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THE ABSORPTION SPECTRA OF METAL-AMMONIA SOLUTIONS

Berkeley, California

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THE ABSORPTION SPECTRA OF METAL-AMMONIA SOLUTIONS

William L. Jolly, Calvin J. Hallada and Marvin Gold

November 1963

The Absorption Spectra of Metal-Ammonia Solutions

(with an addendum on the calcium-ammonia phase diagram)

by

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Introduction

I believe that most of us would agree that very dilute solutions (say 10^{-6} M) of metals in liquid ammonia contain principally ammoniated metal ions and ammoniated electrons which are independent of one another. The question is: what happens when such dilute solutions are made more concentrated? Long ago, Kraus[1] pointed out that conductivity data could be explained in terms of an equilibrium between the ionic species and neutral metal atoms:

$$M^+ + e^- = M.$$

This equilibrium adequately accounted for the behavior of moderately dilute metal-ammonia solutions until it was found that the molar magnetic susceptibility of these solutions decreases with increasing concentration. These latter results were explained by Huster[2] and Sugarman and Freed[3] in terms of an equilibrium between the ionic species and diamagnetic metal atom dimers:

$$2M^+ + 2e^- = M_2.$$

More recently, Becker, Lindquist and Alder[4] showed that the conductivity data and the susceptibility data could be explained by considering both of

the above equilibria. They reported equilibrium constants which indicated that the relative concentrations of the species e^-, M, and M_2 are changing quite rapidly with concentration in the region of 0.01 M. We began measuring the absorption spectra of metal solutions in this same concentration region with the hopes of being able to distinguish the absorption spectra for each of the species and of being able to evaluate the equilibrium constants independently.

The ammoniated electron, e^-, has been described by Ogg[5] and others as an electron in a large cavity. The system is stabilized by the orientation of ammonia molecules on the perifery of the cavity, with the hydrogens pointing inward so as to create a virtual positive charge in the center to hold the electron. Becker Lindquist and Alder[4] described the monomer, M, as an ammoniated metal ion with the electron circulating in an "expanded orbital" on the protons of the coordinated ammonia molecules. These same authors described the dimer, M_2, as a pair of ammoniated metal ions held together by two electrons in a molecular orbital situated largely between the two ions. In view of the above descriptions of the three species e^-, M, and M_2, it seemed reasonable to us that they would have distinctly different absorption spectra.

In this paper I would like to outline our spectrophotometric measurements and to indicate the conclusions that we drew from the results. Complications caused by the formation of two liquid phases arose in the case of calcium solutions, and I would like to conclude by presenting our ~~presenting our~~ preliminary results on the calcium-ammonia phase diagram.

The Absorption Spectra[6]

The first apparatus used in our spectral studies (Apparatus I) is shown in Figure 1. The solution in the absorption cell was maintained at -70° by packing the upper dewar-like chamber with dry-ice so that the solution continuously refluxed. The cell path-length was about 0.5 mm. Smaller path-lengths were not possible with this type of reflux-cooling because of poor circulation of the solution between the cell windows. When path-lengths of about 0.05 mm. were tried in this type of apparatus, the heat generated by the light beam caused bubbles to form between the windows. Since we were thus restricted to a rather long path-length, we could study only very dilute solutions (ca 10^{-3} and lower) in the region of the absorption peak. However we could study solutions as concentrated

as 0.1 M in the visible region of the spectrum, and in Figure 2 we have plotted the absorbancy at 4500 Å against the concentration on a log-log plot. To our great amazement, the extinction coefficients calculated from the individual points deviate from the mean by an average of only ± 1.8%. At that time we thought that perhaps the various species in solution had identical absorption spectra in the visible reason, but that in the infrared, near the absorption peak, we would find changes in the spectrum with changes in concentration.

While we were in the process of building a new type of apparatus for measuring spectra in the region of the absorption peak, Douthit and Dye[7] published a paper in which they reported that sodium obeys Beer's Law up to 0.004 M at the absorption peak. They explained this result by postulating that the monomeric species, M, is a simple ion pair, in which the absorbing species (the electron) exists in practically the same form as it does in very dilute solutions. Donthit and Dye reported that potassium shows a very marked deviation from Beer's Law behavior at concentrations between 0.003 and 0.01 M, and ascribed this deviation to dimer formation.

In spite of the publication of these results, we continued building our apparatus because we wished to extend the measurements to higher concentrations and with sufficient accuracy to permit the calculation of an equilibrium constant in the case of potassium. We also wished to study other metals, such as Li, Cs, and Ca.

Apparatus II is pictured in Figure 3. The path-length for the optical cell was 0.0214 mm. - a dimension so small as to practically prevent circulation of solution between the windows. Therefore the solutions were made up and homogenized in a side vessel and then poured over into the optical cell. The cell was kept cold by placing it in a box flushed with cold nitrogen. The auxiliary apparatus and methods of operation are described in the literature[6].

Typical absorption spectra for sodium solutions at three different temperatures are presented in Figure 4. Although there is some uncertainty as to whether or not the absorbancy on the short wavelength side of the peak increases with increasing temperature[8], it is clear that the absorption peak shifts about 12 or 13 cm^{-1} per degree toward shorter wave numbers as

the temperature is increased. Notice that the absorption curve is quite symmetrical.

The peak wavelength shifts toward longer wavelengths with increasing concentration. A plot of ν_{max} vs. A_{max} is shown in Figure 5 in which we have included the data of Douthit and Dye for more dilute solutions. It is seen that below about 0.005 M, the shift is much more pronounced than it is for higher concentrations, and that the two sets of data are in reasonable agreement where they overlap.

We found that sodium-ammonia solutions follow Beer's Law within an experimental uncertainty of ± 5% for all wavelengths between 4000 Å and the absorption peak (ca 15,250 Å), to the highest concentrations for which we were able to make measurements (0.03 M at the absorption peak and 0.25 M in the visible region). In fact, Beer's Law is obeyed up to ca 0.05 M for wavelengths between the peak and 24,000 Å, but in this wavelength region a positive deviation from Beer's Law was observed at higher concentrations. Within an experimental uncertainty of ± 10%, the absorption spectra of solutions of lithium, potassium, and cesium are identical with those for sodium solutions of similar concentration. A few of the data

are presented in the form of absorbancy-versus-concentration plots in Figures 6, 7, and 8.

In Figure 7 we have plotted a few data for calcium solutions. If we assume that calcium yields two electrons per atom, then we expect the molar extinction coefficient for calcium to be exactly twice that for the alkali metals. One observes from Figure 7 that the experimental values for the extinction coefficients are considerably less than twice that for the alkali metals. For a while we thought we had evidence for Ca_2^{2+} or Ca^+ ions. However these runs were marred by experimental difficulties, not the least of which was the fact that two liquid phases formed when making up the more concentrated solution. We have recently repeated the calcium runs, and in Figure 9 we present our results. The data show that calcium obeys Beer's Law up to 0.025 M and that the molar extinction coefficients are two times those of the alkali metal solutions at wavelengths in the vicinity of the absorption peak. Hence there appears to be nothing abnormal about the spectrum of calcium. In the last section of this paper, we describe our study of the calcium-ammonia phase diagram which was occasioned by this work.

Because Clark, Horsfield and Symons[9] reported the appearance of shoulders at 6700 and 8000 Å in the absorption spectra of ammonia solutions of sodium and sodium iodide, we repeated these measurements using higher concentrations of sodium iodide. Our results are presented in Figure 10. It will be noted that there are no indications of shoulders on the NaI + Na curve, and that the addition of sodium iodide causes the absorption peak to shift to shorter wavelengths.

Interpretation of the Spectra

How can we account for the fact that the spectra of the metal solutions are only slightly affected by changes in concentration below 0.25 M? I think it is clear that the nature of the absorbing species cannot change much over this concentration range; and since, in very dilute solutions, we must attribute the absorption process to a 1s ——> 2p transition of the electron-in-a-cavity, we are led to the conclusion that the electron-in-a-cavity retains its identity even though species such as M and M_2 are being formed. As we have mentioned earlier, this is readily explained for the M species by describing it as an ion pair in which an ammoniated metal ion

and an ammoniated electron are held together by coulombic forces with little distortion of either the ammoniated ion or the ammoniated electron. The M_2 species may be pictured as a quadrupolar ionic assembly of two ammoniated ions and two ammoniated electrons[10]. Presumably the electrons and ions are held in a square or rhombic configuration. The probability density for the electron in the ammoniated electron extends with decreasing intensity through several solvent layers. Hence the wave functions for the two electrons in the dimer will overlap sufficiently so that the singlet state will be lower in energy than the triplet by more than kT.

Apparently the ammoniated electron retains its structure in any other species which may form in metal solutions: M^-, M_2^+, M_4, etc. However, in highly concentrated solutions, one would expect that the nature of the ammoniated electrons would change because of the unavailability of sufficient ammonia molecules to properly coordinate both the metal ions and the electrons. Perhaps the deviations from Beer's Law which we observed at wavelengths around 21,000 Å for concentrations greater than 0.05 M indicate the formation of high polymers with incipient metallic bonding. If we assume that the metal

ion and the electron each coordinate six ammonia molecules, the solution will be depleted of "solvent" molecules at 2.8 M. It is interesting that at 3 M, the conductance of a sodium-ammonia solution is increasing very rapidly with increasing concentration.

The slight shift of the spectrum toward shorter wavelengths upon adding sodium iodide to a sodium solution may be due to the formation of a species such as Na_2^+:

$$Na_2 + Na^+ \longrightarrow Na_2^+ + Na.$$

Since this reaction corresponds to an increase in the concentration of unpaired electrons, it would be interesting to have quantitative data on the paramagnetic susceptibility of sodium-sodium iodide solutions.

The Calcium-Ammonia Phase Diagram[11]

In our study of the spectra of calcium solutions, we wished to use solutions as concentrated as possible while avoiding liquid-liquid phase separation. Therefore we initially determined the boundary between the one-liquid and two-liquid regions on the ammonia-rich side of the Ca-NH_3

phase diagram. The results showed that this boundary lies in the region of rather dilute solutions and that it is very steep, suggesting an extremely high consolute temperature. Our interest in this system was thereby aroused, and we made measurements on the calcium-rich side of the two-phase region as well as some attempts to determine the consolute temperature and concentration.

Low-temperature conductivity studies. - The conductivity cell pictured in Figure 11 A was used to determine the boundary between the one-liquid and two-liquid regions on the dilute side at -63.8° and - 45.0°. The composition was varied by adding and removing ammonia from the cell. The data are plotted in Figure 12. The sloping portions of the curves correspond to the single-phase regions and the horizontal portions correspond to the two-phase regions. From the points of intersection one reads off the boundary concentrations, which are 0.031 and 0.078 mole % calcium at -63.8 and -45.0°, respectively.

High-temperature conductivity studies. - The conductivity cell pictured in Figure 11B was used to determine the boundary for the compositions 0.32 and 0.44 mole % calcium. The resistance was followed while lowering the temperature.

The data are plotted in Figure 13. From the cusp-like points, one reads off the temperatures -4 and +7° for 0.32 and 0.44 mole % calcium, respectively.

Vapor pressure studies. - As one removes ammonia from an equilibrated mixture of calcium and ammonia in the two-liquid region, the vapor pressure remains constant as long as both phases are present. When all the dilute phase disappears, continued removal of ammonia causes the concentrated phase to become more concentrated with a consequent decrease in vapor pressure. When calcium hexammoniate precipitates out, continued removal of ammonia brings about no further decrease in vapor pressure until the saturated solution disappears. Further removal of ammonia should cause an abrupt drop in the pressure of ammonia to the equilibrium pressure over the Ca - $Ca(NH_3)_6$ system. Pressure measurements of the type described above were carried out in order to obtain points on the phase diagram in the more concentrated region. In the low temperature runs, the pressures were measured with an ordinary mercury manometer. In a run at 0°, the pressures were measured both with a Bourdon gage and with a differential mercury manometer

(the pressure difference between the sample and pure liquid ammonia was measured). The low-temperature data are plotted in Figure 14. These data and the data obtained at 0° yield the phase boundary compositions presented in Table 1.

Table 1.

Phase Diagram Points Obtained from Vapor Pressures

Temperature, °C.	Mole % Ca at Phase Boundaries	
− 63.5	4.8	10.0
− 45.0	4.0	10.5
− 36.0	3.8	10.7
0.0	3.25	11.0

Visual determinations. - In a sealed glass tube containing calcium and ammonia in amounts corresponding to 1.19 mole % Ca, the two liquid phases disappeared when the temperature was raised above 42° and reappeared when lowered below this temperature. In a similar experiment with a mixture corresponding to 2.44 mole % Ca, the two liquid phases persisted up to 50°.

All our data, as well as two points calculated from pressure measurements

of Okabe[12], are presented in Figure 15. It will be noted that the two-liquid region for calcium differs in two respects from the corresponding regions for the alkali metals. The consolute temperature is very much higher for calcium (>50°); and the consolute composition (which apparently lies between 1.19 and 3.25 mole % Ca) is much lower (on a mole % basis) than the average consolute composition found for the alkali metals.

Acknowledgment

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(to be placed as footnotes)

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6. Most of the experimental work discussed in this section was performed by M. Gold and C. J. Hallada. Experimental details may be found in the references (a) M. Gold and W. L. Jolly, Inorg. Chem., 1, 818 (1962) and (b) C. J. Hallada and W. L. Jolly, ibid., in press.

7. R. C. Douthit and J. L. Dye, J. Am. Chem. Soc., 82, 4472 (1960).

8. Professor Dye has pointed out that the dimensions of the absorption cell may vary with the internal pressure (which of course is the vapor pressure of ammonia over the solutions in the case of our measurements). Unfortunately we did not check this possibility with Apparatus II. With Apparatus III (that used for obtaining the calcium spectra) we found

that the change in pressure corresponding to changing the temperature from -45° to -65° caused a decrease in the effective path length of 7%.

9. H. C. Clark, A. Horsfield and M. C. R. Symons, J. Chem. Soc., 2478 (1959).

10. M. Gold, W. L. Jolly, and K. S. Pitzer, J. Am. Chem. Soc., 84, 2264 (1962).

11. The experimental work was performed by Dr. C. J. Hallada.

12. T. Okabe, Kogyō Kagaku Zasshi, 60, 1438 (1957).

Figure Captions

Figure 1. - Apparatus I for measuring spectra of extremely dilute solutions.

Figure 2. - Log-log plot of absorbancy at 4500 Å vs. concentration for sodium solutions at -70°.

Figure 3. - Apparatus II for measuring spectra of relatively concentrated metal solutions.

Figure 4. - Absorption curves for alkali metals at -65, -55, and -45°.

Figure 5. - Wave number at maximum vs. absorbancy at maximum for alkali metals at -65°.

Figure 6. - Absorbancy at 10,000 Å vs. concentration for alkali metals at -65°.

Figure 7. - Absorbancy at 15,250 Å vs. concentration for alkali metals and calcium at -65°.

Figure 8. - Absorbancy at 21,000 Å vs. concentration for alkali metals at -65°.

Figure 9. - Absorbance vs. concentration for calcium at -45° for three different wavelengths.

Figure 10. - Absorption curves for 0.0203 M sodium solution with and without added sodium iodide.

Figure 11. - Conductivity cells for determining the calcium-ammonia phase diagram.

Figure 12. - Resistance-vs.-composition curves for calcium-ammonia mixtures at -45.0° and -63.8°.

Figure 13. - Resistance-vs.-temperature curves for two different calcium-ammonia mixtures.

Figure 14. - Pressure-vs.-composition curves for calcium-ammonia mixtures at three different temperatures.

Figure 15. - A portion of the calcium-ammonia phase diagram.

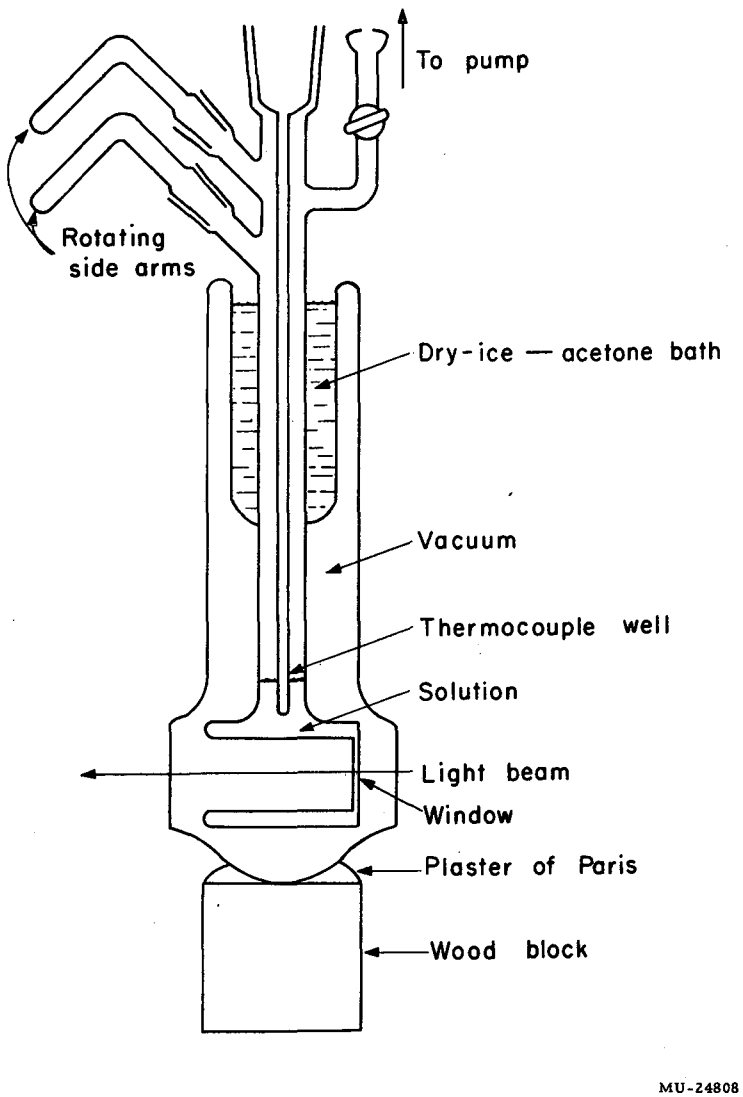

To pump
Rotating side arms
Dry-ice — acetone bath
Vacuum
Thermocouple well
Solution
Light beam
Window
Plaster of Paris
Wood block
MU-24808

Fig. 1

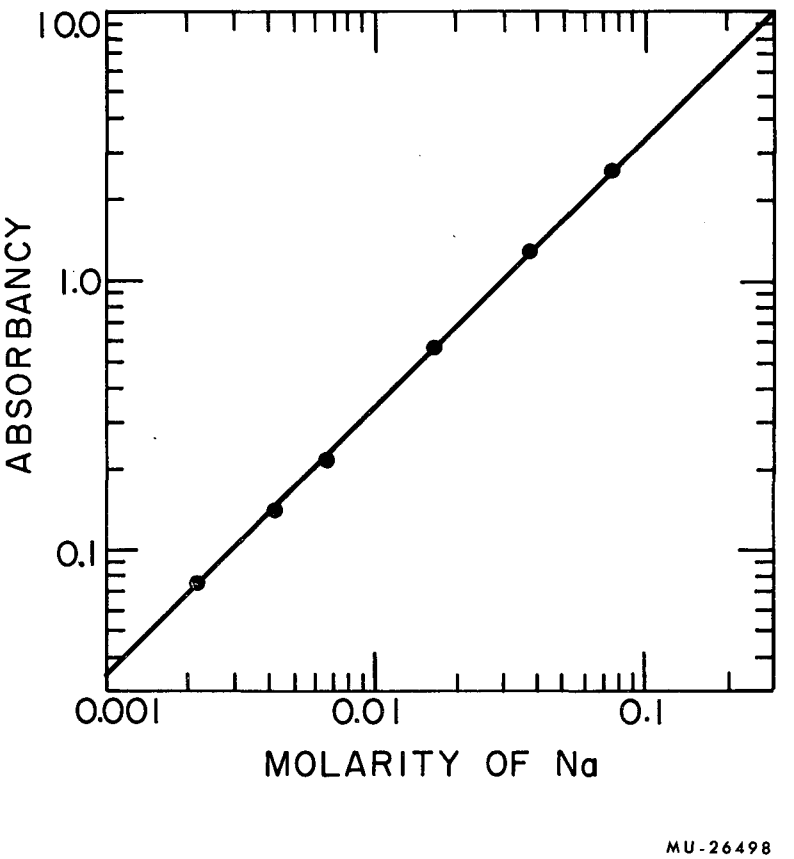


Fig. 2

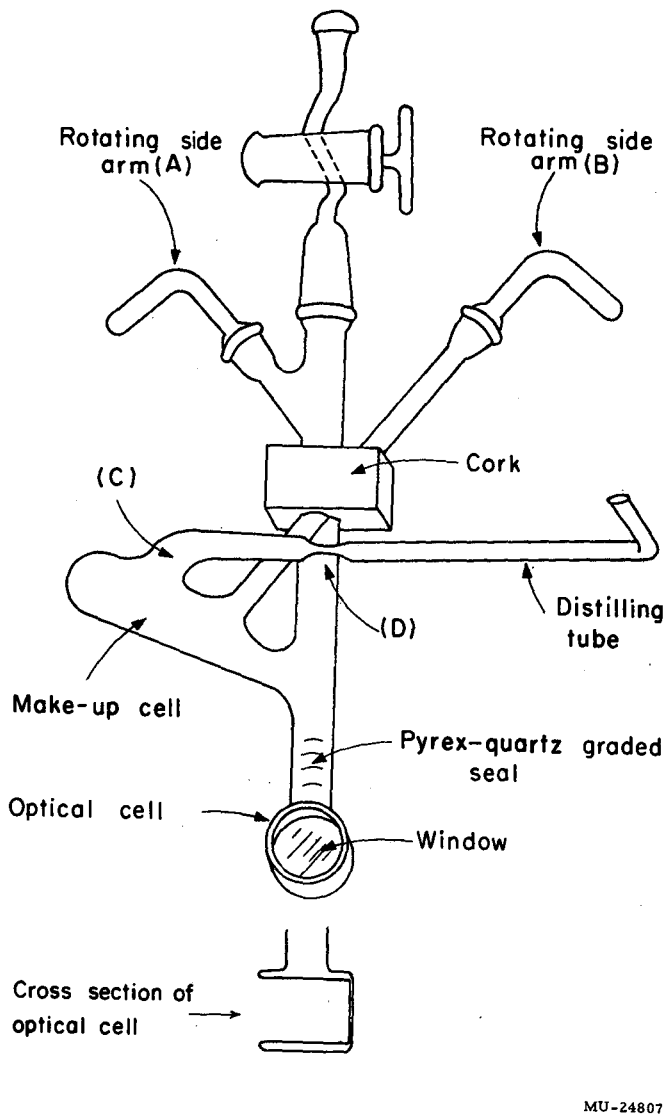

Rotating side arm (A)
Rotating side arm (B)
Cork
(C)
(D)
Distilling tube
Make-up cell
Pyrex-quartz graded seal
Optical cell
Window
Cross section of optical cell
MU-24807

Fig. 3

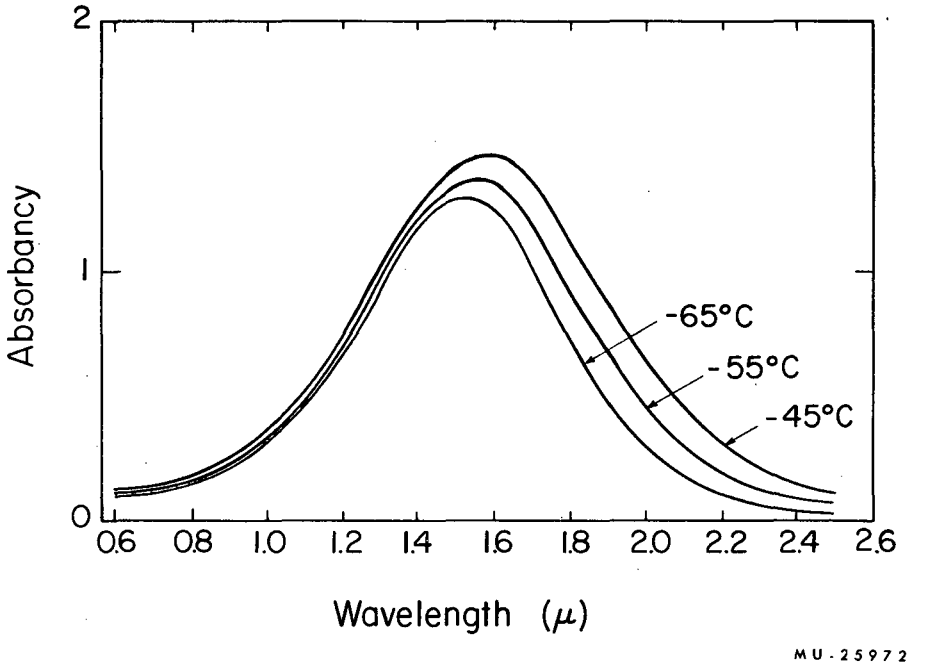

2
1
0
Absorbancy
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
Wavelength (μ)
-65°C
-55°C
-45°C
MU-25972

Fig. 4

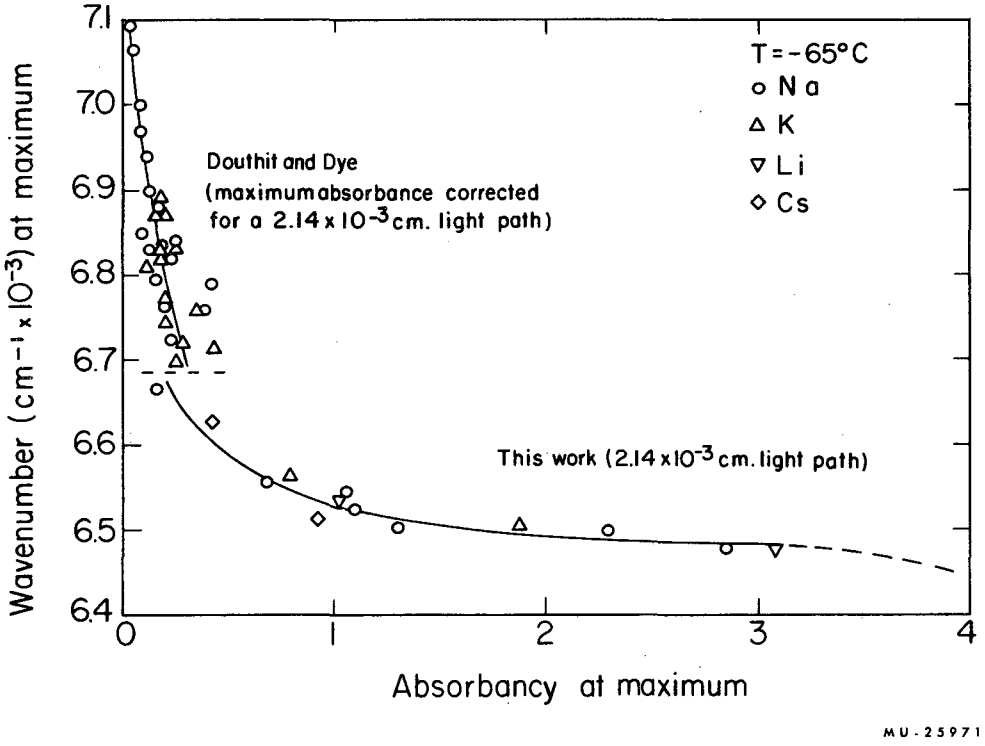

T = -65°C
o Na
Δ K
∇ Li
◇ Cs
Douthit and Dye
(maximum absorbance corrected
for a 2.14 x 10⁻³ cm. light path)
This work (2.14 x 10⁻³ cm. light path)
Wavenumber (cm⁻¹ x 10⁻³) at maximum
Absorbancy at maximum
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
0
1
2
3
4
MU-25971

Fig. 5

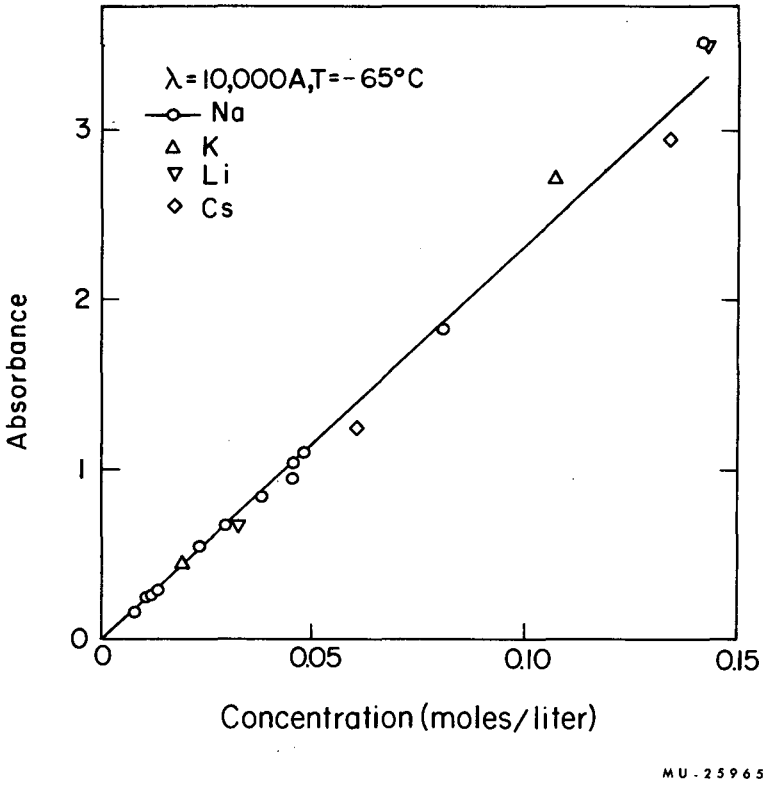

λ = 10,000A, T = -65°C
Na
K
Li
Cs
Absorbance
0
1
2
3
0
0.05
0.10
0.15
Concentration (moles/liter)
MU-25965

Fig. 6

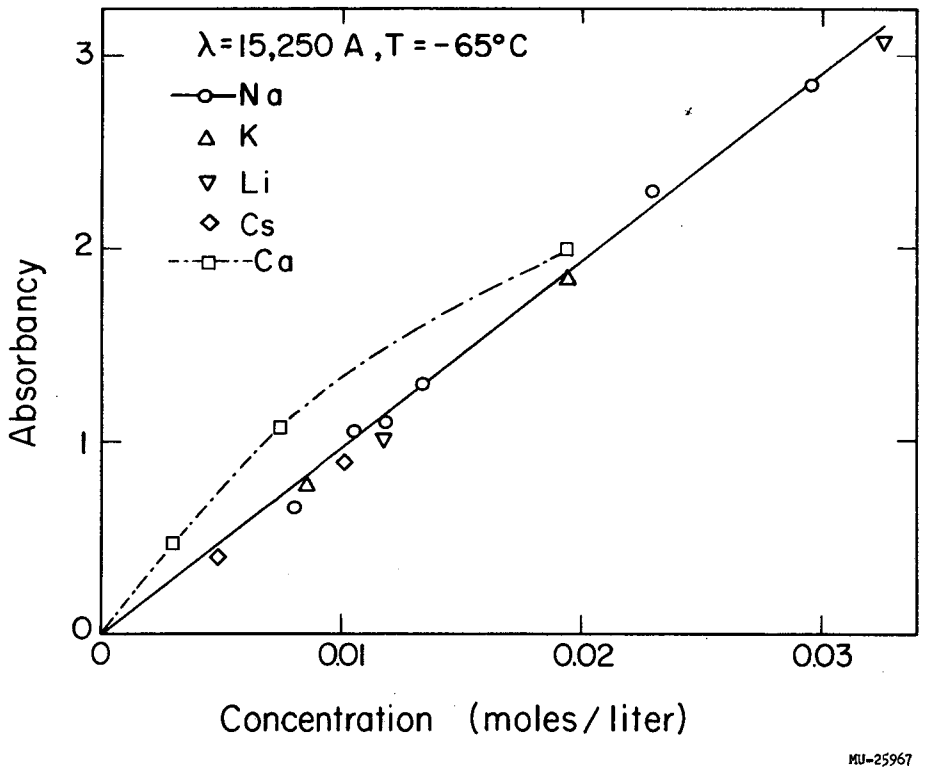
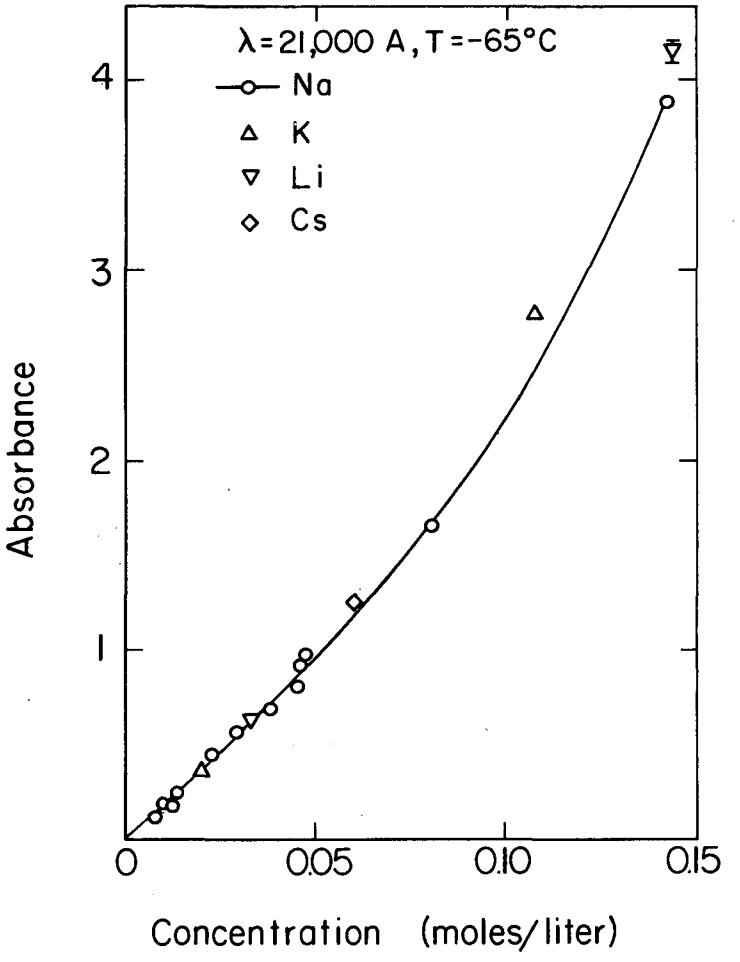

λ=15,250 A ,T = -65°C
Na
K
Li
Cs
Ca
Absorbancy
0
1
2
3
0
0.01
0.02
0.03
Concentration (moles/liter)
MU-25967

Fig. 7



MU-25969

Fig. 8

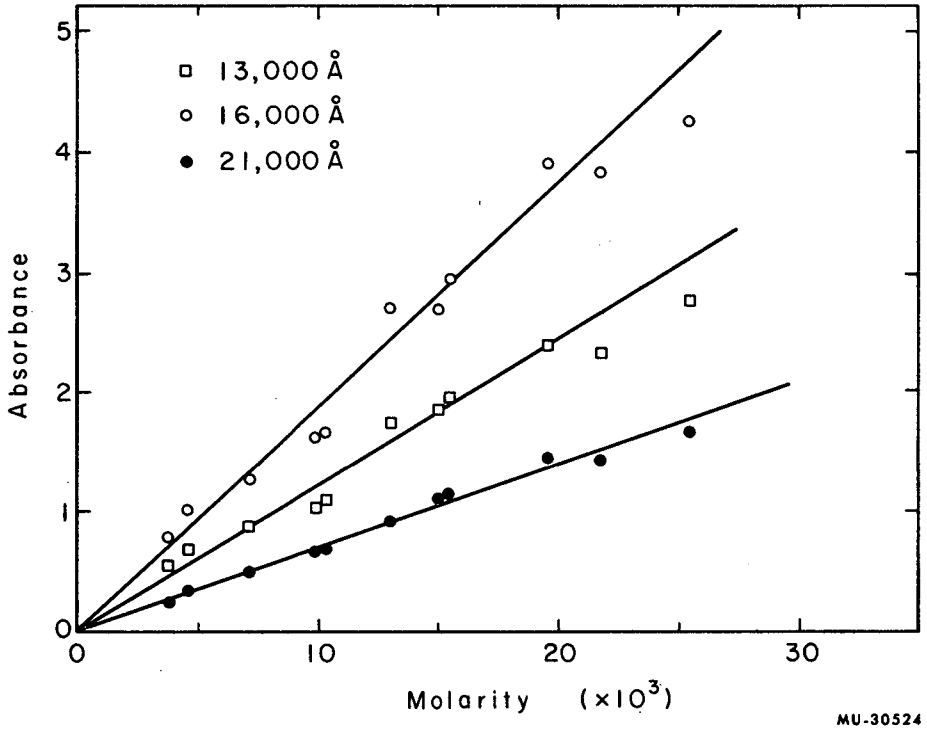

13,000 Å
16,000 Å
21,000 Å
Absorbance
Molarity (×10³)
0
1
2
3
4
5
0
10
20
30
MU-30524

Fig. 9

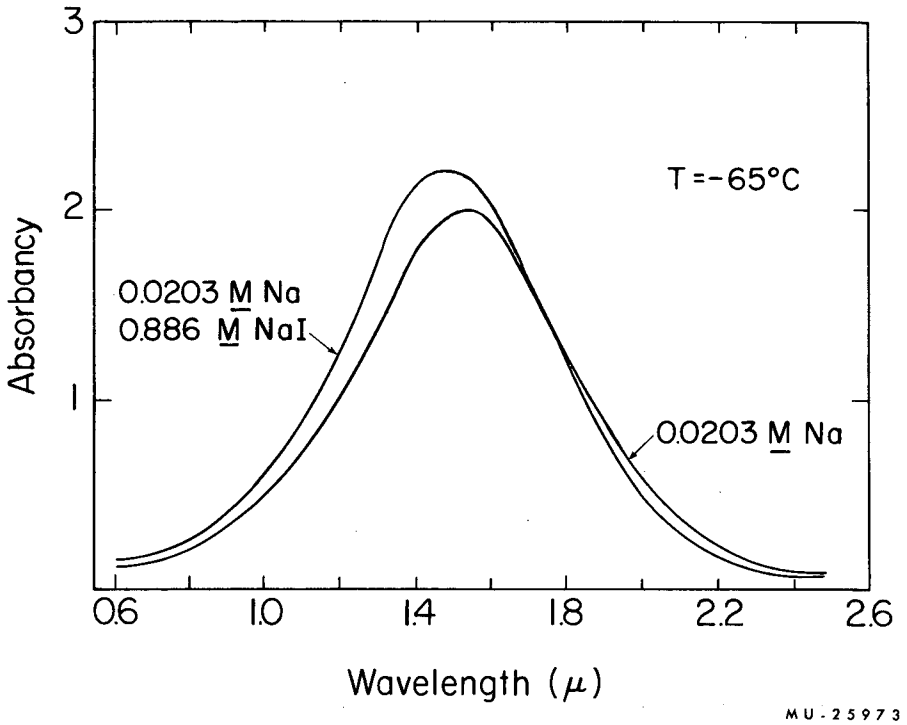

3
2
1
Absorbancy
T=-65°C
0.0203 M Na
0.886 M NaI
0.0203 M Na
0.6
1.0
1.4
1.8
2.2
2.6
Wavelength (μ)
MU-25973

Fig. 10

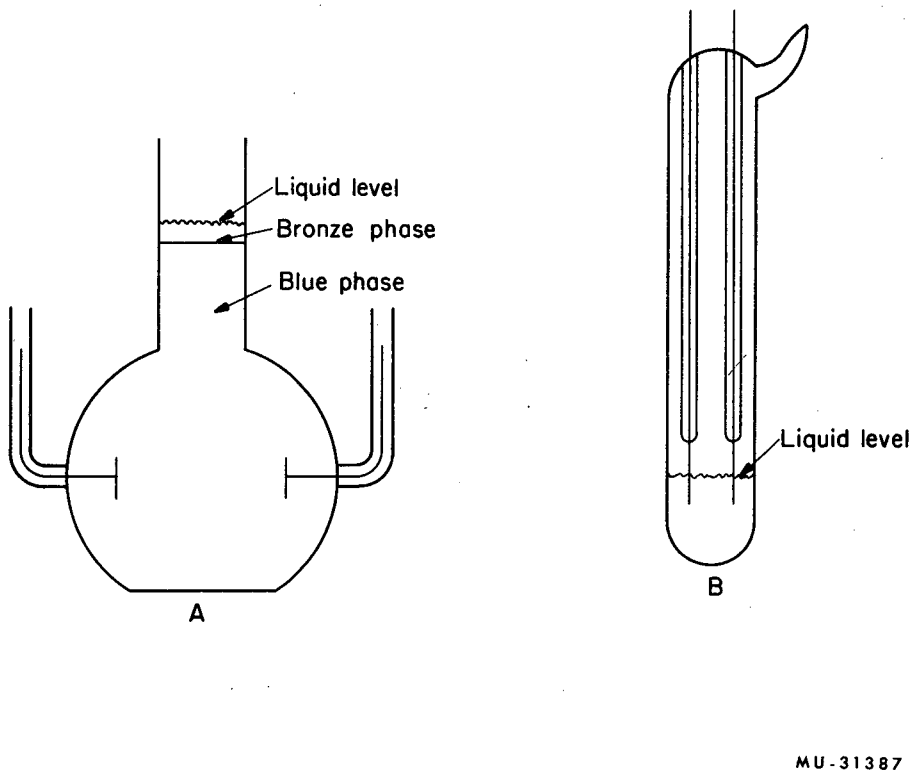

Liquid level
Bronze phase
Blue phase
A
Liquid level
B
MU-31387

Fig. 11

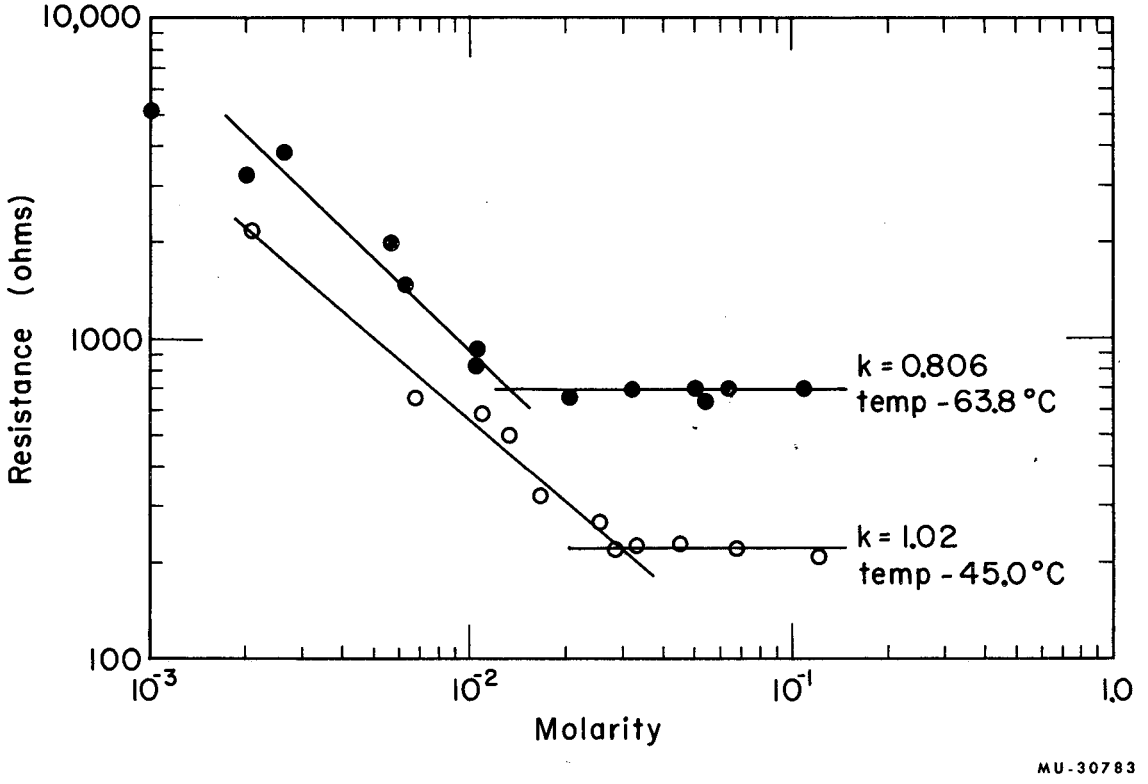
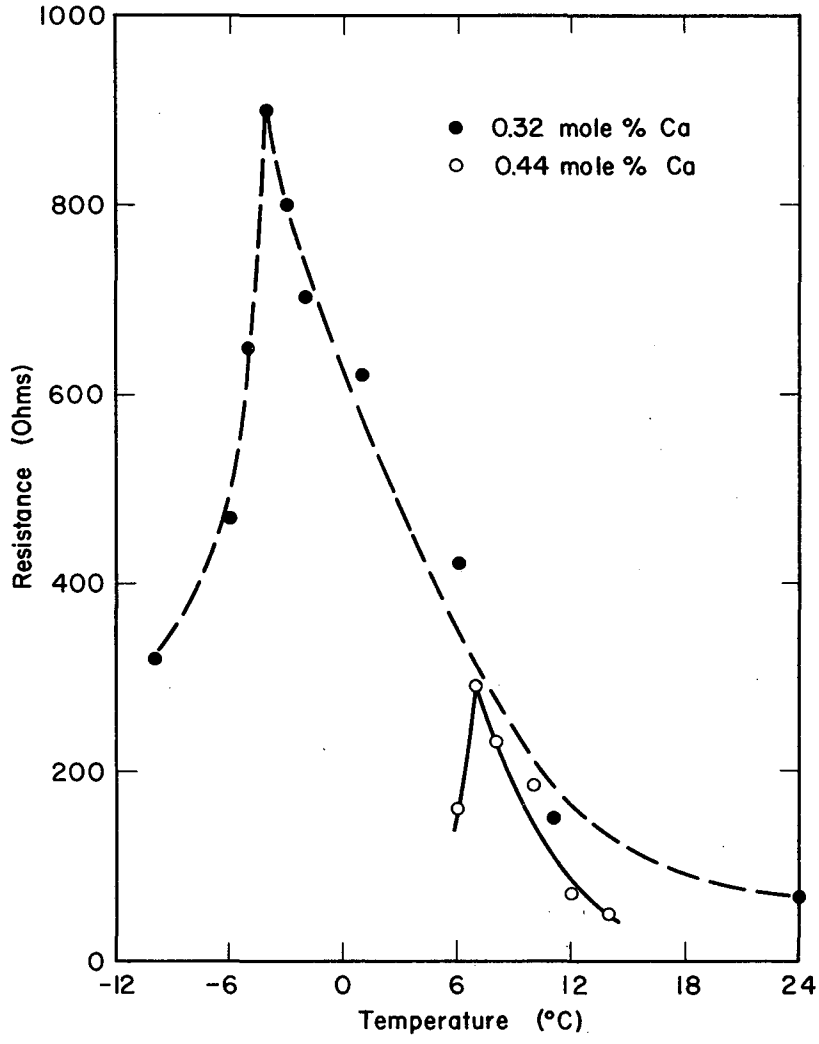

10,000
1000
100
Resistance (ohms)
10^{-3}
10^{-2}
10^{-1}
1.0
Molarity
k = 0.806
temp - 63.8 °C
k = 1.02
temp - 45.0 °C
MU-30783

Fig. 12



MU-31388

Fig. 13

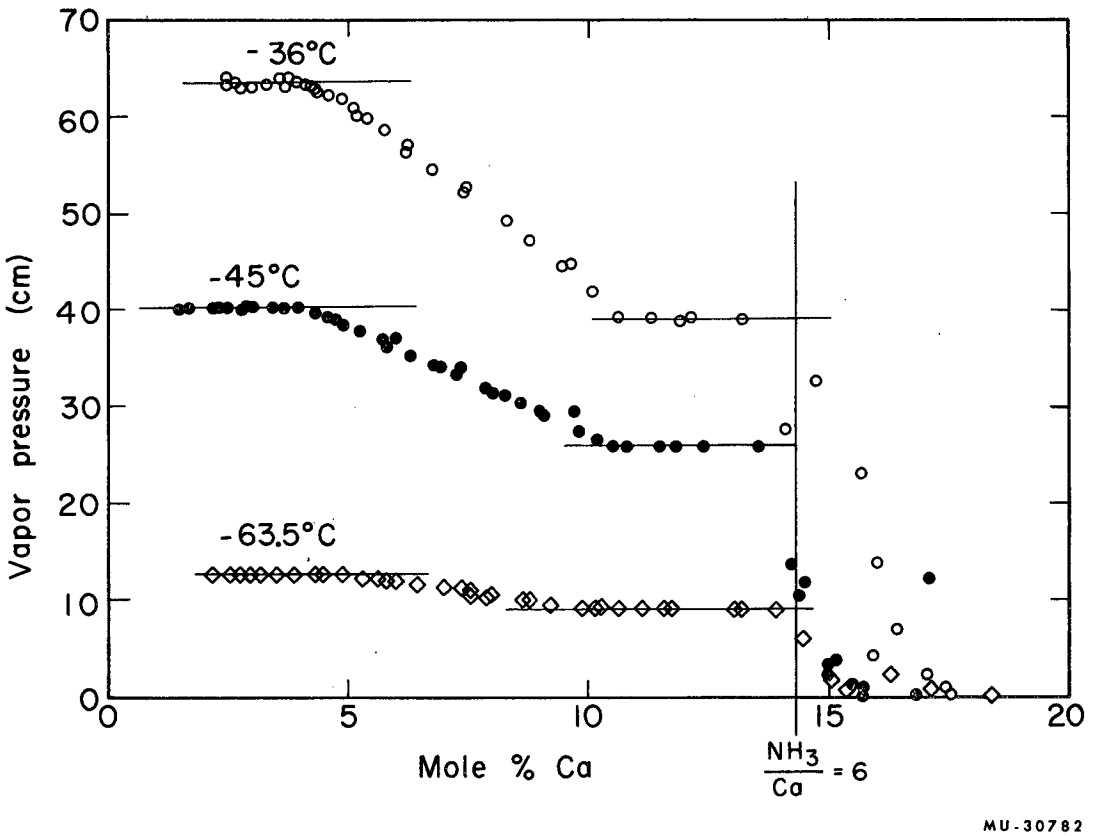

70
60
50
40
30
20
10
0
Vapor pressure (cm)
- 36°C
-45°C
-63.5°C
0
5
10
15
20
Mole % Ca
NH3/Ca = 6
MU-30782

Fig. 14

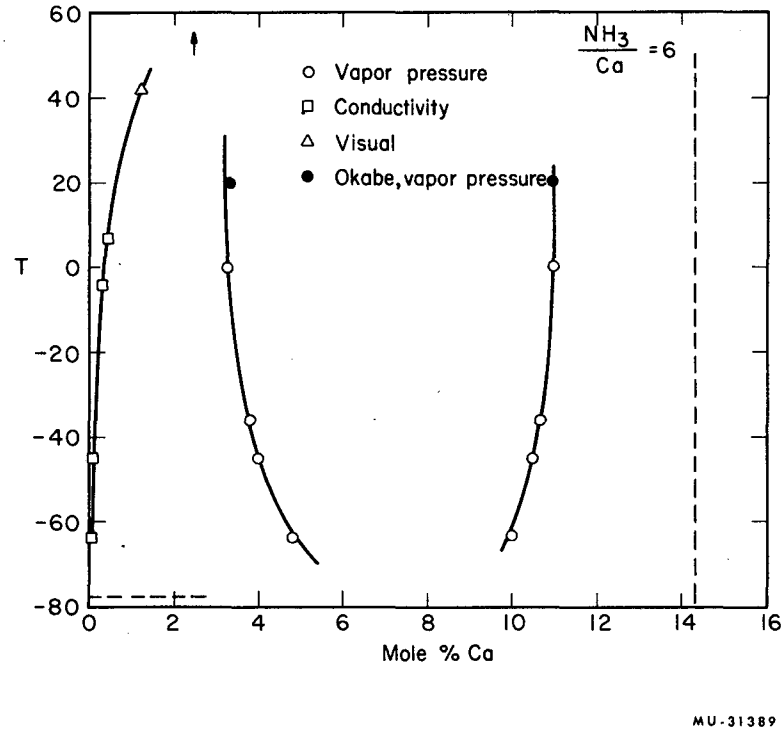

60
40
20
T 0
-20
-40
-60
-80
0
2
4
6
8
10
12
14
16
Mole % Ca
Vapor pressure
Conductivity
Visual
Okabe, vapor pressure
NH3/Ca = 6
MU-31389

Fig. 15

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