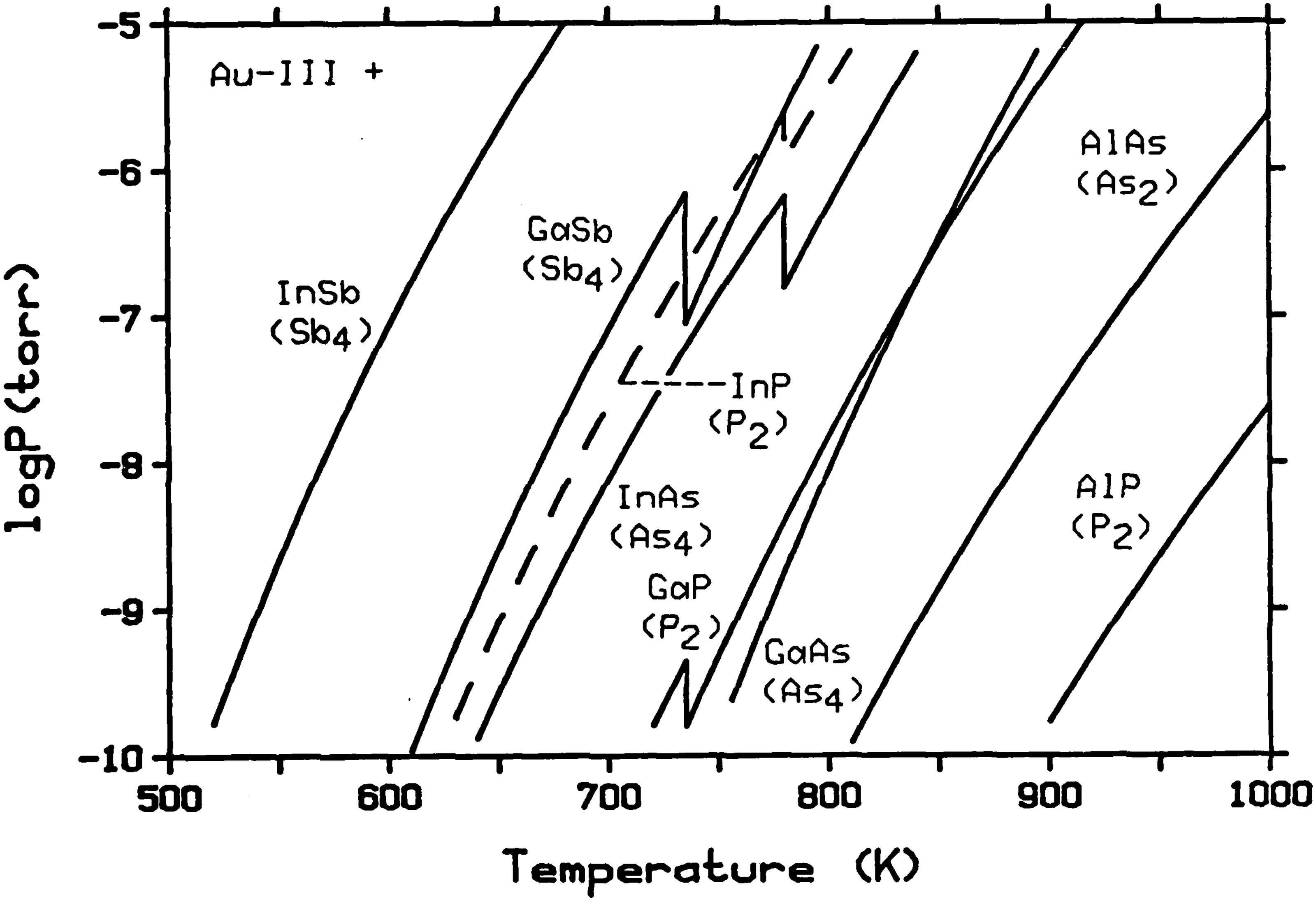
Au-III +
InSb
(Sb$_4$)
GaSb
(Sb$_4$)
InP
(P$_2$)
InAs
(As$_4$)
GaP
(P$_2$)
GaAs
(As$_4$)
AlAs
(As$_2$)
AlP
(P$_2$)
-5
-6
-7
-8
-9
-10
500
600
700
800
900
1000
logP (torr)
Temperature (K)

Fig. 6