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Metal hydride research is becoming a rapidly growing branch of materials science, due in part to the challenges presented by this field for modifying metal hydrides in such a way as to make them truly useful. Binary metal hydrides have of course been known for a very long time, but it was not until about ten years ago, with the discovery of the  $AB_5$  compounds, at the Phillips Laboratories in Eindhoven, that intermetallic hydrides with truly unusual properties began to be developed. These properties are now very familiar to us: (1) the hydrogen dissociation pressures are one to several atmospheres near ambient temperatures; (2) the kinetics of absorption and desorption are extremely rapid, in many cases being limited by the heat transfer characteristics of the materials; (3) the reactions are thermally reversible; (4) the amount of hydrogen stored in these materials is very large, approaching in many cases the volumetric density of liquid hydrogen itself. The intermetallic hydrides are therefore essentially unique in all of chemistry, particularly in displaying thermally reversible reactions with good kinetics. Their ability to store very large amounts of hydrogen is an added bonus.

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All these facts were known, in the early 1970's and it was natural to ask "What can be done with these materials? They are certainly interesting from a scientific point of view; they have fascinating physico-chemical properties; but will they remain laboratory curiosities?" In part, the burden of this paper is to review those factors one must learn to control in order to modify the materials to make them useful. We want to be able to do a kind of materials engineering that will enable one to tailor the properties of the materials for specific tasks. Essentially, that is the problem we faced when we began to work in this field. We had to ask ourselves the question: "What modifications of metal hydrides are required to make these materials optimally useful in particular applications such as chemical heat pumps?" The solution to this problem has turned out to be more generally applicable to other types of metal hydrides than originally anticipated. By gaining an understanding of the factors controlling the free energies of formation of the hydrides, one can, in fact, modify the alloys in such a way as to impart certain desired properties.

The familiar phase diagram of the LaNi<sub>5</sub>-H<sub>2</sub> system is shown in Fig. 1. The diagram is characterized by so-called alpha and beta regions with a rather flat plateau in the region where the alpha phase is being converted to beta. Another characteristic is the increasing hydrogen pressure with increasing temperature. Hysteresis loops are associated with the adsorption and desorption of hydrogen.

The compound,  $\text{LaNi}_5$  has created so much interest, in part because the hydrogen dissociation pressures are in the range of from one to ten atmospheres at temperatures between  $15^\circ\text{C}$  and  $75^\circ\text{C}$ .

It occurred to us sometime ago that the  $\text{AB}_5$  hydrides could be useful for chemical heat pump systems. A chemical heat pump is essentially a thermally activated engine. With a pair of hydrides having different dissociation pressures at some given temperature, one can, by applying a thermal gradient, cause hydrogen to be transferred from one to the other, and therefore construct a "chemical" heat pump which functions in the same way as an absorption refrigerator whose essential components are a generator, a condenser, an absorber and an evaporator (Fig. 2). To make such a system work it is essential to have a pair of metal hydrides possessing very specific properties.

How do we obtain the right pair of metal hydrides? If we examine a series of van't Hoff plots (Fig. 3) displaying the logarithm of the hydrogen dissociation pressure plotted against the inverse of the absolute temperature, one has a series of straight lines with different slopes. The different slopes, of course, reflect different enthalpies of hydriding, each one characteristic of a particular metal hydride. We wish to construct a chemical heat pump operating in a temperature regime convenient, for example, for solar energy applications having a high temperature input of about  $100^\circ\text{C}$  and a low temperature input of perhaps 4 to  $10^\circ\text{C}$ . In that temperature regime, it is easy to see that the enthalpies of the hydrides useful for

such a device are limited to a very narrow range of values. In order not to be burdened with thick walled vessels, one does not want to operate at pressures that are excessively high, but prefers to be in about the one atmosphere to ten atmosphere pressure range, thus again narrowing the choice of the range of enthalpies of hydriding to between 7 and 10 kcal/mole of hydrogen absorbed.

Surveying the periodic table of elements, we find that the binary hydrides fall essentially into two classes: those too stable for our purposes, such as  $\text{CaH}_2$  or  $\text{TiH}_2$  on the one hand, and the unstable hydrides such as  $\text{FeH}$  and  $\text{NiH}$  on the other. The intermetallic hydrides, because they are composed of elements forming stable and unstable hydrides, bring the enthalpies into a very convenient range for our purposes. If we examine the thermodynamics for the operation of a chemical heat pump in more detail, we find essentially three types of situations (Fig. 3.). First, the pair of metal hydrides can have different slopes, that is, different enthalpies, but the same entropy. Second, they could have different slopes and different intercepts, that is, different enthalpies and different entropies. Third, they could have the same slope and different intercepts, or the same enthalpies but different entropies. One could operate with materials having any of these different enthalpy-entropy characteristics, but the optimal heat pump action would occur for the situation in which the enthalpies of the two hydrides are different, and the entropies are the same. Furthermore, if we examine the relationships between the enthalpies and the

temperatures, we find that the ratio of the enthalpies of the pair of hydrides  $\Delta H_{m_1} / \Delta H_{m_2}$  is equal to the ratio of the (absolute) high and intermediate temperatures,  $T_h / T_m$ , over which one wishes to operate the heat pump. Once a temperature regime has been chosen, the ratio of the enthalpies of the two hydrides is fixed by the laws of thermodynamics. These relationships are universally applicable to all chemical heat pump systems, whether based on hydrides or ammoniates or alcoholates. Another relationship that can be derived is that the square of the intermediate temperature is equal to the product of the high and low temperatures,  $T_m^2 = T_h \times T_l$ . We can use these equations to determine the values which the enthalpies of the pair of hydrides have to have. Table I gives some illustrative calculations of this sort. If one wants to operate at a rejection temperature of 50°C, and have a high temperature input of 109°, then the low temperature is fixed at 0°C. The second hydride has to have an enthalpy of 8.3 kcal/mole if the first hydride has an enthalpy of 7 kcal/mole. In other words, if  $\Delta H_{m_2}$  is chosen to be that of  $\text{LaNi}_5\text{H}_6$ , then the other hydride has to have an enthalpy of 8.3 kcal/mole in order to operate the heat pump with an optimum C.O.P. in a temperature regime with  $T_m = 50^\circ$ ,  $T_l = 0^\circ$ , and  $T_h = 109^\circ\text{C}$ . And so it goes: the lower the temperature from which one wishes to pump heat, the higher the input temperature and the higher the enthalpy of the second hydride has to be. For pumping from -10°C, the enthalpy would have to be 8.6 kcal/mole while for pumping from -20°C, it would have to be 8.9 kcal/mole of  $\text{H}_2$  absorbed.

These examples illustrate how closely one needs to control the thermodynamic properties of the pair of hydrides in order to use them in an optimal fashion in a chemical heat pump. The first problem one faces in trying to put this idea into practice is to be able to "manufacture" hydrides having appropriate enthalpies and entropies.

How can this be done? When we first began work on this question about five years ago, the answer was unknown. We did know that there were a number of properties that influence to some degree the free energy of hydride formation, and therefore the hydrogen dissociation pressures. Among these are, in the case of  $\text{LaNi}_5$ , the lanthanum to nickel ratio, as determined by the Eindhoven group. In surveying the literature, one found studies of the thermodynamic properties of quite a few of the  $\text{AB}_5$  series of compounds. Plotting the logarithm of their dissociation pressures against the crystallographic cell volume, one obtained a reasonably good correlation, reminiscent of the interstitial-hole volume relationship found by Lundin, for example, at the Denver Research Institute a number of years ago. This correlation was observed not only in the  $\text{AB}_5$  system, but in other intermetallic hydride systems as well.

The crystal structure of  $\text{LaNi}_5$  may be described in terms of two different layers: one layer contains both La and Ni atoms; the other layer is composed entirely of Ni atoms, and so on.

When one substitutes Group IIIA or IV metals--Aluminum, Gallium, Indium, Silicon, Germanium and Tin, for Ni in the  $\text{AB}_5$  structure, the atoms of these elements go into the second layer, the

one which in  $\text{LaNi}_5$  is composed only of Ni atoms.

Austin Dwight, working at the Argonne Laboratory, found a number of years ago, that the element Al substitutes for Ni in  $\text{LaNi}_5$  and is particularly effective in increasing the cell volume of  $\text{LaNi}_5$  because aluminum is a larger atom than Ni. The cell volume for the composition  $\text{LaNi}_4\text{Al}$  relative to  $\text{LaNi}_5$  has increased some 4 to 5 percent (Fig. 4).

The result of such substitutions on hydride properties is shown in Fig. 5 and 6 and in Table II. The composition  $\text{LaNi}_{4.6}\text{Al}_4$  for example has a substantially lower hydrogen decomposition pressure than  $\text{LaNi}_5$ :  $\sim 1$  atm at  $48^\circ\text{C}$  compared to  $\sim 5$  atm for  $\text{LaNi}_5$ .

A systematic study substituting Al for Ni was carried out. It turned out that the enthalpy of hydriding is a linear function of the Al content (Fig. 7). Since there is also a linear relationship between the Al content and the cell volume, the enthalpy changes linearly with either the Al content or the cell volume. Furthermore, the entropy changes in these reactions are virtually identical across the series of Al-substituted intermetallics and therefore the logarithm of the hydrogen dissociation pressure which is proportional to the free energy change is a linear function of the Al content as well. It is possible then to change the hydrogen dissociation pressure at some given temperature by almost three orders of magnitude by going from  $\text{LaNi}_5$  to  $\text{LaNi}_{3.5}\text{Al}_{1.5}$  in a continuous fashion. One therefore has a sensitive means of control over a parameter which is so important for heat pump applications. Analogous work has been done by us with all of the

Group IIIA and IVA elements. All behave similarly in a qualitative sense but differ in some details associated with specific chemical bonding and electronic factors. The salient result of this work is that we now know, by changing the chemical composition of the hydrides, how to "tailor" the thermodynamic properties and therefore, the hydrogen dissociation pressures, to an extent that enables us, in fact, to build a chemical heat pump.

The HYCSOS Metal Hydride Chemical Heat Pump System is shown in Fig. 8. There are four vessels containing 10 pounds each of the appropriate hydride filling the interstices between four nesting coils of tubular heat exchangers. The four vessels constitute the four elements of an absorption refrigerator referred to earlier. The status of this system has progressed to an engineering development effort which is being carried out industrially.

Another and totally different application of hydrides is in a very low pressure regime, as low as  $10^{-11}$  or  $10^{-12}$  atms. Of course, the more stable the hydride, in a thermodynamic sense, the lower the dissociation pressure. In the case of the heat pump systems, we were working with materials with enthalpies of 7 to 10 kcal; but for materials like zirconium hydride, the enthalpies are ~40 kcals, making the hydrogen dissociation pressure so low, that the substances are in fact hydrogen getters.

One often needs to pump hydrogen down to very low partial pressures in vacuum systems, and one may employ a hydrogen getter for this purpose. The materials suitable for such an

application must have very special characteristics. As stated earlier, many elements and compounds form stable hydrides but very few of them perform the functions of "bulk" getters which implies an ability to absorb hydrogen at ambient temperatures with good kinetics. Sublimed titanium, for example, can be an active hydrogen getter, however, once the surface of that film has been saturated with hydrogen, the bulk of the titanium will react with hydrogen only very slowly. A material that has been available commercially as a bulk hydrogen getter is ST-101, an alloy of Zr and Al made by SAES Getters, in Milan, Italy.

We have developed a new family of hydrogen getters that give one a similar kind of flexibility in terms of hydrogen pumping in vacuum systems that one now has in chemical heat pump applications.  $ZrV_2$  forms a well-known Laves phase hydride. Replacing some of the V in  $ZrV_2$  with Fe, just as substituting some of the Ni with Al in the  $AB_5$  compounds, changes the hydrogen dissociation pressures and thus modifies the thermodynamics of the hydrogen reaction in a very well defined way. If one plots the cell volume versus the enthalpy, one observes linear behavior. Since the Fe additions change the cell volume, changes in the hydrogen decomposition pressure are induced analogous to the situation in the  $LaNi_{5-x}Al_x$  system. This effect is shown in the three curves in Fig. 9 representing three different ternary Cr substitutions in  $ZrV_2$ . Very similar observations were seen with Fe substitutions. Substituting Cr for V in the  $ZrV_2$  phase increases the hydrogen dissociation pressure in a predictable way. However, the

situation with the Laves phase hydrides is quite different than in the case of the  $AB_5$ 's. Because one does not have an alpha-beta transformation, there is a continuous range of solid solutions as hydrogen is added to  $ZrV_2$  perserving the alpha pahase over the entire composition range. Consequently there is no plateau region and the pressure continuously increases with increasing H/M ratio.

But the pressures are in a very convenient and interesting range for getter applications. In Fig. 10 we have compared ST-101, the material that I mentioned as the only commercially available hydrogen getter, with these two Fe-andCr-substituted Laves phase alloys.

There are certain applications for hydrogen getters which require one to operate in a particular temperature regime, both for pumping and for regenerating the getter, for example, for in-torus pumping in a Tokamak fusion device. The Tokamak Fusion Test Reactor (TFTR) now under construction at the Princeton Plasma Physics Laboratory near Princeton, New Jersey is designed to demonstrate break-even fusion. In this machine one needs to getter hydrogen isotopes to minimize hydrogen recycling. Both deuterium and, in the later stages of operation of this machine, tritium as well need to be pumped. Since the gettering is being done in the torus of the Tokamak, one would like the temperature at which the regeneration takes place to be, say  $400^\circ\text{C}$ . One therefore searches for a material that can getter hydrogen at  $200^\circ\text{C}$  and which could be regenerated at  $400^\circ$ . Comparing the pressure composition characteristics of ST-101 (the straight line), with the points representing

the situation for the Cr and Fe substitutions in Laves phase alloys (Fig. 10) it is seen that the latter may have pressure temperature characteristics desirable for Tokamak applications. Again, we have achieved a degree of flexibility in tailoring hydride materials, this time for getter applications.

The present situation in the field of metal hydrides is rich in potential applications. There are storage applications; there are the thermal energy applications, such as heat pumps, thermal to electric converters and compressors. Other possible uses involve getters, selective hydrogen absorbers, hydrogen purifiers, and various applications in nuclear reactors as moderators and hydrogen scavengers. Targets in rotating neutron sources and storage materials for tritium are applications already in use. Other possibilities include uses for deuterium isotope separation. The power of the intermetallic hydrides to act as hydrogenation catalysts has already been demonstrated and hydrides as superconductors have received a good deal of attention.

Where is intermetallic hydride research going in the 1980's? One needs to discover in more detail the relationship between thermodynamic, kinetic, structural and compositional properties. That is certainly a large and formidable task. We would like to be able to synthesize new and possibly lightweight and less expensive intermetallic hydrides for automotive applications. This will depend on the development of entirely new hydride materials using novel synthetic routes. Processing of hydride materials in the amorphous state and as composites and compacts

may overcome the severe problem encountered in rapid cycling applications due to the poor heat transfer of the hydride powders. Work along those lines is going on in various laboratories. And we need breakthroughs leading to new classes of hydride materials. I am confident that we have not yet seen the end of significant discoveries in metal hydride research.

Finally, I would like to conclude by making just a few brief observations about the future of hydrogen.

I think that metal-hydrides are part of the overall hydrogen economy: hydrogen as a fuel and as an energy carrier. Historically, one of the problems with hydrogen has been the public perception that hydrogen is so dangerous a material that it can never safely be used as an energy carrier. The Columbia spaceship may represent a turning point in this perception. I listened to the television broadcast of the Columbia take-off, and I was impressed by the fact that none of the reporters mentioned that half the power to the spacecraft was provided by hydrogen. The technological breakthrough represented by pumping 100,000 gallons of liquid hydrogen into the propulsion engines, burning it with oxygen in a completely controlled way, providing 5 million pounds of thrust, two pounds for every pound of weight on the rocket is staggering. Eventually, however people will become aware of the fact that several times a year, a critical component of the largest space effort in the U.S. is powered by hydrogen. And therefore, I feel that hydrogen will become environmentally less threatening

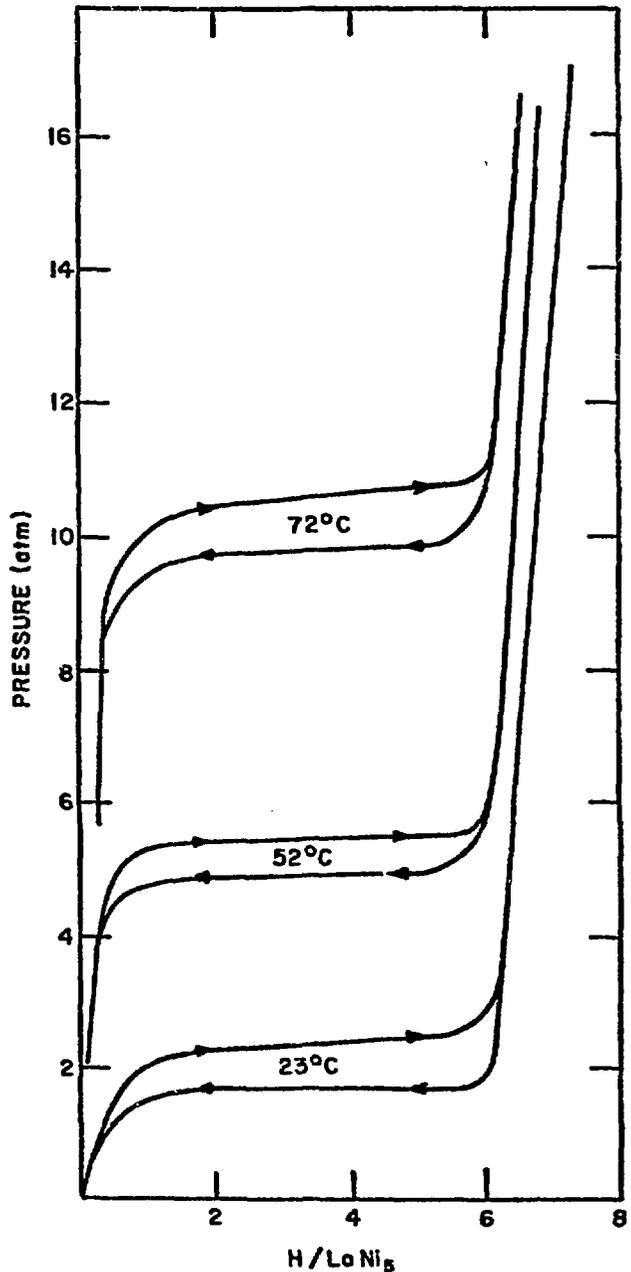
as it will be shown to be safe if proper precautions are taken. One can anticipate metal hydrides to play an important role in the safe handling and use of hydrogen. Let's hope so--they are among the most fascinating substances on which to do scientific research!

**Acknowledgement:**

My colleagues George Lamich, Marshall Mendelsohn and Irving Sheft in the Chemistry Division of Argonne National Laboratory have participated in all aspects of the work described above.

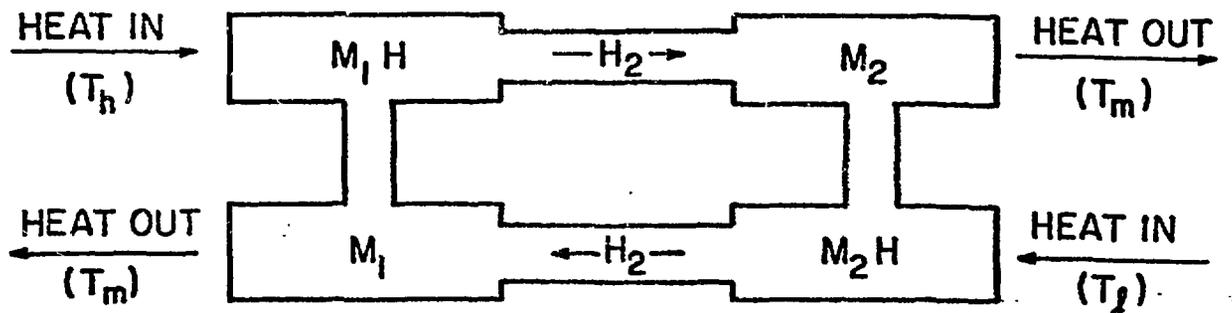
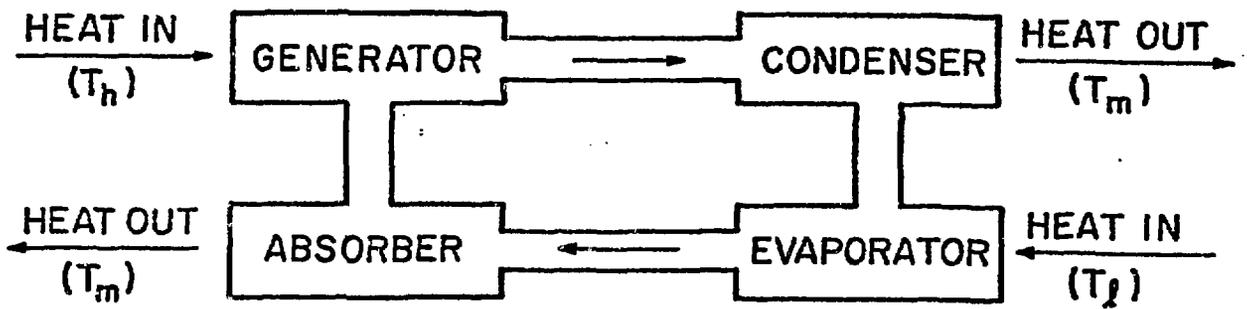
### Figure Captions

- Fig. 1. Absorption-desorption isotherm for  $\text{LaNi}_5 + \text{H}_2$ .
- Fig. 2. Two metal hydride refrigerator cycle.
- Fig. 3. Three examples of chemical heat pump thermodynamic relationships.
- Fig. 4. Cell volume *vs* Al content in  $\text{LaNi}_{5-x}\text{Al}_x$ .
- Fig. 5. Desorption isotherms for  $\text{LaNi}_{4.6}\text{Al}_{0.4}$ .
- Fig. 6.  $\log P_{\text{plateaus}}$  *vs*  $1000/\text{temperature}$ .
- Fig. 7.  $\Delta H$  *vs*  $X$  in  $\text{LaNi}_{5-x}\text{Al}_x$ .
- Fig. 8. HYCSOS Metal Hydride Chemical Heat Pump.
- Fig. 9. Composition (Torr-liter  $\text{H}_2/\text{gm}$  alloy) *vs* pressure (atm).
- Fig. 10. Composition (Torr-liters  $\text{H}_2/\text{gm}$  alloy) *vs* pressure (atm).



Absorption-desorption isotherm for LaNi<sub>5</sub> + H<sub>2</sub>.

Fig. 1.



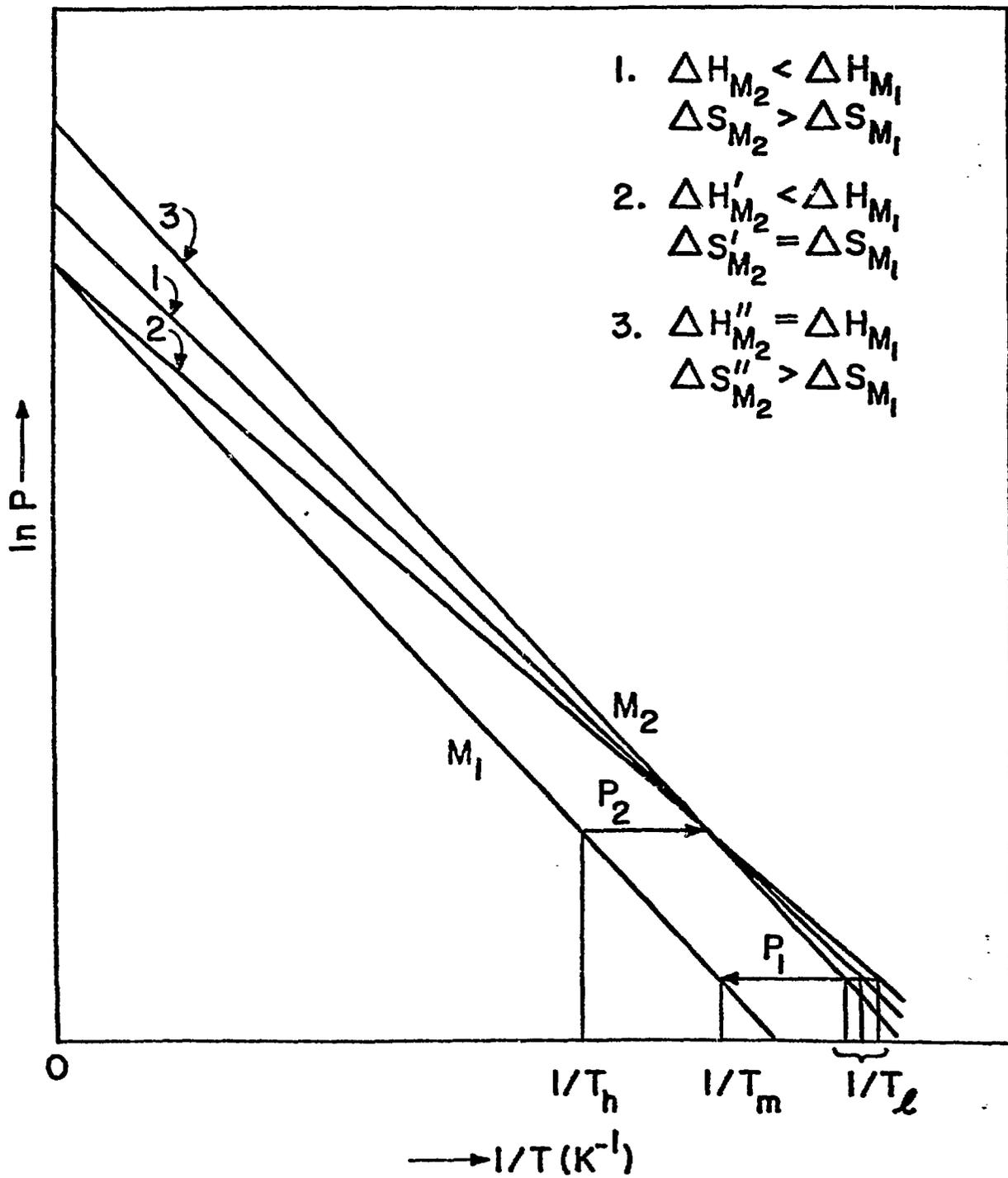


Fig. 3

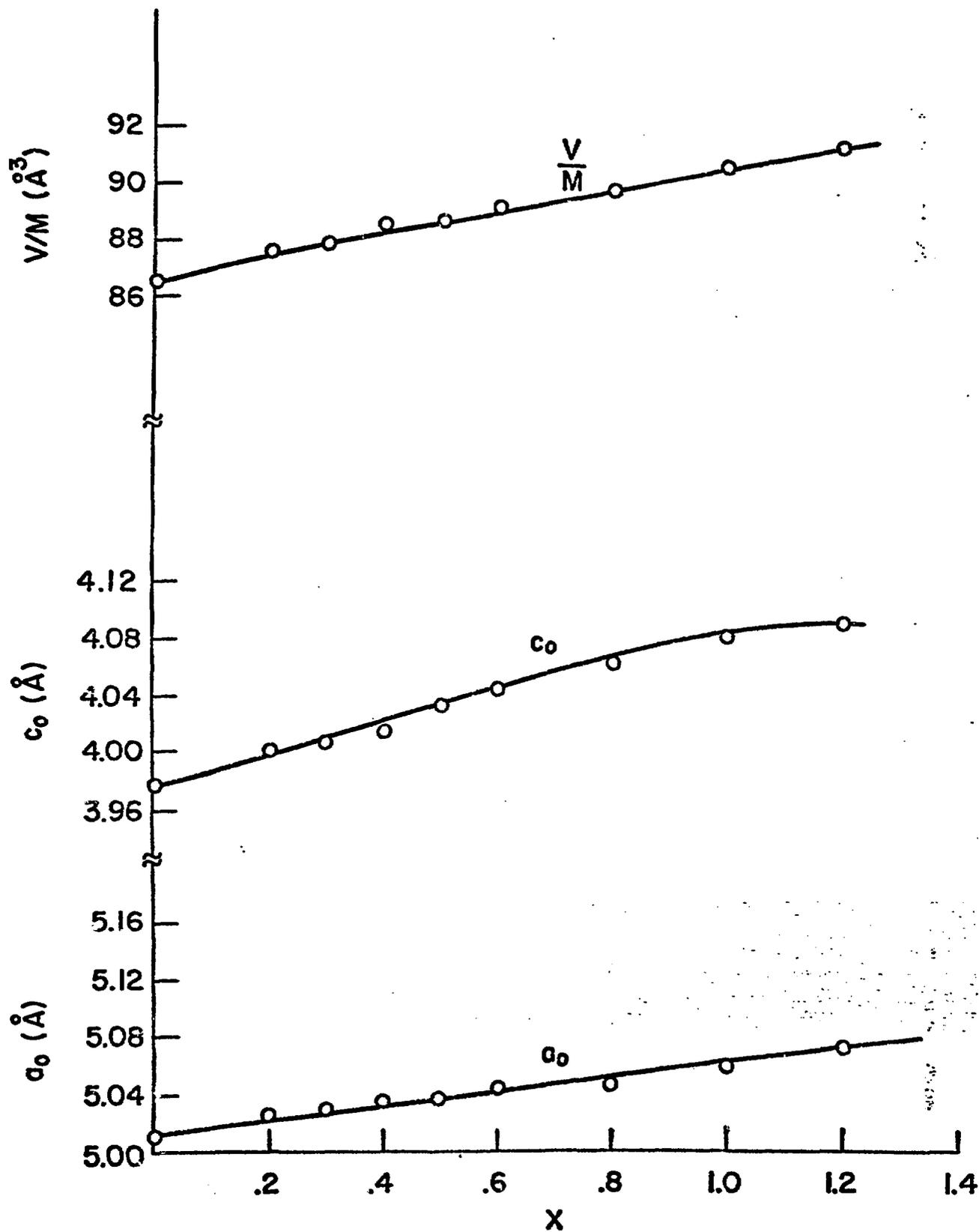


Fig. 4.

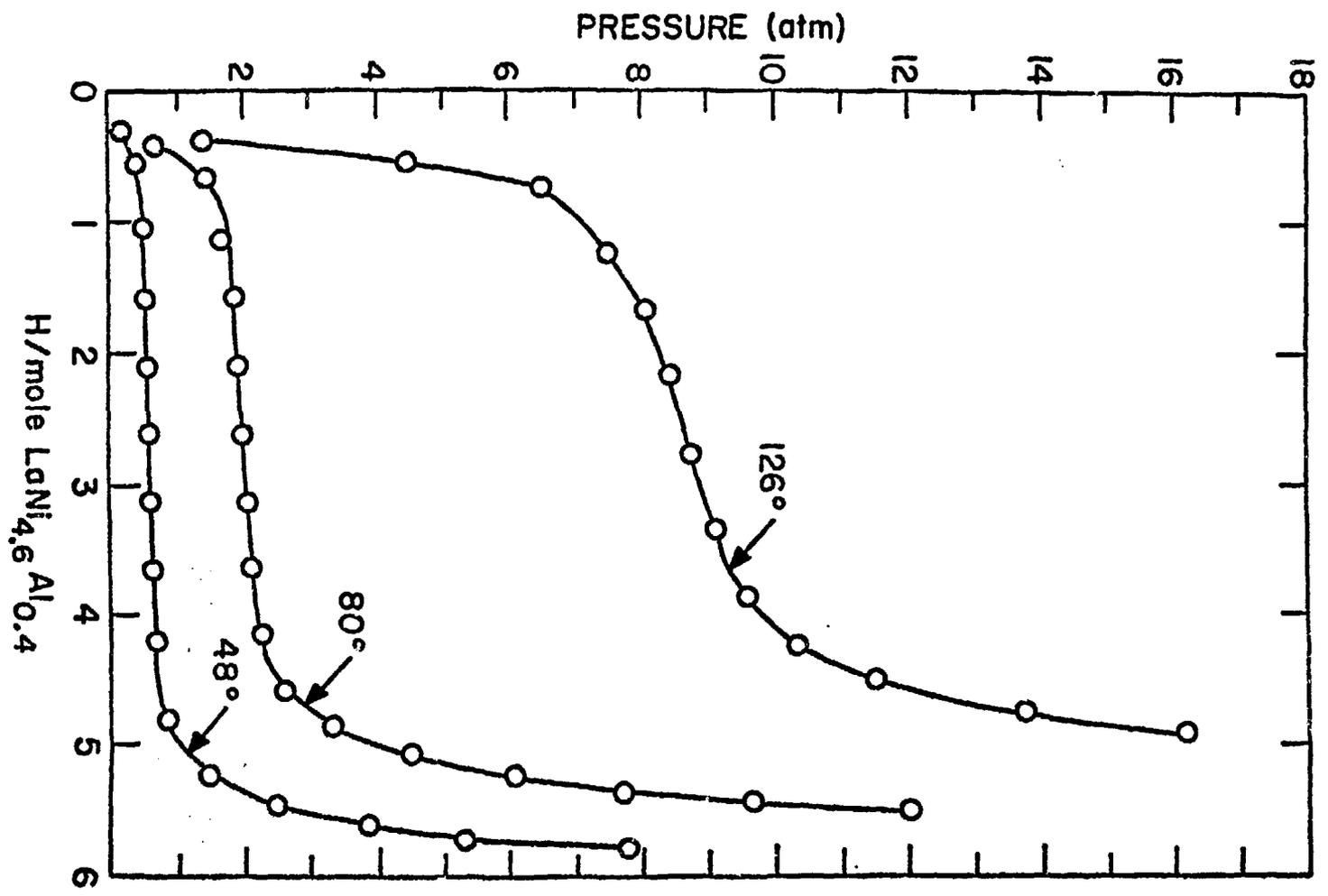


Fig. 5.

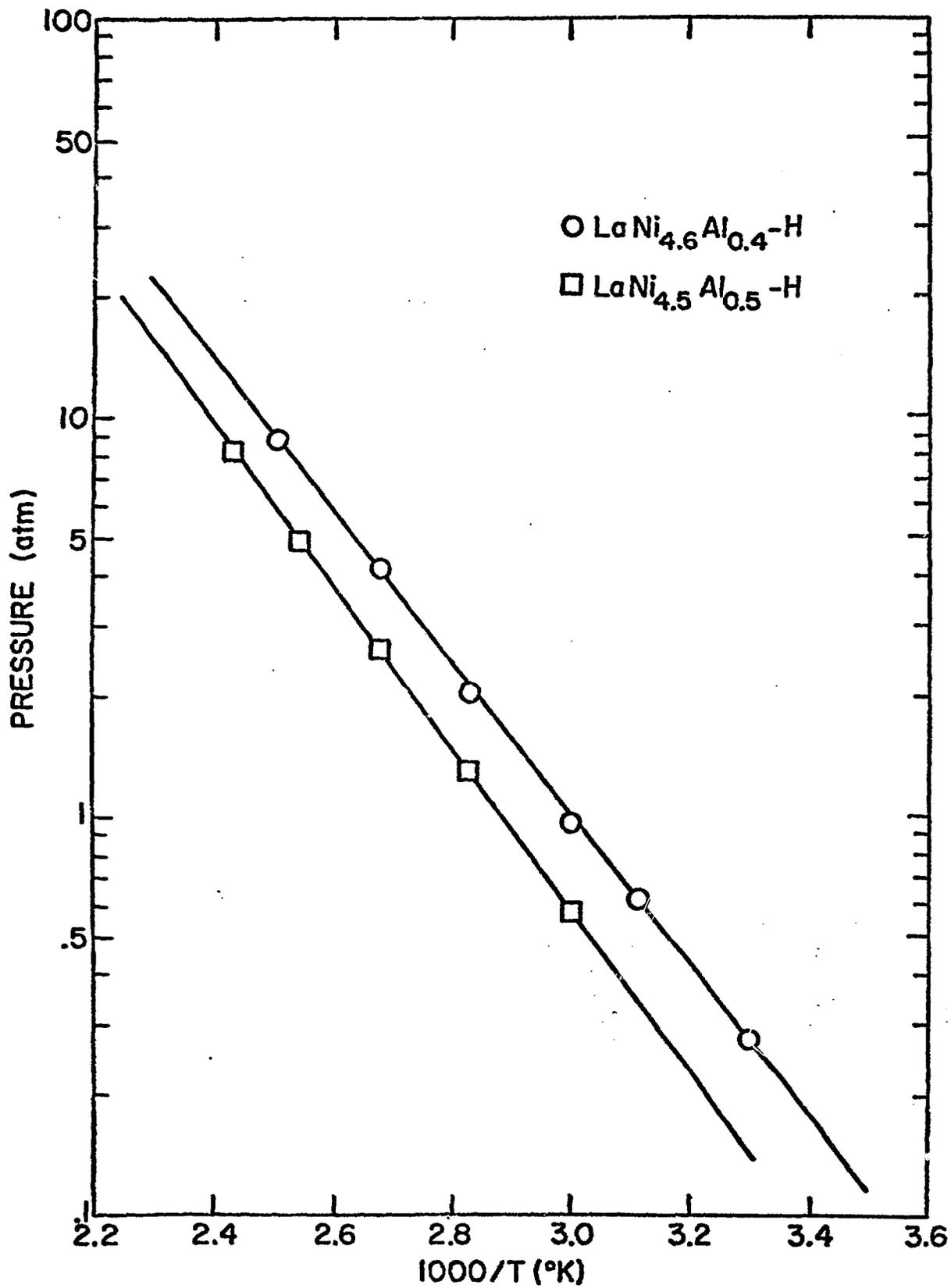


Fig. 6.

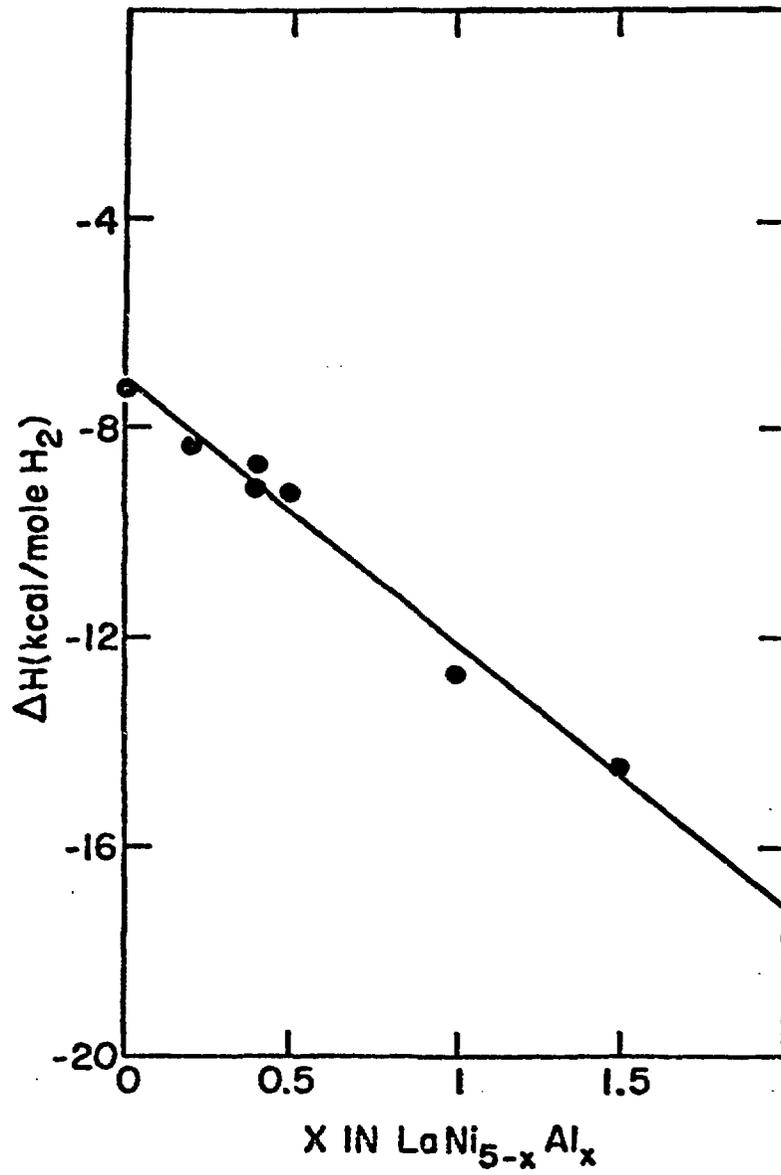


Fig. 7. }

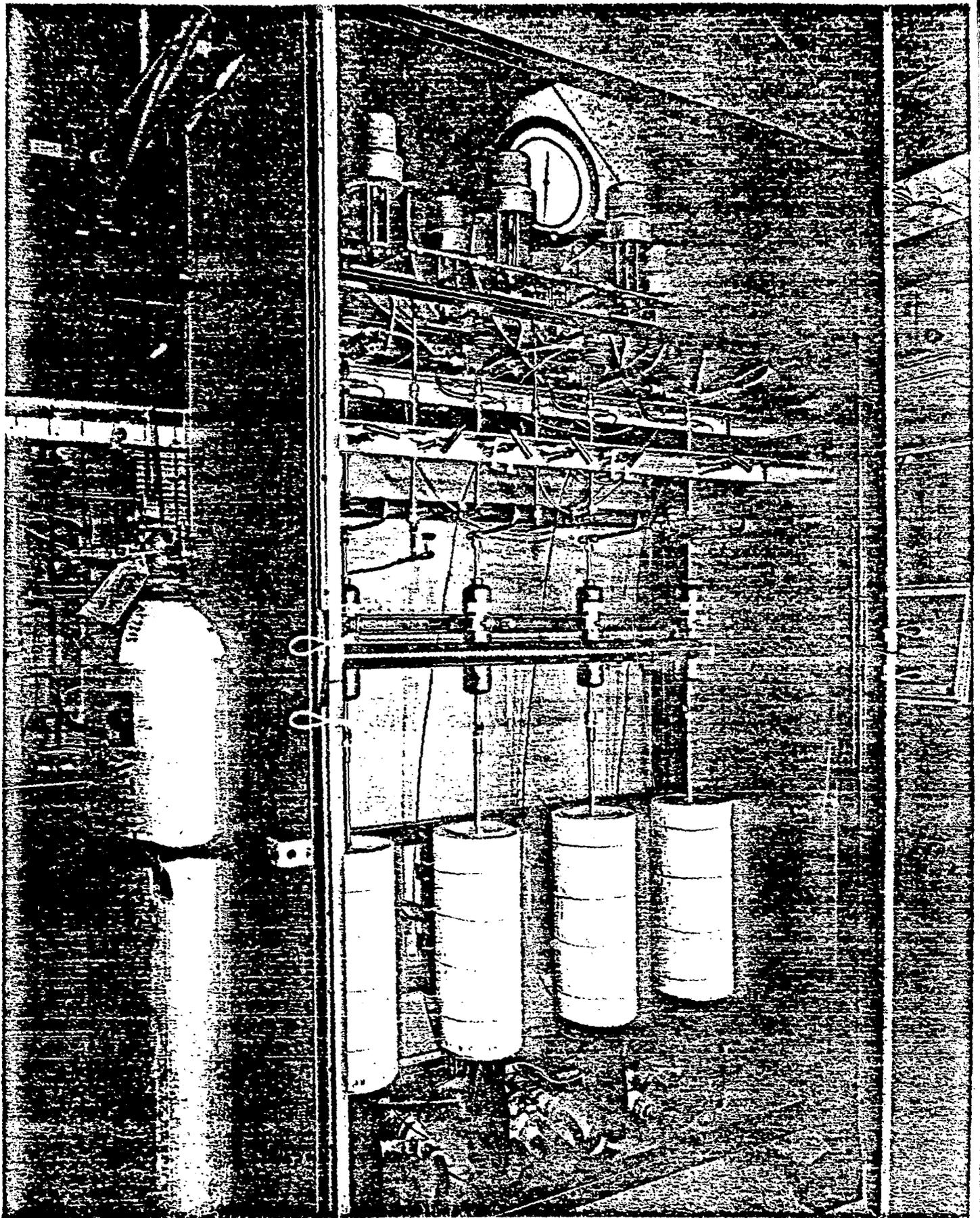


Fig. 8.

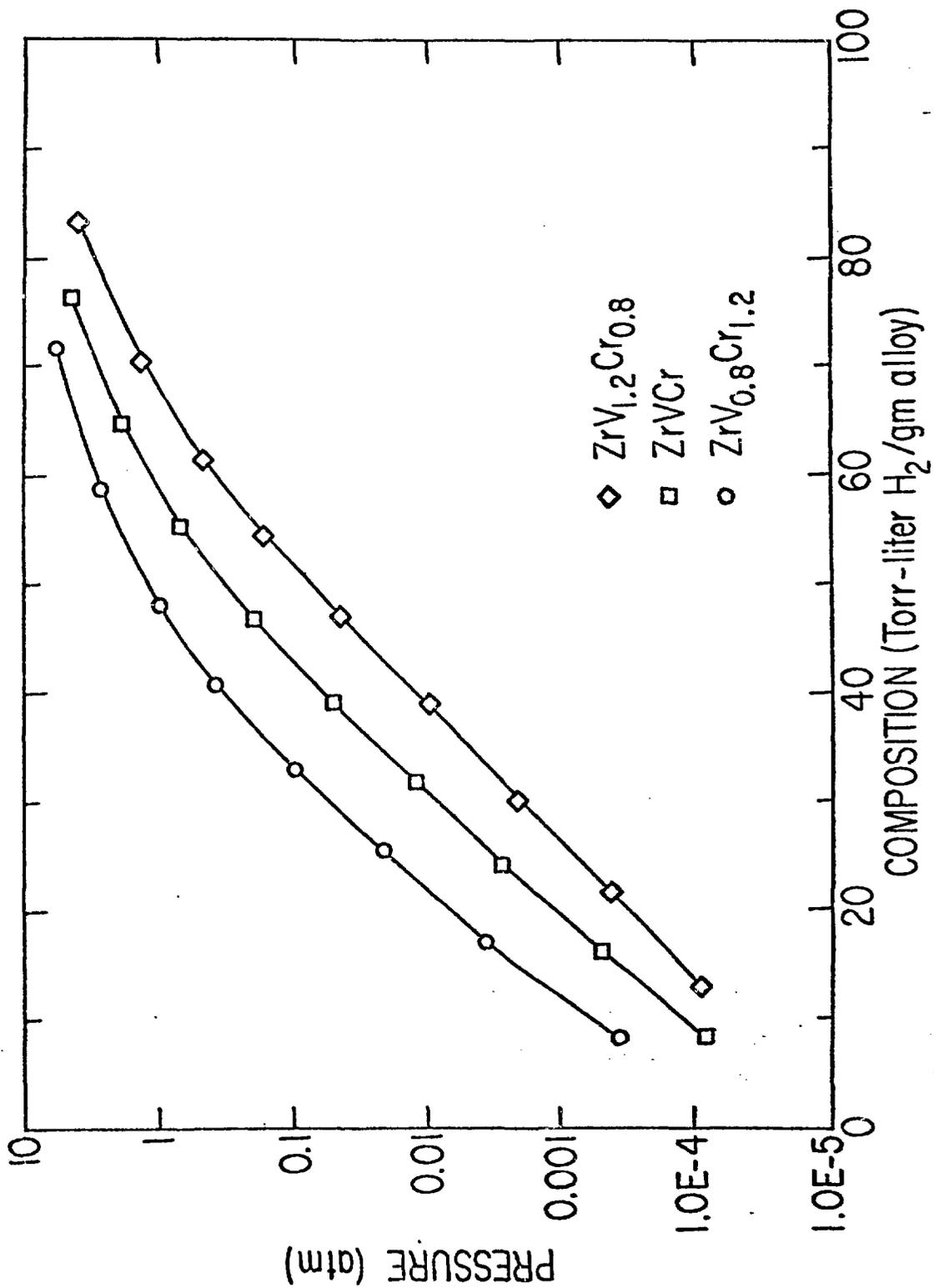


Fig. 9.

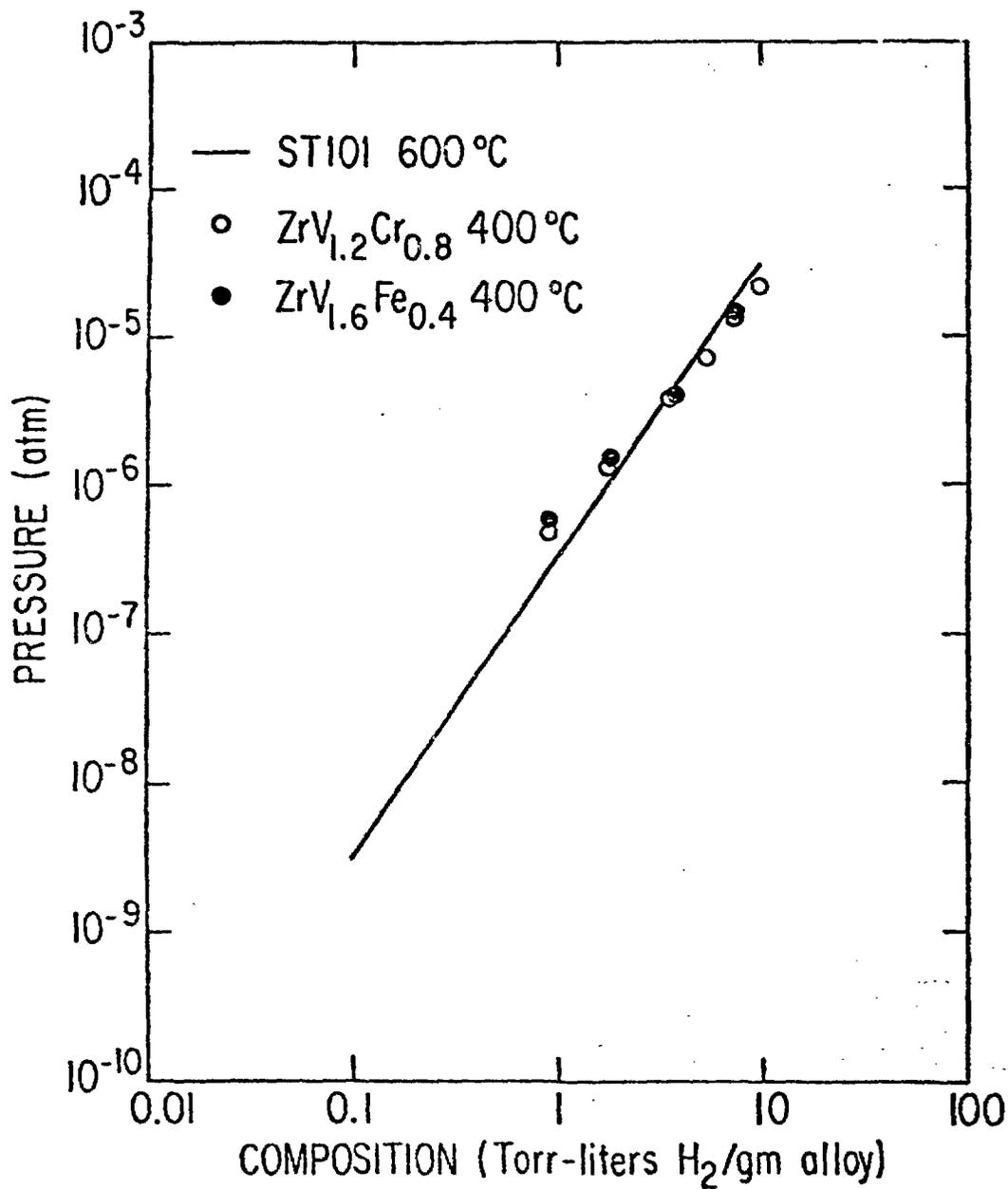


Fig. 10.

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