

AD-A192 141

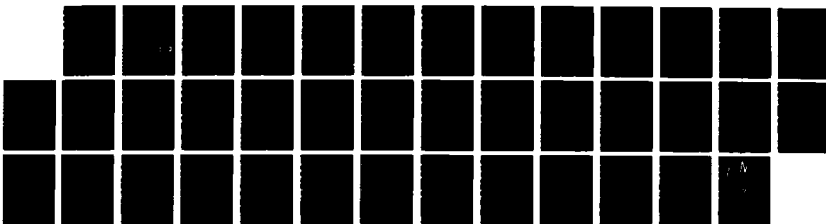
CALCULATIONS OF THE GASEOUS SPECIES IN HALIDE ACTIVATED
CEMENTATION PACKS(U) OHIO STATE UNIV RESEARCH
FOUNDATION COLUMBUS S C KUNG ET AL FEB 88

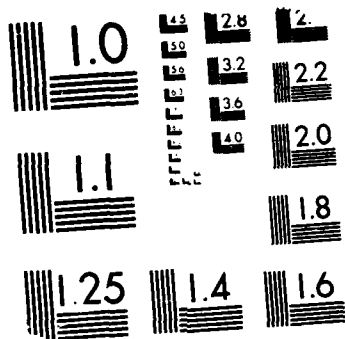
1/1

UNCLASSIFIED

N00014-87-K-0030

F/G 11/6 1 ML





MICROCOPY RESOLUTION TEST CHART
SERIAL ... STANDARDS 1963 A

4

DTIC FILE COPY

AD-A192 141

RF Project 765839/719131
Technical Report (Reprint)

CALCULATIONS OF THE GASEOUS SPECIES IN HALIDE
ACTIVATED CEMENTATION PACKS

S. C. Kung and Robert A. Rapp
Department of Metallurgical Engineering

DEPARTMENT OF THE NAVY
Office of Naval Research
Arlington, Virginia 22217

Contract No. N00014-87-K-0030

DTIC
ELECTE
MAR 23 1988
S H D

February 1988



The Ohio State University
Research Foundation

1314 Kinnear Road
Columbus, Ohio 43212

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

88 2 29 087

CALCULATIONS OF THE GASEOUS SPECIES IN HALIDE
ACTIVATED CEMENTATION PACKS

S. C. Kung and Robert A. Rapp
Department of Metallurgical Engineering

DEPARTMENT OF THE NAVY
Office of Naval Research
Arlington, Virginia 22217

Contract No. N00014-87-K-0030

February 1988



The Ohio State University

Department of
Metallurgical Engineering
141A Fontana Laboratories
116 West 19th Avenue
Columbus, Ohio 43210
Phone 614 422-2491

February 1, 1988

Editorial Office of Elsevier Sequoia
Mayfield House
256 Banbury Road
Oxford OX2 7DH
UNITED KINGDOM

Dear Sir:

Enclosed please find three (3) copies of the manuscript
"Calculations of the Gaseous Species in Halide Activated
Cementation Packs," by S. C. Kung and R. A. Rapp, which is
herewith submitted for publication in Thin Solid Films. We look
forward to your review and acceptance.

Sincerely

Robert A. Rapp
Professor

RAR/ds
Enclosure

cc: S. C. Kung
G. R. St. Pierre
✓ R. A. Rapp

CALCULATIONS OF THE GASEOUS SPECIES IN HALIDE
ACTIVATED CEMENTATION PACKS

S. C. Kung* and Robert A. Rapp
Department of Metallurgical Engineering
The Ohio State University
Columbus, Ohio 43210

ABSTRACT

The equilibrium partial pressures of gaseous species in cementation packs using pure condensed Al(l), Cr(s), and Si(s) metals, activated by various halide salts under Ar or reducing environments containing different amounts of hydrogen, have been calculated. The analyses indicate that the presence of hydrogen gas in the system does not significantly alter the equilibrium partial pressures of gaseous species for a pack containing Al at unit activity. However in the absence of aluminum, the vapor pressures of chromium - and silicon-halides are maximized in a hydrogen-free inert gas environment. The vapor pressures for the volatile chlorides of Fe are significantly higher than those for Ni or Co, so that displacement reactions leading to the loss of Fe from the substrate are expected for coating processes involving higher halide activities, e.g., chromizing or siliconizing.

Keywords: cementation pack, activator, coating.

*Currently address: Inland Steel Company, Research Department,
East Chicago, IN.

For	
I	
d	
ion	
by	<i>per letter</i>
Distribution/	
Availability Cod	
Dist	Avail and/or Special
A-1	

INTRODUCTION

The pack cementation process is commonly used to form diffusion coatings which improve the oxidation and corrosion resistance of various heat-resistant alloys at elevated temperatures. The addition of Al, Cr, or Si to the substrate changes the surface composition locally and improves the alloy resistance to corrosive environments. The process consists of arranging the parts to be coated in a semi-sealed retort filled with an appropriate mixture of powders normally comprised of a masteralloy, a halide-salt activator, and an inert oxide filler. The process is conducted isothermally for an extended period to allow the active elements in the masteralloy to react with the activator salt, so that volatile products are formed. The metal halide molecules diffuse through the pack to the substrate where surface reactions deposit the metallic components for diffusion into the substrate. Procedures for the pack cementation coating process and the role of each constituent have been discussed elsewhere¹⁻³ and are not treated in this paper.

Although various cementation packs have been developed and used for at least fifty years, the detailed coating mechanisms and the predominant chemical reactions at the substrate surface are not well established. This lack of understanding limits the possibility for engineering the pack system and predicting the surface composition and the resulting concentration profiles. Efforts have been made by

Levine and Caves¹, Seigle et al⁴⁻⁹, Nciri and Vandembulke¹⁰, and recently Kung and Rapp¹¹ to study the coating rates in aluminization packs, and models have been proposed to reveal the coating process.

To analyze the coating mechanism in a cementation pack, the partial pressures of the gaseous species diffusing in the pack must be known. It is customary to assume that a local equilibrium between the masteralloy and the activator salt exists in the pack at the coating temperature. The gaseous diffusion of the vapor species from the equilibrium pack to the substrate and solid-state diffusion in the substrate limit the coating rate for the cementation process. It is therefore necessary to describe well the thermodynamics of the pack containing the desired masteralloy and activator. Levine and Caves¹ calculated and compared the equilibrium partial pressures of gaseous species in an aluminization pack using various halide salts as the activators. Their system, containing pure Al as the masteralloy, was further modified by Seigle et al⁴ who considered the active gaseous species in the pack under a protective atmosphere of H₂ with a total pressure of 1 atm.

When the masteralloy is a binary alloy powder, e.g., Cr-Al, Cr-Si, Al-Si, etc, both elements could be codeposited into the substrate simultaneously if each element has significant and comparable partial pressures for their halides. The desired surface composition for the coated substrate can be achieved by careful control of the masteralloy composition (i.e., the thermodynamic activities of the metallic components) and the choice of an activator salt of suitable stability.

This has been demonstrated by Rapp et al² who successfully codeposited Al and Cr into pure Fe and a 2.5 Cr-1 Mo alloy steel to achieve Kanthal-like surface compositions which produced protective Al_2O_3 scales upon oxidation. As the number of components in the masteralloy (or in the pack) is increased, the constituent gaseous species become more numerous as well. For example, in a pack containing a binary masteralloy of Cr and Al, both elements react with the activator salt to form the corresponding gaseous halide species. The partial pressures of these metallic halides are directly proportional to the activities of Cr and Al in the masteralloy, which deviate greatly from ideal behavior.¹² Furthermore, for a binary masteralloy, the equilibrium partial pressures of the individual gaseous species in the pack are not generally the same as those calculated individually using the same activity for each element with the given activator. In other words, the mutual presence of halides from two metallic elements affects their equilibrium partial pressures in certain packs. Shifts in the equilibrium gas composition result from the competition between the several metallic components in the chemical reactions with the activator salt to reach a minimum Gibbs energy while maintaining a total pressure of 1 atm.

Table 1 lists the calculated equilibrium partial pressures of gaseous species in a NaCl-activated pack assumed to contain pure Al(l), Cr(s) and Si(s) metals, as well as those containing only a single metal as the source of the components. This artificial condition assumes that the three metallic components will not form an alloy in

the pack. These calculations were made by using a computer program, SOLGASMIX, which will be discussed shortly. According to the calculations, the shifts in the equilibrium gaseous compositions are evident, particularly for the gaseous halides of Cr and Si. Specifically, when Al is present, the very stable volatile Al chlorides maintain a very low chlorine activity in the pack; under these conditions, the pressures of the Cr and Si chlorides are very low. In the absence of Al, packs with either Cr or Si maintain a much higher chlorine activity, so that the pressures of their chlorides become significant. Because of this competition, the thermodynamic calculations are complicated and normally require the aid of advanced computer iterations. Nciri and Vandenbulke¹⁰ studied the equilibrium partial pressures of gaseous species in packs containing binary masteralloys of Al-Cr, Al-Ni, and Al-Fe. Their calculations were carried out using a computer program developed by Erikssen.¹³ Based on their calculated results, the possibility of codeposition of other metals in the presence of Al was discussed.

For many engineering metals and alloys, it is beneficial to deposit multiple protective elements into the surface by a single-step coating process using a multicomponent masteralloy, e.g., Cr-Al, Cr-Si, Al-Si, Al-Cr-Si, etc. Because of the several components involved, the chemical competition among these coating elements and the shifts of equilibrium vapor pressures need to be considered. To engineer such cementation packs, a knowledge of the thermodynamics of volatile halides in the system is essential; the recent compilation by

Pankratz¹⁴ is particularly useful. Such data can then be used to determine suitable compositions of the masteralloy, the choice of the activator, and perhaps the coating temperature. This paper discusses the factors important for pack cementation systems intended for simultaneous depositions of Al, Cr, or Si using one of the following potential halide-salt activators: NaCl, NaF, AlF₃, or AlCl₃, under either pure Ar or H₂-containing atmospheres.

THERMODYNAMIC CALCULATIONS

The illustrative pack systems considered here contain excess pure Al, Cr, and Si powders as the source metals. These metals are assumed to coexist in the pack in their pure condensed forms without any tendency to alloy during coating; therefore, their activities are assumed to remain unity at all times. Clearly, this is an artificial representation, introduced here to show the significant differences in halide stabilities for Al, Cr, and Si. Except for AlCl₃, the activators (NaCl, NaF, and AlF₃) are stable as condensed phases at the coating temperatures. In addition to the gas phase, a total of 5 phases, i.e., gas, Al, Cr, Si, and a condensed activator, are present in these systems.

The existence of a condensed activator phase in the pack regulates the degrees of freedom of the system. The partial pressures of metallic halides are chemically determined by both the activities of

the coating metals in the masteralloy and the partial pressure of halogen resulting from the most reactive salt/alloy reaction, i.e., $M + 1/2 X_2 = MX_i(v)$. When the activities of the active metals are constant (unity assumed for this study), the partial pressures of MX_i become only a function of P_{X_2} . If a stable condensed halide activator is present in the pack at a given temperature, the partial pressure of X_2 is fixed and stays time-invariant. As a result, the vapor pressures of metallic halides are also fixed at constant values.

For the $AlCl_3$ activator, however, the salt is unstable upon heating and decomposes completely at elevated temperatures (melting point at 465.7 K, triple point at 467 K with a vapor pressure of 2.3 atm). Because of the lack of a condensed activator phase in this system, the partial pressures for an $AlCl_3$ -activated pack become greatly dependent upon the amount of the activator and the venting pressure for the system. The $AlCl_3$ vapor would tend to escape from a vented coating system and the residual activator in the pack would decrease with time, resulting in gas and pack compositions which vary as a function of time. Thus, the calculations for the $AlCl_3$ -activated pack represent only the equilibrium condition for a pack vented to 1 atmosphere, or for a system otherwise constantly supplied with a flowing stream of $AlCl_3$ gas under a total pressure of 1 atm.

The thermodynamic calculations for cementation packs with various activators were carried out by using a computer program, SOLGASMIX, evolved from Eriksson¹³ and modified at The Ohio

State University. The program is capable of considering several phases simultaneously, e.g., a gas in equilibrium with several condensed phases. The program redistributes the elements to predefined species of known thermodynamic stabilities to reach a state of minimum Gibbs energy. The program requires the input of standard Gibbs energies of formation for all possible compounds in the system and the initial amounts of elements involved. Table 1 lists the standard Gibbs energies of formation used for this study, with a standard state of condensed phases specified as the stable phase of the pure element or compound at the given temperature under 1 atm total pressure. The standard state for vapors is unit fugacity. The initial amounts of the system are input as follows:

$$\begin{aligned}n(\text{Al}) &= 1 \text{ mole, } n(\text{Cr}) = 1 \text{ mole, } n(\text{Si}) = 1 \text{ mole,} \\n(\text{activator}) &= 0.01 \text{ mole, and } n(\text{inert gas}) = 1 \times 10^{-4} \text{ mole.}\end{aligned}$$

The molar number of inert gas in the pack is chosen using the ideal gas law for a container normally used in this laboratory for pack cementation coatings. However, the exact amounts of these components are not critical because the equilibrium partial pressures of gaseous species are independent of the input values as long as none of the components are significantly consumed to result in activities less than unity, and the total pressure remains constant at 1 atm. The inert filler, Al_2O_3 powder, is extremely stable and does not react significantly with other components. It is therefore excluded in the thermodynamic calculations. The partial pressures of ternary gaseous species are thermodynamically negligible and are also excluded in this study.

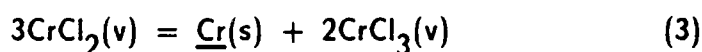
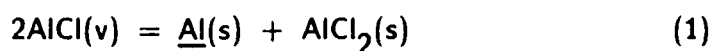
RESULTS AND DISCUSSION

Figure 1(a) to (c) show the partial pressures of the gaseous species in packs using NaCl as the activator in pure Ar, in a 5% H₂/Ar gas mixture, and in pure H₂, respectively, as a function of temperature. The gas phase is comprised predominantly of Ar or/and H₂, with the partial pressures of other gaseous species ranging from 1×10^{-20} to 1 atm. Because of their high thermodynamic stability (more negative Gibbs energies of formation), the partial pressures of aluminum chlorides are several orders of magnitude higher than those for chromium chlorides or silicon chlorides. The vapor pressure of Al at any temperature is relatively low compared to those for the aluminum chlorides. This low P_{Al} dictates that the transport of Al from the pack to the substrate must be governed by the diffusion of its chloride species, rather than a direct deposition by Al vapor. On the other hand, the vapor pressures of gaseous chromium chlorides and silicon chlorides are relatively low and comparable to their metallic vapors, because of the very low chlorine activity dictated by the presence of Al. The components Cr and Si can not be codeposited with Al in a pack with unit Al activity.

Because of the large differences in the thermodynamic stabilities among the volatile halides for these coating elements, the calculated partial pressures of Table 2 for the dominant aluminum halides in the presence of Al are essentially the same as in the presence or absence of Cr and Si. However, the calculated vapor

pressures for the chromium chlorides and silicon chlorides exhibit significantly higher pressures for packs in equilibrium with Cr or Si individually, in the absence of Al.

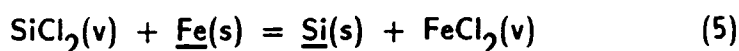
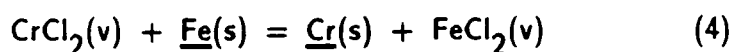
One mode of deposition of metals at the substrate surface is the disproportionation of lower halides (lower halogen content) into higher halides, as indicated in Eqs. (1)-(3).



This mechanism is particularly important when the halide vapor pressure of the substrate element is low and when the coating component has higher and lower halides of comparable vapor pressures.

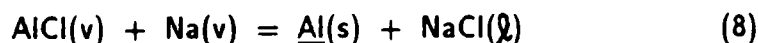
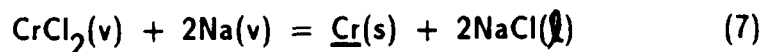
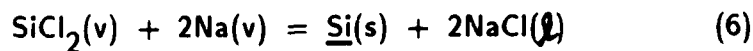
However, if the halide vapor pressures for the substrate element is comparable to the coating halides, displacement reactions at the substrate surface are possible. Figures 2(a)-(c) present the partial pressures of gaseous species for different pure metal substrates (Fe, Ni, and Co) in 5% H₂/Ar when condensed NaCl is present at their surfaces. The calculations ignore any interactions with gaseous chlorides generated from the pack. The thermodynamic activity of the substrate metal at the surface would decrease with coating time because of the addition of coating elements to the surface; therefore, the vapor pressures of the substrate chlorides would also decrease with time.

Figures 2(a)-(c) indicate that an Fe substrate exhibits the highest vapor pressure of metallic chloride, about 2 orders of magnitude higher than those for Ni or Co, which are quite low. When the vapor pressure of the substrate chloride is comparable to the partial pressures of the coating chlorides from the pack, e.g., FeCl_x vs. CrCl_x or SiCl_x , displacement reactions at the substrate would become important, i.e.,



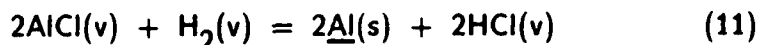
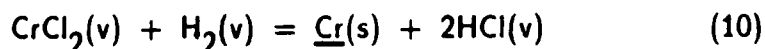
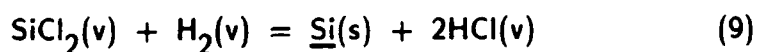
According to such reactions, iron chloride vapor should escape from the substrate surface, at the same time, allowing the active elements to be coated into the surface. The calculated results in Figs. 2(a)-(c) imply that displacement reactions, with loss of substrate material, would only be significant for Fe and its alloys in packs of relatively high chlorine activity. The existence of a displacement reaction would be important in deciding the substrate dimensions and weight changes upon coating.

Liquid NaCl in the pack forms high partial pressures of the gaseous species Na, NaCl, and Na_2Cl_2 . The large amounts of the Na and NaCl vapors with high diffusivities assist in *accepting* chlorine *at* the substrate surface by the following reactions:



← These additional surface reactions, resulting from the introduction of Na as a component to the pack, could affect the overall coating kinetics. In such a pack, a thin fused salt film is expected to exist on the substrate surface.

When hydrogen gas is introduced into the system, the partial pressures of the Al, Cr, and Si chloride vapors are only slightly affected in the presence of pure Al. No important differences can be observed in the plots of Figs. 1(b) and 1(c) compared to Fig. 1(a). Thus, despite the formation of HCl in the gas phase, the existence of hydrogen does not noticeably shift the equilibrium of a cementation pack when pure Al is present. However, when Al is absent in the pack, the partial pressures of Cr and Si chlorides can be significantly *(compared to an Ar environment)* decreased, as hydrogen is introduced. Table 3 gives a comparison of the equilibrium vapor pressures for NaCl-activated packs at 1400 K in a pure H₂ environment using Al/Cr/Si, Cr/Si, Cr, or Si as the masteralloy. These data, calculated with SOLGASMIX, indicate an increase of approximately two orders of magnitude in the partial pressures of Cr and Si chlorides is expected when Al is absent. Such *, especially for the Ar environment of Table 2,* changes in thermodynamic equilibria, would accelerate the deposition of Cr and Si from the pack to the substrate. The formation of HCl in the ^{H₂} gas phase at the substrate could significantly alter the coating kinetics according to the following reactions supporting chlorine removal:



With the presence of hydrogen, however, a significant acceleration in kinetics is expected only for the transfer of Si and Cr according to Eqs. (9) and (10), where the partial pressures of these metallic chlorides are much lower than those for the HCl and H₂ gases. On the other hand, the partial pressure of HCl is relatively insignificant compared to those of aluminum chlorides for unit Al activity. Therefore, the coating rate of Al in the presence of H₂ should remain unchanged, and Eq. (11) is not important. Kung and Rapp¹¹ have studied the NaCl-activated aluminization of Fe and demonstrated only a small effect from the addition of hydrogen.

If AlCl₃ is used as the activator in the pack, the thermodynamics of this system are simplified by eliminating the Na component. However, this activator is unstable at high temperatures and does not persist as a condensed phase. Figures 3(a)-(c) give the calculated partial pressures of various vapor species for vented AlCl₃-activated packs under a total pressure of 1 atm. Compared to the NaCl-activated packs shown in Figs. 1(a)-(c), the partial pressures of metallic chlorides are, in general, two orders of magnitude higher. Clearly, these higher vapor pressures result from the higher chlorine activity in the AlCl₃-activated system. Despite the absence of the reactions of Eqs. (6)-(8) involving Na(g) and NaCl(l), an increase in the overall coating ^{rate} is expected because of the high metallic halide vapor pressures. Kung and Rapp¹¹ showed that the aluminization of pure iron was faster in an AlCl₃-activated pack than in a NaCl pack for short coating durations. The coating mechanism, however, was

later reversed when the coating time was prolonged, because the activator escaped from the pack system. Similar to the NaCl-activated pack, the addition of hydrogen to the AlCl_3 pack does not shift the equilibrium of gaseous species significantly.

Generally, fluoride salts and their vapors are both thermodynamically more stable than the corresponding chlorides, and the vapor pressures for gaseous fluorides in cementation packs are higher than those for the corresponding chlorides. In the interest of the pack stability afforded by a condensed activator, it is more convenient to use fluorides as activators for pack cementation processes. Figures 4(a)-(c) plot the equilibrium partial pressures of gaseous species as a function of temperature in packs using NaF as the activator. The partial pressures of chromium fluorides are not included in these plots because data for their standard Gibbs energies of formation are lacking in the literature. Nevertheless, the vapor pressures of chromium fluorides in the system should be minor and the exclusion of these species from the thermodynamic calculations would not shift other gaseous species noticeably, especially for the semi-log plots shown.

According to the calculations, condensed AlF_3 tends to form in a NaF-activated pack at lower temperatures (< 1100 K). This condensation disappears as the coating temperature exceeds 1100 K. The vapor pressures of fluorine gas are not shown in the figures because their calculated values fall below the scale range (i.e., $\log P < -20$). The partial pressures of corresponding species in the NaF

pack of Figs. 4(a) -(c) are higher than those in the NaCl pack of Figs. 1(a)-(c), indicating the expectation for deposition at faster coating rates. Seigle et al⁴ found that the vapor pressures of gaseous halides were highest in the NaF-activated pack and decreased with the activator type in the order of NaCl, NaBr, and NaI. The coating mechanisms at the substrate surface in a NaF pack are similar to those in a NaCl pack. As for the previous example, the introduction of hydrogen to the NaF system should not result in an observable effect on the pack thermodynamics in the presence of pure Al.

The use of AlF_3 as the activator again decreases the number of components involved in the pack system. But in contrast to AlCl_3 , solid AlF_3 is thermodynamically stable and remains as a condensed phase in the studied temperature range. Figures 5(a)-(c) show the results calculated for AlF_3 -activated packs under various gaseous environments. Again, chromium fluorides are not plotted because the data are not available, and the fluorine gas pressures are small and off the scale. The absence of gaseous sodium vapor and its compounds in the gas phase provides slightly higher partial pressures for the metallic fluorides compared to those in the NaF pack. No significant effect from the introduction of hydrogen gas is observed in the presence of pure Al.

DISCUSSION

For all the systems, aluminum halides exhibit higher partial pressures compared to the metallic halides of Cr and Si in equilibrium

with the corresponding condensed pure metals. The direct transport of metallic Al vapor from the pack to the substrate would always be comparatively negligible. When condensed NaCl and its vapors are present in the gas according to Fig. 1, the reaction of aluminum monochloride with sodium vapor to form a condensed NaCl film at the substrate can become important. In general, regardless of the activator, the thermodynamics of aluminization and the Al deposition kinetics are essentially unaffected by the addition of hydrogen to the system for a pack with unit Al activity.

Because of the differing relative abundances of the volatile silicon chlorides (Fig. 1) and silicon fluorides (Fig. 4), a disproportionation reaction seems possible for the chlorides, but not for fluorides. However, for chromizing an iron substrate, the disproportionation reaction cannot be important because ^{of} the significant difference in partial pressures between CrCl_2 and CrCl_3 . Instead, a displacement reaction between the Fe of the substrate and the Cr halide molecules arriving from the pack must play a predominant role. When sodium and its halides are present, the majority of chromizing and siliconizing processes are probably achieved by the reactions of their metal halides with Na for a Ni or Co substrate, or with iron for an iron substrate. Furthermore, when hydrogen is introduced into the pack, ~~de~~creases in the rates of chromizing and siliconizing are expected *despite* the availability of hydrogen to form and desorb HCl at the substrate surface.

For many engineering applications, it would be desirable to coat the substrate with a specific proportion of two or three elements simultaneously by a single coating step, generally with a higher concentration of Cr and less of Al and/or Si at the substrate surface. This requires modification of the cementation pack by choosing proper masteralloy compositions and activators. The masteralloy must exhibit an Al activity on the order of 10^{-3} times those for Cr or Si to bring the respective metal halide pressures to the same order of magnitude. Fortunately, activities in the Cr-Al system exhibit a large negative deviation from the ideal behavior. Based on such calculations, the composition of a masteralloy suitable for codeposition of, for example, 20 Cr, 4 Al, and a small amount of Si needs to be very high in Cr content, moderate in Si, and extremely low in Al activity. Pure condensed silicon in the pack should provide a slow coating rate of Si because of its low halide pressures, and therefore, might be used directly with a Cr-Al binary masteralloy for simultaneous coating, providing the alloying process between the Si metal and Cr-Al alloy is slow. In general, fluoride activator salts provide higher metallic halide vapor pressures in the pack than chlorides, and hence higher coating rates. However, as pointed out earlier, subtle differences in specific surface reactions are expected for the chlorine- or fluorine-activated packs.

CONCLUSIONS

The thermodynamics of cementation packs using different halide salts as the activators under different reducing environments have been analyzed and discussed. The coating metals Al, Cr, and Si were considered, for ease of comparison, to exist at unity activity in the same pack. In general, the fluoride salts react with Al, Cr, and Si metals to form higher partial pressures of metallic fluorides than the corresponding chloride salts. The vapor pressures of Al halides are much higher than those for Cr and Si. ^{In the presence of Al at unit activity,} the use of 5% H₂/Ar or pure hydrogen gas does not significantly shift the thermodynamics of the packs from those under pure Ar gas. However, *in the absence of aluminum at high activity, the deposition of Cr and Si should be accelerated by an inert gaseous environment.*

Upon simultaneous deposition of Al and Cr or/and Si, a *much* higher composition and activity of Cr in the masteralloy is required. The approximate design of such packs, based on the thermodynamic data in the literature, should be possible. The most important requirement is the selection of a suitable binary Cr-Al or ternary Cr-Si-Al masteralloy or perhaps a mixture of a Cr-rich binary Cr-Al alloy and pure Si. The selection of a proper activating salt, or salt mixture to form a solution, can then be used to tune the resulting ratios of the coated components and the overall coating rates.

ACKNOWLEDGEMENT

This work was supported by the Office of Naval Research (A. J. Sedriks, project monitor) under contract No. N00014-87-K-0030.

REFERENCES

- (1). S. R. Levine and R. M. Caves, *J. Electrochem. Soc.*, 121 (1974) 1051.
- (2). R. A. Rapp, D. Wang, and T. Weisert, *Simultaneous Chromizing and Aluminizing of Iron and Iron Base Alloys by Pack Cementation Process*, Metallurgical Coating, M. Khobaib and R. Krutenat, eds., TMS-AIME, Warrendale, 1987, p. 131.
- (3). L. L. Seigle, *Surface Engineering*, R. Kossowsky and S. C. Singhal, eds., Martinus Nijhoff Publishers, Boston, 1984.
- (4). L. L. Seigle, B. K. Gupta, R. Shankar and A. K. Sarkhel, *Kinetics of Pack Aluminization of Nickel*. NASA Contract Report 2939, prepared for Lewis Research Center under Contract NGR-33-016-160, NASA Scientific and Technical Information Office, 1978.
- (5). D. C. Tu and L. L. Seigle, *Thin Solid Films*, 95 (1982) 47.
- (6). R. Sivakumar and L. L. Seigle, *Met. Trans.*, 13A (1982) 495.
- (7). B. K. Gupta, A. K. Sarkhel and L. L. Seigle, *Thin Solid Films*, 39 (1976) 313.
- (8). B. K. Gupta and L. L. Seigle, *Thin Solid Films*, 73 (1980) 365.
- (9). N. Kandasamy, F. J. Pennisi and L. L. Seigle, *Thin Solid Films*, 84 (1981) 17.
- (10). B. Nciri and L. Vandenbulke, *J. Less-Common Metals*, 95 (1983) 55.
- (11). S. C. Kung and R. A. Rapp, *Surface and Coatings Technology*, 32 (1987).

- (12). W. Johnson, K. Komarek and E. Miller, Trans Met. Soc.,
AIME, ²⁴²(1968) 1685.
- (13). G. Eriksson, Chem. Scr., 8 (1975) 100.
- (14). L. B. Pankratz, "Thermodynamic Properties of Halides," U.
S. Dept. of the Interior, Bureau of Mines, Bulletin 674, 1984.

List of Figures

- Figure 1: Equilibrium Partial Pressures of Gaseous Species in NaCl-Activated Pack Containing Pure Al, Cr, and Si in (a) Ar, (b) 5% H₂ + Ar, and (c) H₂.
- Figure 2: Equilibrium Partial Pressures of Gaseous Species at Substrate Surface in Gas 5% H₂/Ar. When NaCl is Present, (a) Fe, (b) Ni, and (c) Co.
- Figure 3: Equilibrium Partial Pressures of Gaseous Species in AlCl₃-Activated Pack Containing Al, Cr, and Si in (a) Ar, (b) 5% H₂ + Ar, and (c) H₂.
- Figure 4: Equilibrium Partial Pressures of Gaseous Species in NaF-Activated Pack Containing Al, Cr, and Si in (a) Ar, (b) 5% H₂ + Ar, and (c) H₂.
- Figure 5: Equilibrium Partial Pressures of Gaseous Species in AlF₃-Activated Pack Containing Al, Cr, and Si in (a) Ar, (b) 5% H₂ + Ar, and (c) H₂.

TABLE 1

STANDARD GIBBS FREE ENERGIES OF FORMATION⁽¹⁾ (cal/mole)

Temperature (K)

Gas Phase	1000	1200	1400
Al	47132	41623	36202
Cr	59688	52938	46286
Si	72248	65278	58367
Na	3529	0	0
NaCl	-55766	-57493	-55678
Na ₂ Cl ₂	-132477	-129950	-120415
NaF	-82662	-84297	-82389
Na ₂ F ₂	-189611	-186610	-175672
AlCl	-32136	-35188	-35137
AlCl ₂	-74971	-75687	-76309
AlCl ₃	-127587	-124475	-121315
Al ₂ Cl ₆	-250614	-238053	-225547
AlF	-82590	-85486	-88241
AlF ₂	-172559	-172945	-173235
AlF ₃	-275137	-271515	-267838
Al ₂ F ₆ ⁽²⁾	-561189	-546836	-532504
CrCl ₂ ⁽²⁾	-46053	-48672	-51704
CrCl ₃ ⁽²⁾	-67823	-65055	-64228
CrCl ₄ ⁽³⁾	-77349	-72505	-67663
CrF ₂ ⁽³⁾			
CrF ₃ ⁽³⁾			
CrF ₄ ⁽³⁾			
SiCl	22227	17402	12656
SiCl ₂	-49229	-50827	-52357
SiCl ₃	-84895	-83213	-81505
SiCl ₄	-126892	-120772	-114674
SiF	-29370	-34042	-38634
SiF ₂	-148033	-149286	-150466
SiF ₃	-249123	-246945	-244735

SiF ₄	-351701	-344827	-337958
HCl	-24091	-24387	-24672

Condensed Phases

NaCl(l)	-76222	-72419	-65778
NaF(s)	-112347	-107123	-99400
AlF ₃ (s)	-298803	-286403	-274125

(1) Data obtained from L. B. Pankratz, Thermodynamic Properties of Halides, BurMines Bull. 674.

(2) Data from both (1) and C. Wagner and V. Stein, Z. Physikal Chem. bd. 192, Heft 3/4.

(3) Data could not be found.

TABLE 2

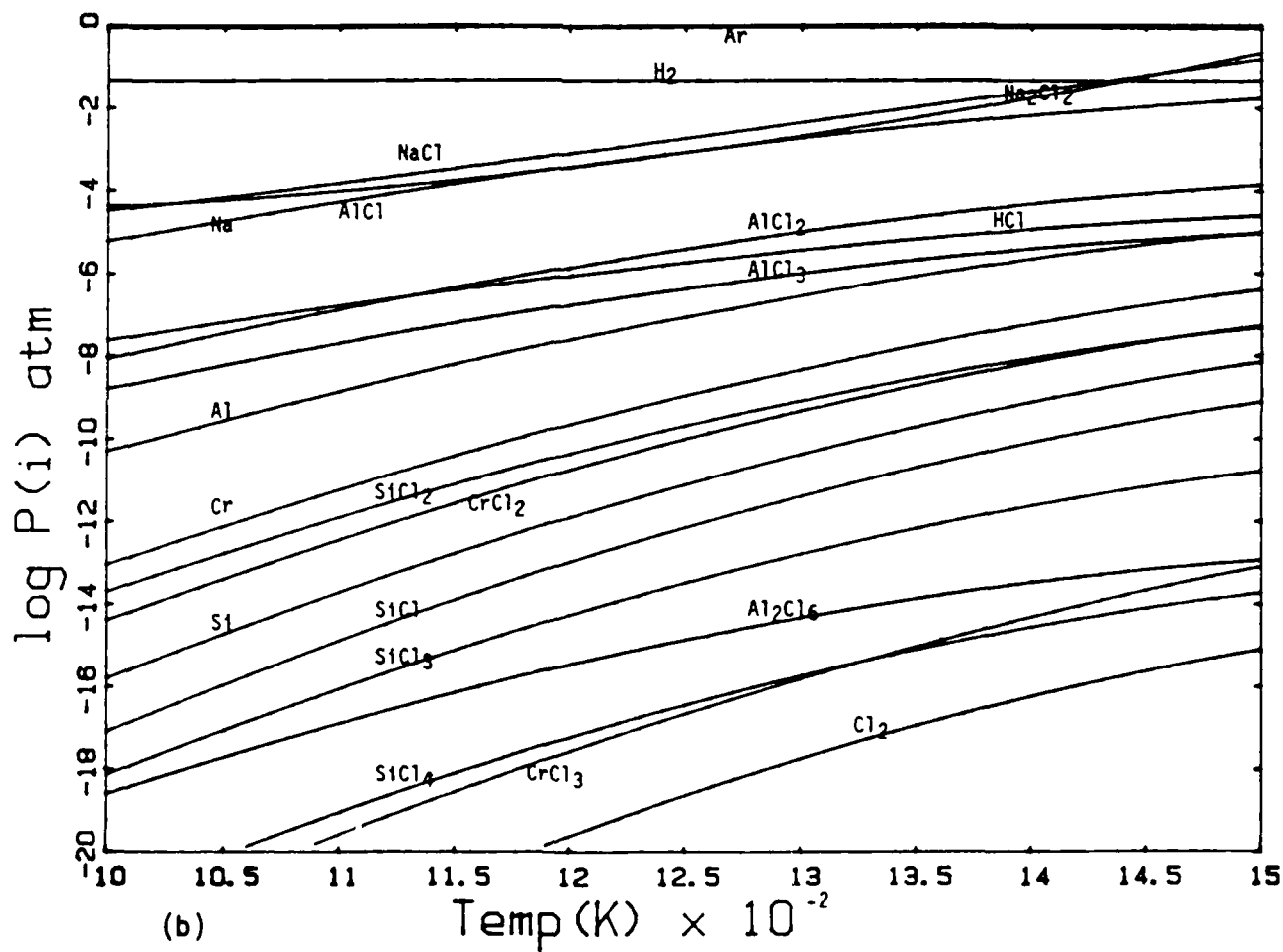
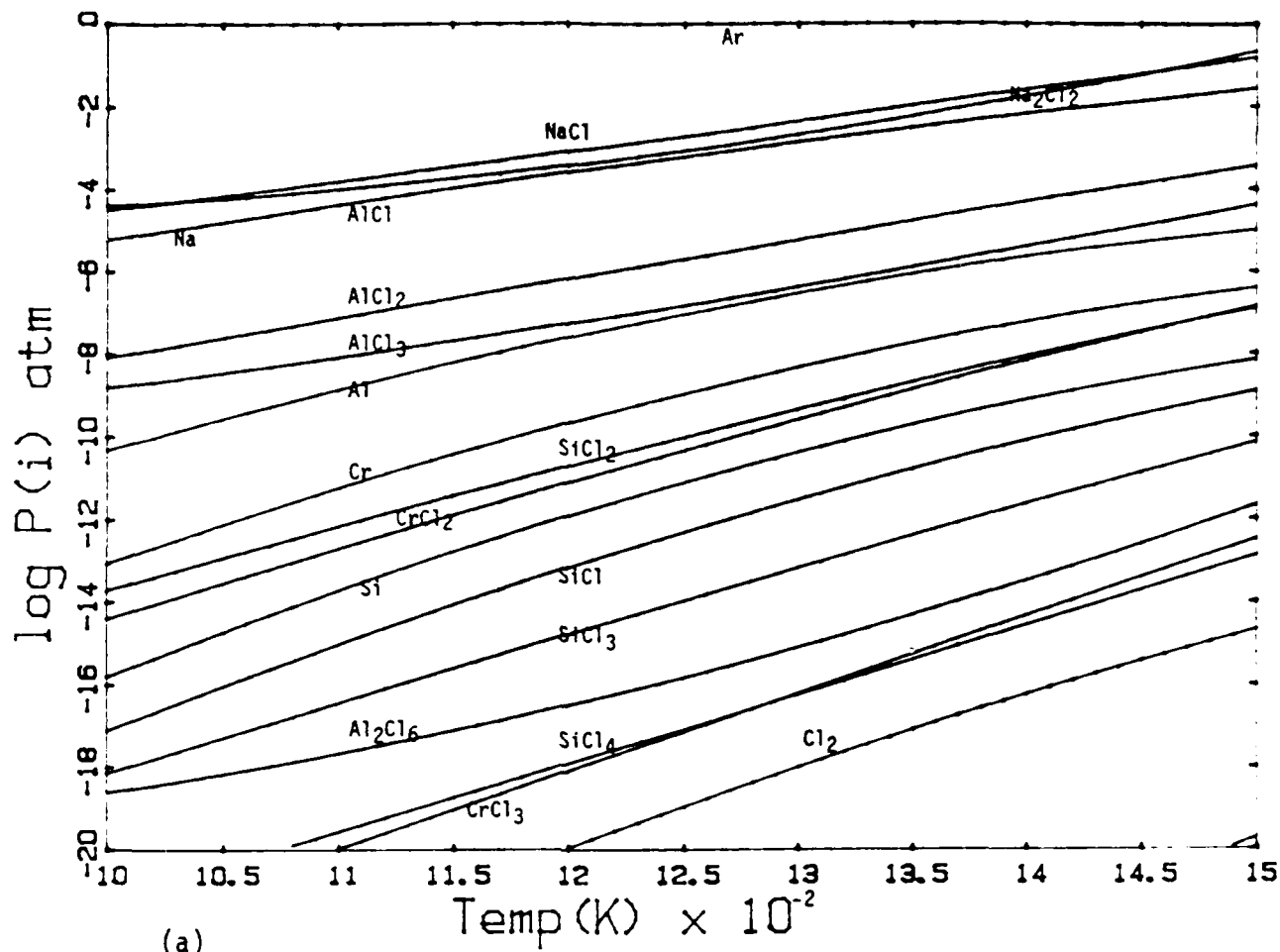
Comparison of equilibrium partial pressures of gaseous species for a NaCl-activated pack containing simultaneously pure Al/Cr/Si and a pack containing only a single metal of Al, Cr, or Si at 1400 K under Ar atmosphere.

<u>GAS Species</u>	<u>Al/Cr/Si</u>	<u>(Partial pressures in atm.)</u>		
		<u>Al only</u>	<u>Cr only</u>	<u>Si only</u>
Ar	0.94129E+00	0.94129E+00	0.95513E+00	0.95512E+00
Cl ₂	0.59080E-16	0.59080E-16	0.37396E-12	0.31292E-12
Al	0.22317E-05	0.22317E-05		
Cr	0.59514E-07		0.59514E-07	
Si	0.77364E-09			0.77364E-09
Na	0.70132E-02	0.70131E-02	0.88149E-04	0.96364E-04
NaCl	0.26505E-01	0.26505E-01	0.26505E-01	0.26505E-01
Na ₂ Cl ₂	0.18231E-01	0.18231E-01	0.18231E-01	0.18231E-01
AlCl	0.69047E-02	0.69048E-02		
AlCl ₂	0.48279E-04	0.48280E-04		
AlCl ₃	0.39374E-05	0.39374E-05		
Al ₂ Cl ₆	0.33153E-13	0.33153E-13		
CrCl ₂	0.69624E-08		0.44071E-04	
CrCl ₃	0.47169E-14		0.23755E-08	
CrCl ₄	0.12750E-21		0.51084E-14	
SiCl	0.81290E-10			0.59161E-08
SiCl ₂	0.88044E-08			0.46634E-04
SiCl ₃	0.24022E-11			0.92599E-06
SiCl ₄	0.27811E-14			0.78022E-07

TABLE 3

Comparison of equilibrium partial pressures of gaseous species for a NaCl-activated pack containing simultaneously pure Al/Cr/Si and a pack containing only Cr/Si, Cr, or Si at 1400 K under H₂ atmosphere.

<u>GAS Species</u>	<u>(Partial pressures in atm.)</u>			
	<u>Al/Cr/Si</u>	<u>Cr/Si</u>	<u>Cr only</u>	<u>Si only</u>
H ₂	0.94124E+00	0.95404E+00	0.95404E+00	0.95404E+00
HCl	0.52772E-04	0.60949E-03	0.61064E-03	0.61040E-03
Cl ₂	0.58640E-16	0.77171E-14	0.77463E-14	0.77400E-14
Al	0.22317E-05			
Cr	0.59514E-07	0.59514E-07	0.59514E-07	
Si	0.77364E-09	0.77364E-07		0.77364E-09
Na	0.70394E-02	0.61363E-03	0.61247E-03	0.61272E-03
NaCl	0.26505E-01	0.26505E-01	0.26505E-01	0.26505E-01
Na ₂ Cl ₂	0.18231E-01	0.18231E-01	0.18231E-01	0.18231E-01
AlCl	0.68790E-02			
AlCl ₂	0.47920E-04			
AlCl ₃	0.38935E-05			
Al ₂ Cl ₆	0.32419E-13			
CrCl ₂	0.69107E-08	0.90945E-06	0.91289E-06	
CrCl ₃	0.47685E-14	0.71990E-11	0.72398E-11	
CrCl ₄	0.12561E-21	0.21754E-17	0.21919E-17	
SiCl	0.80987E-10	0.92906E-09		0.93044E-09
SiCl ₂	0.87390E-08	0.11501E-05		0.11535E-05
SiCl ₃	0.23755E-11	0.35862E-08		0.36022E-08
SiCl ₄	0.27399E-14	0.47452E-10		0.47734E-10



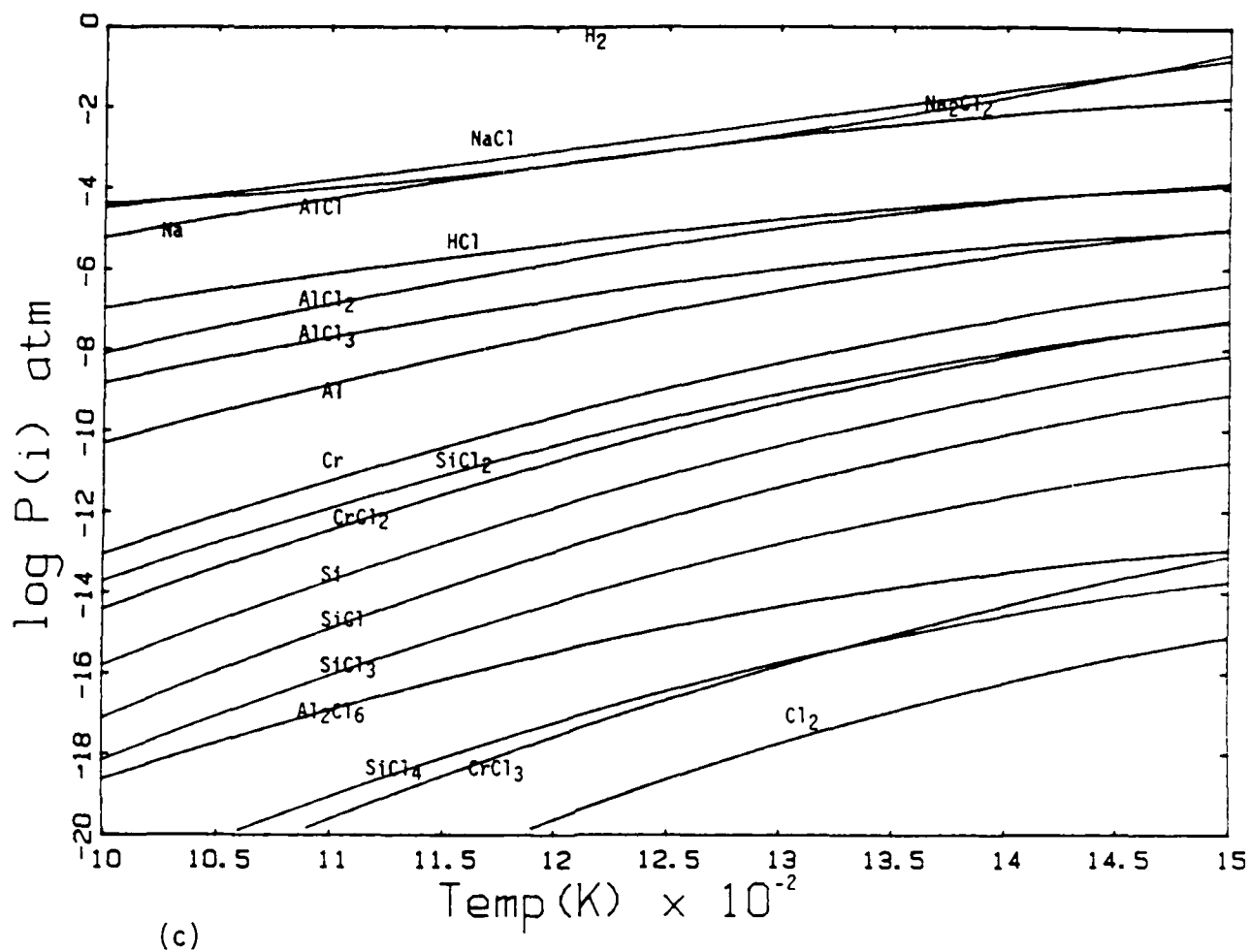
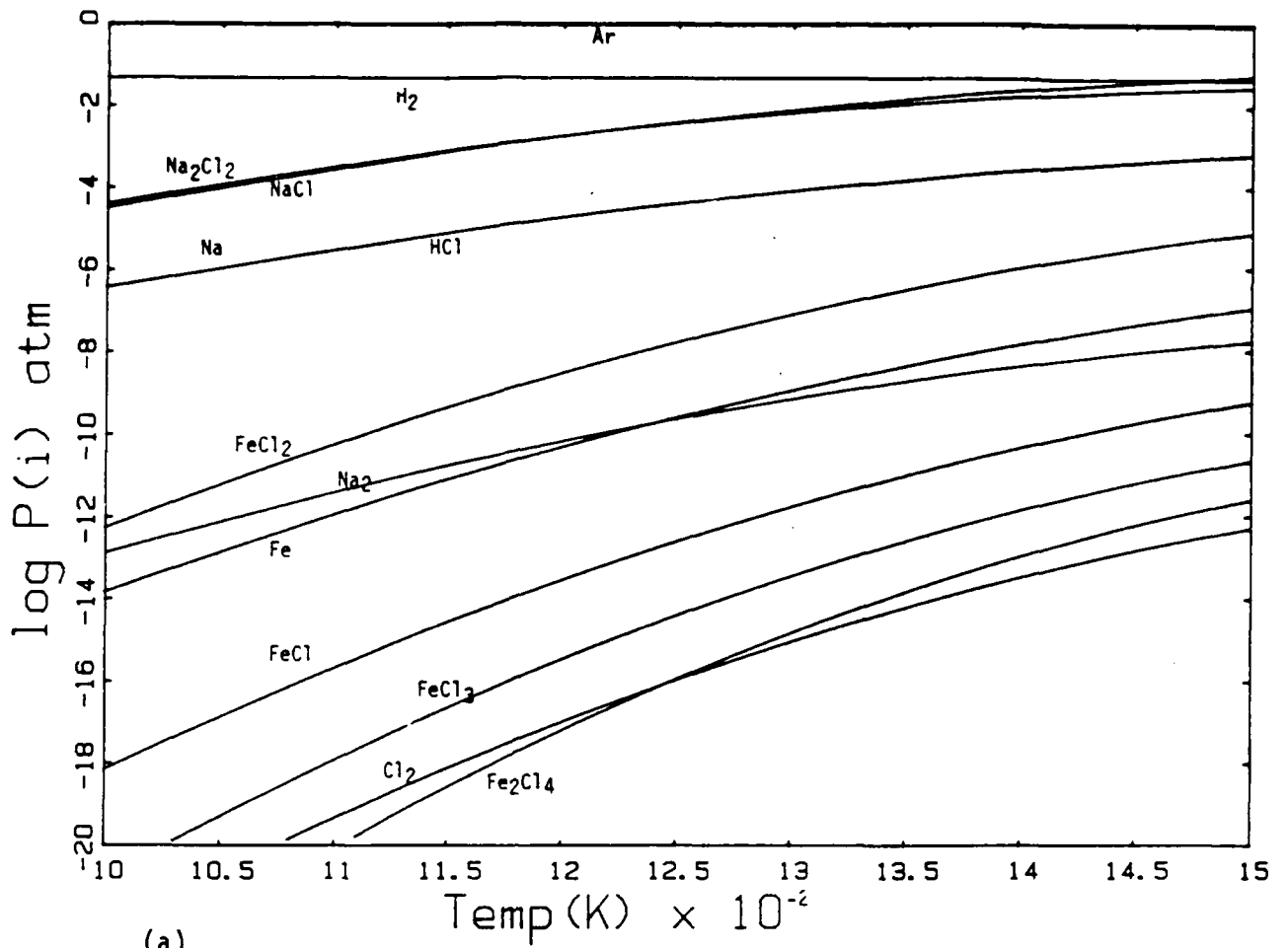
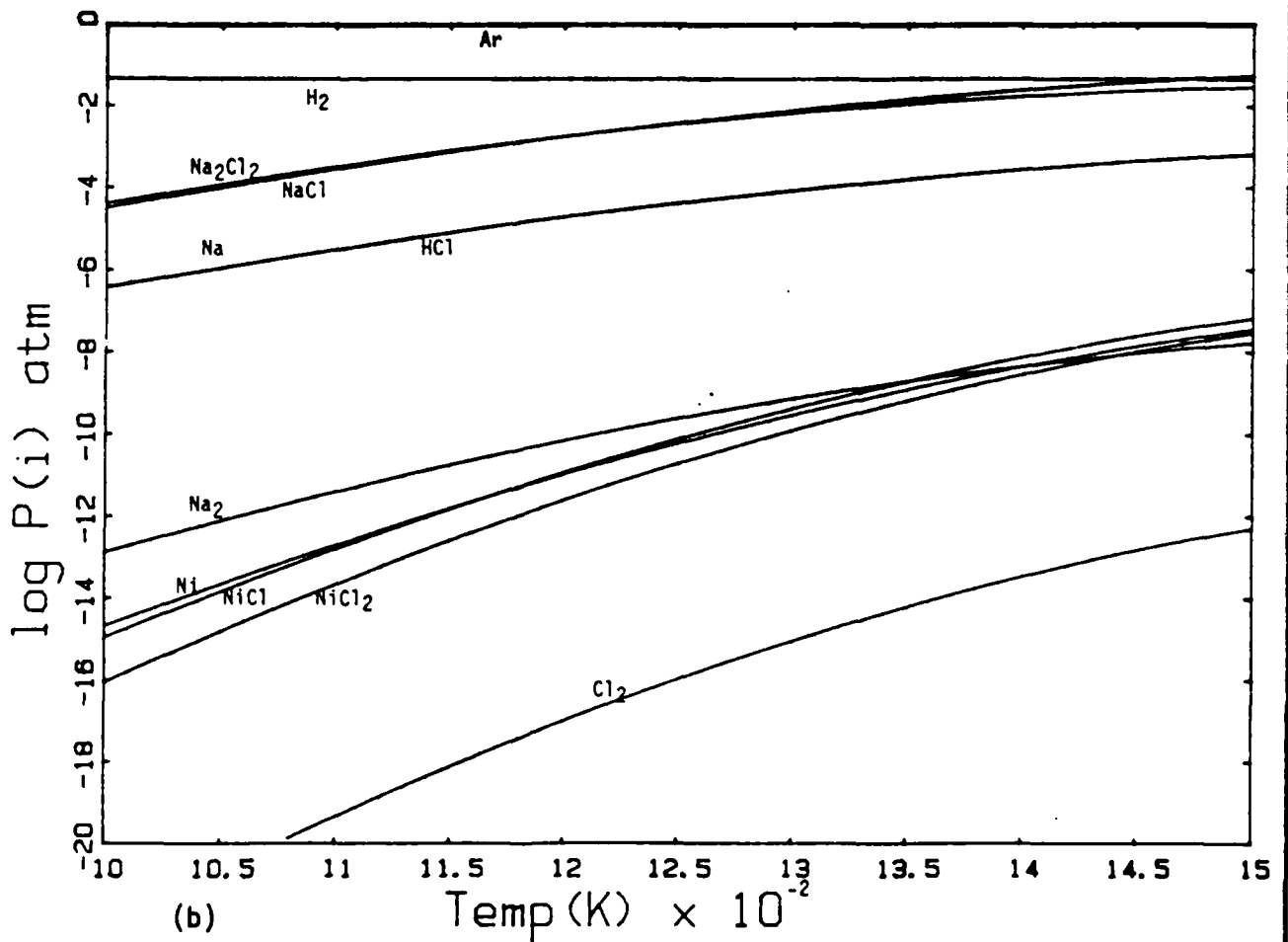


Figure 1 - Equilibrium Partial Pressures of Gaseous Species in NaCl-Activated Pack Containing Pure Al, Cr, and Si in (a) Ar, (b) 5% H₂ + Ar, and (c) H₂.



(a)



(b)

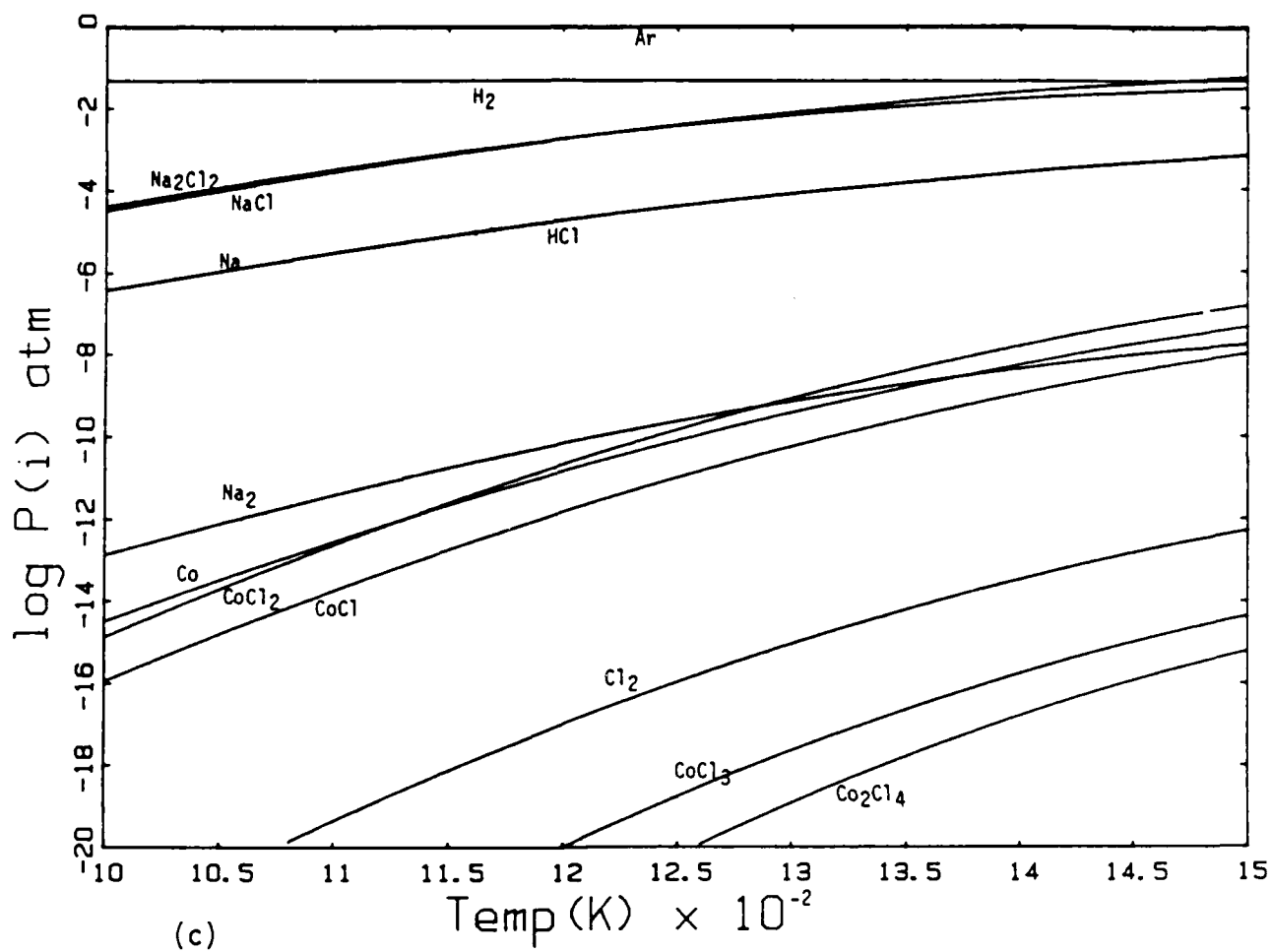
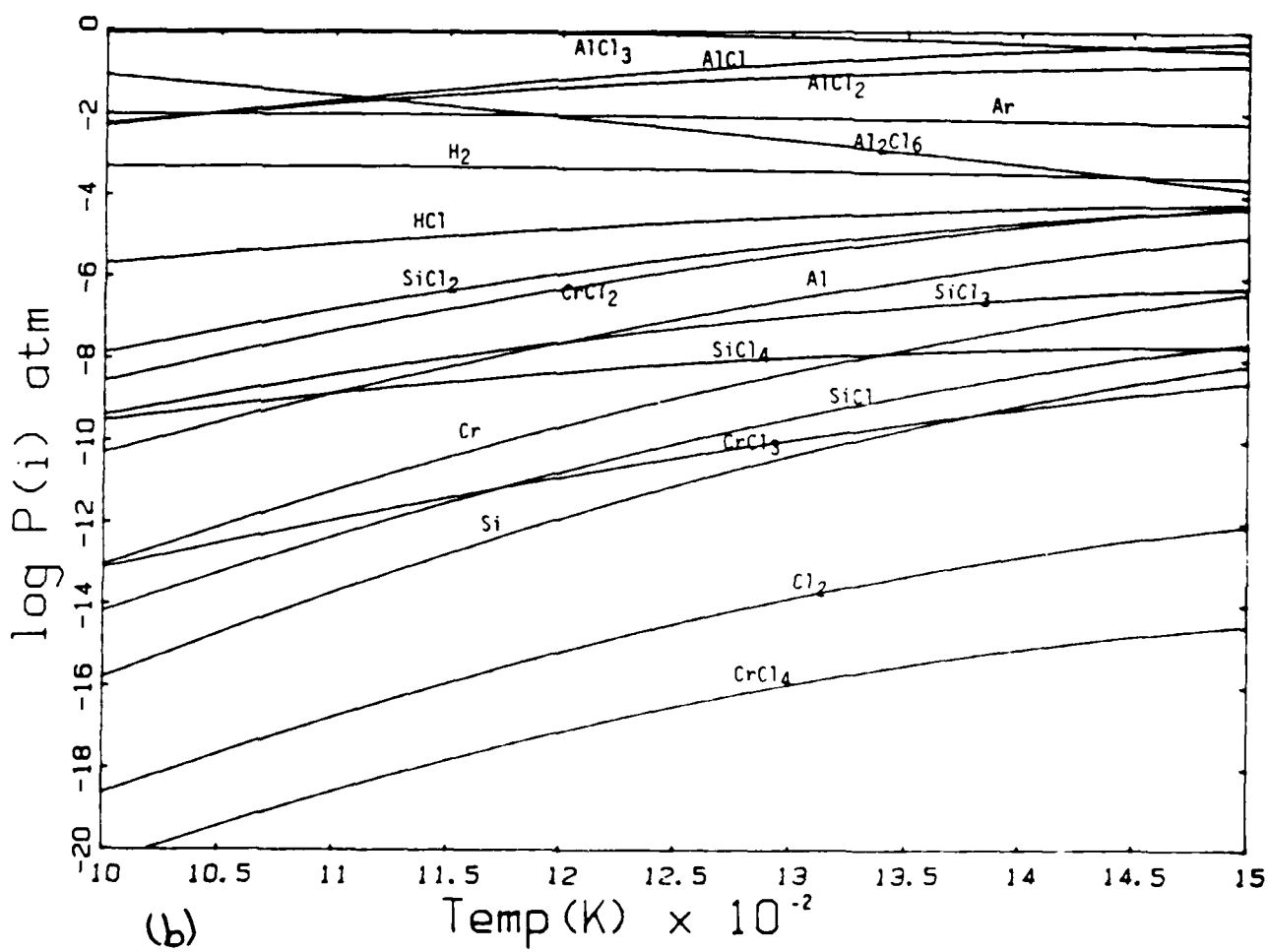
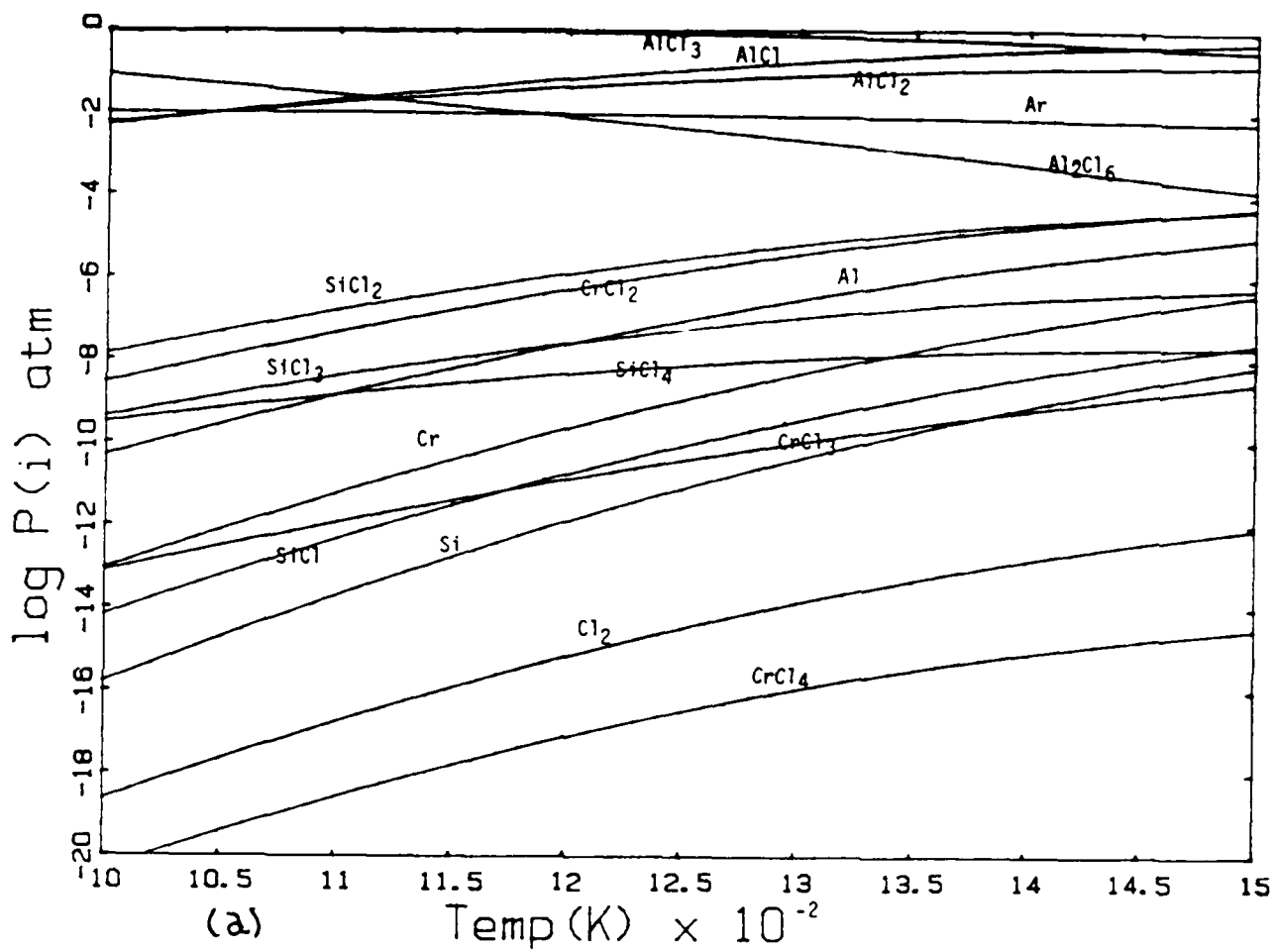


Figure 2: Equilibrium Partial Pressures of Gaseous Species at Substrate Surface in gas 5% H₂/Ar. When NaCl is Present, (a) Fe, (b) Ni, and (c) Co.



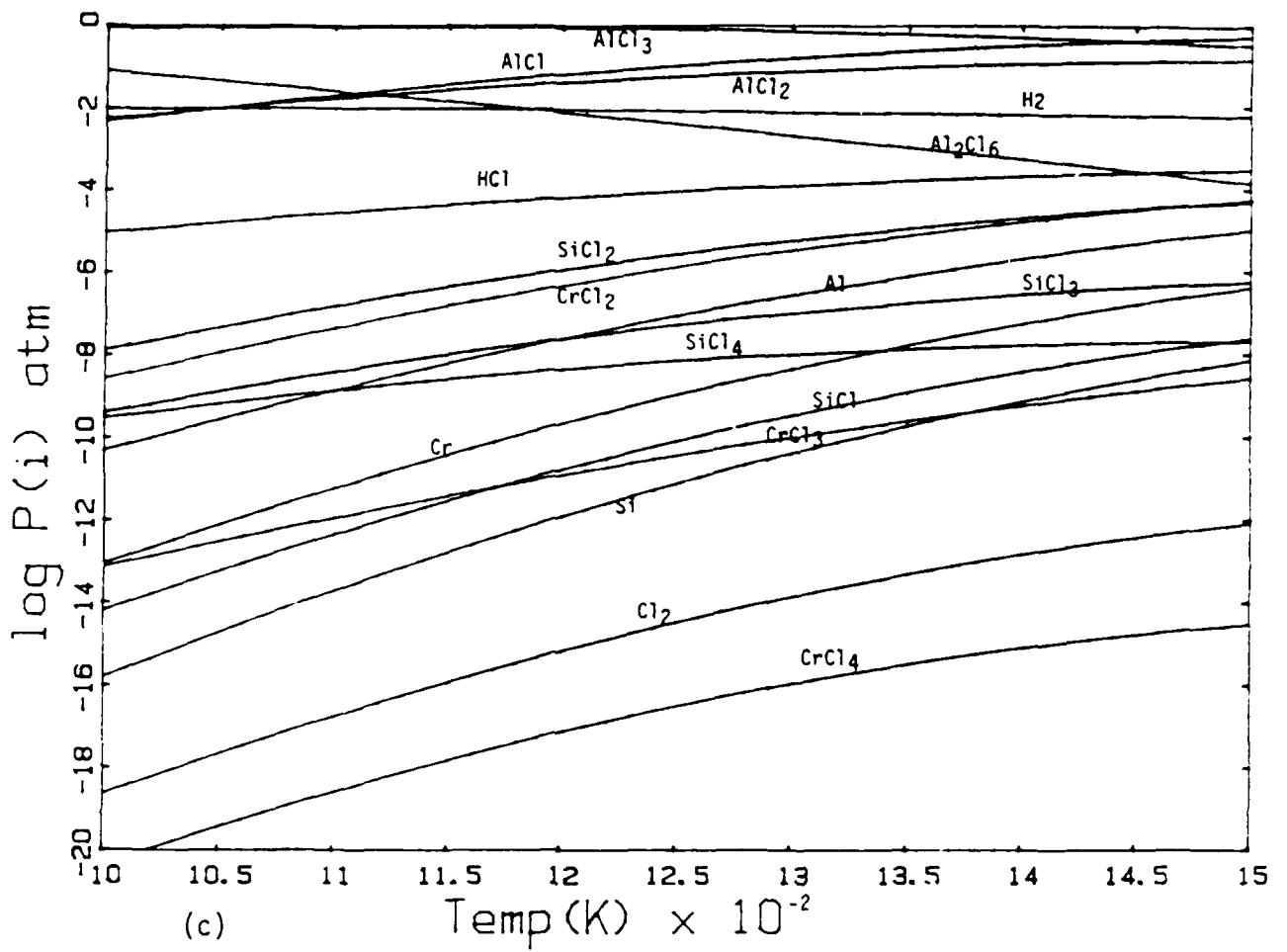
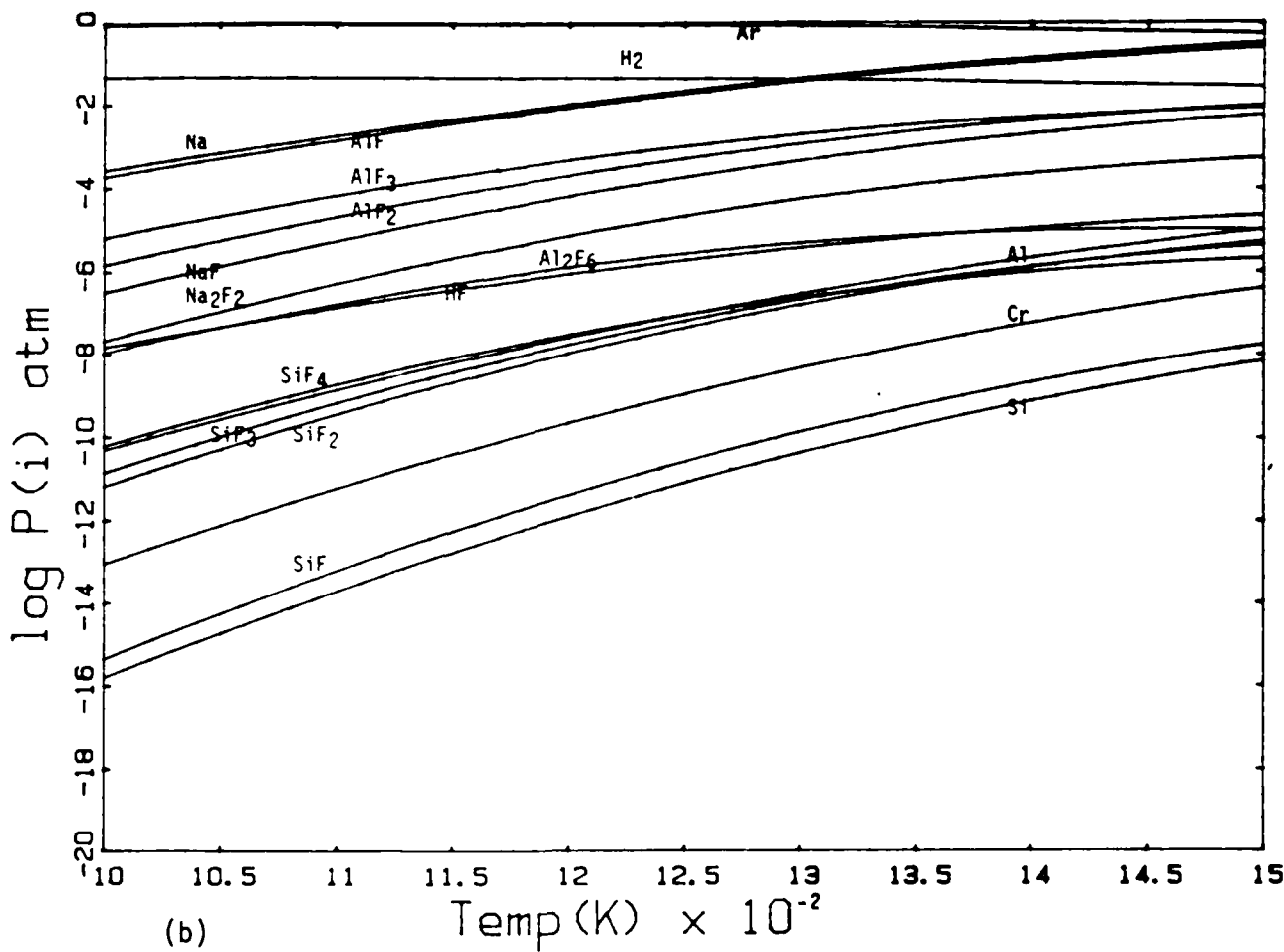
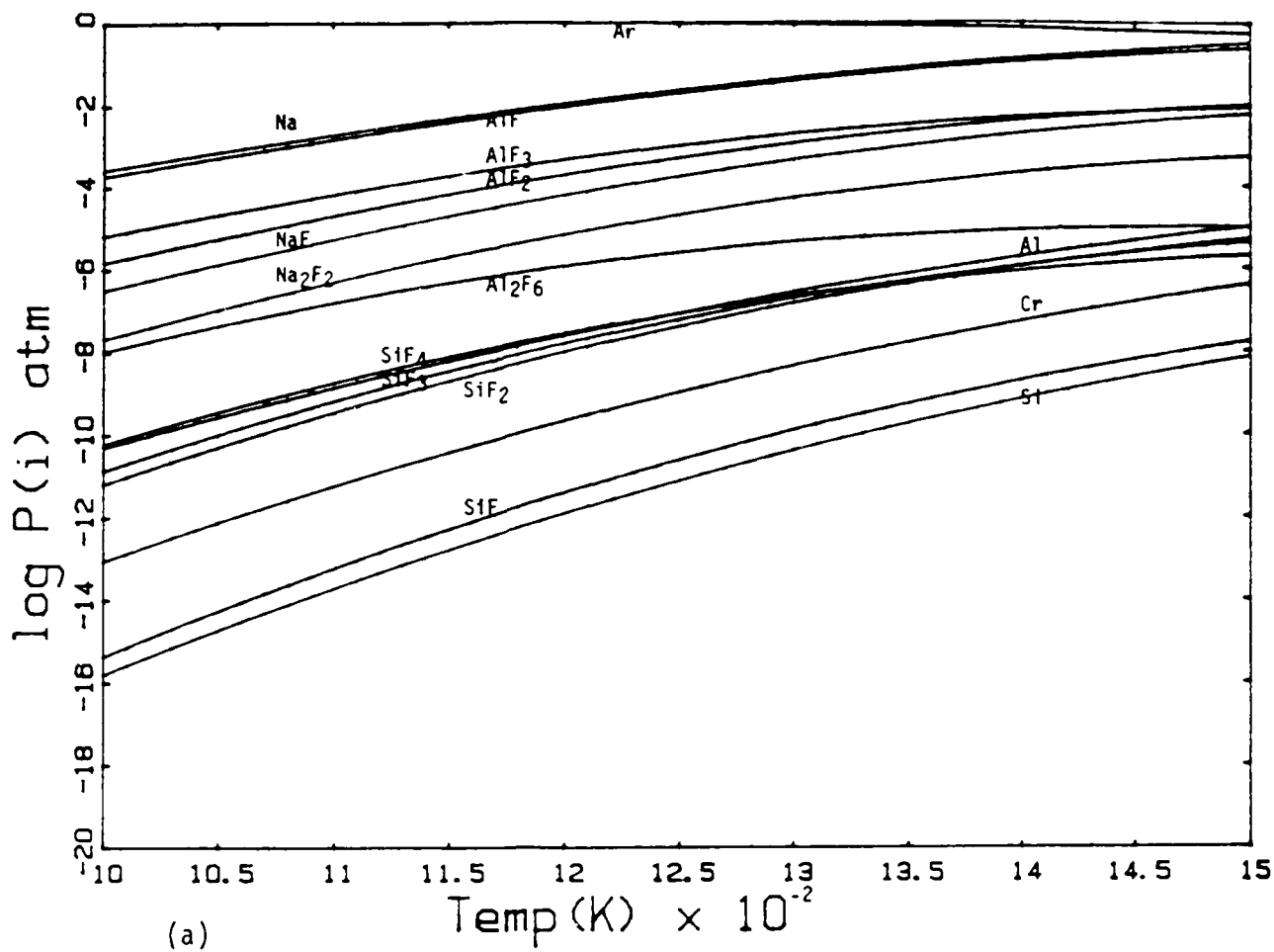
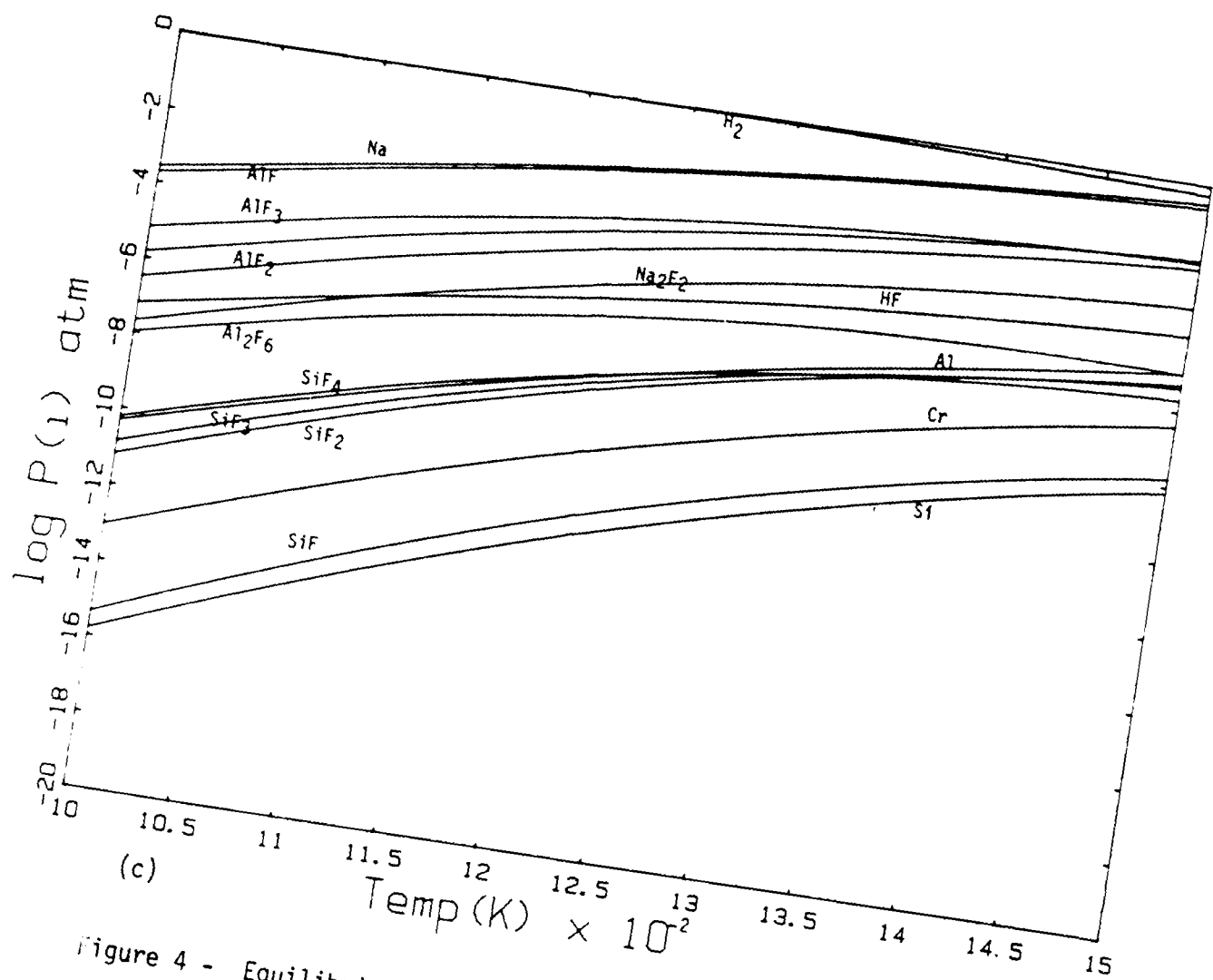
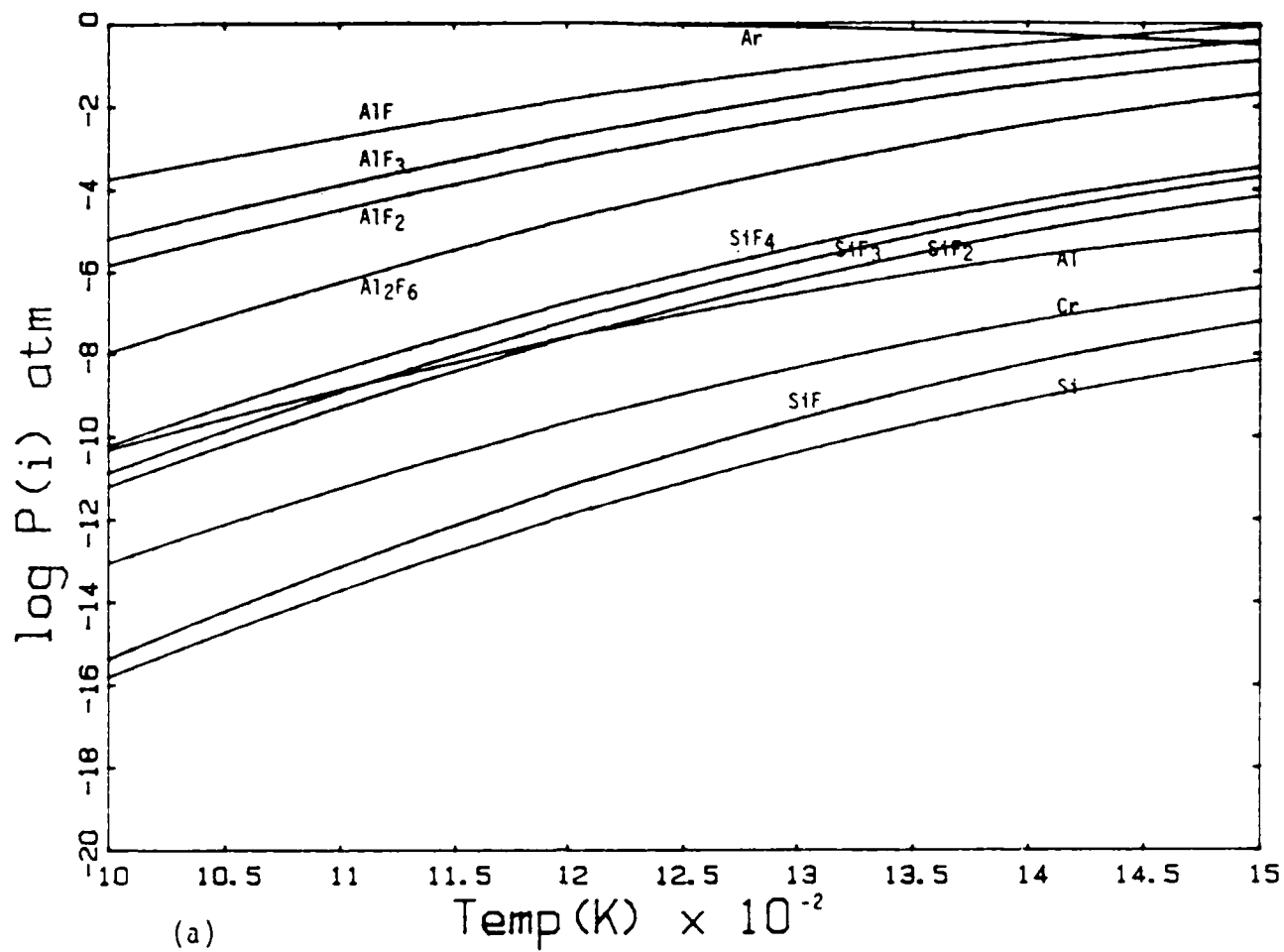


Figure 3 - Equilibrium Partial Pressures of Gaseous Species in AlCl_3 -Activated Pack Containing Al, Cr, and Si in (a) Ar, (b) 5% H_2 + Ar, and (c) H_2 .

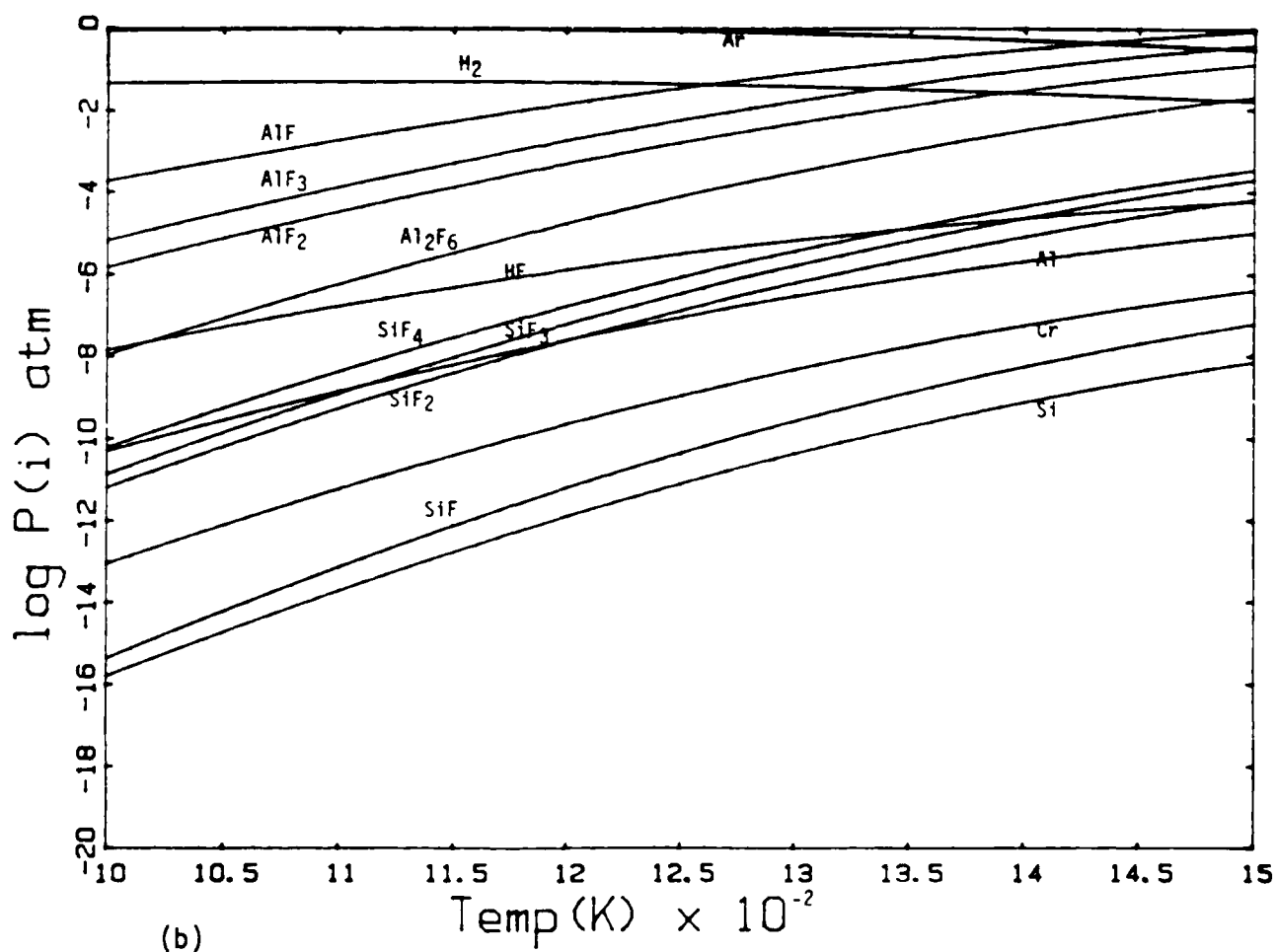




(c)
 Figure 4 - Equilibrium Partial Pressures of Gaseous Species in NaF-Activated Pack Containing Al, Cr, and Si in (a) Ar, (b) 5% H₂ + Ar, and (c) H₂.



(a)



(b)

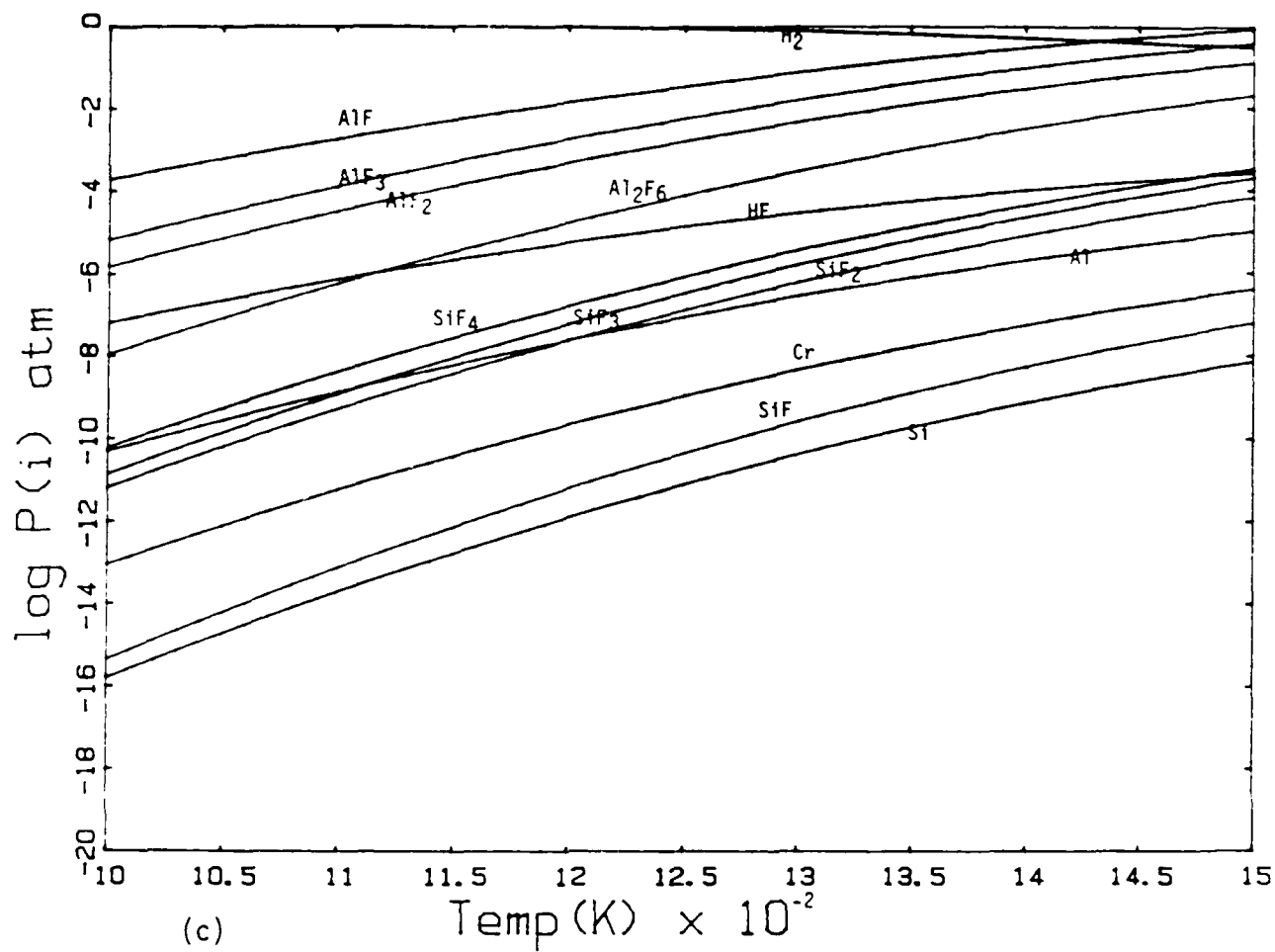


Figure 5 - Equilibrium Partial Pressures of Gaseous Species in AlF₃-Activated Pack Containing Al, Cr, and Si in (a) Ar, (b) 5% H₂ + Ar, and (c) H₂.

END

DATE

FILMED

5-88

DTIC