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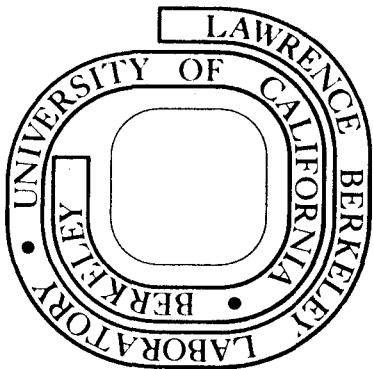
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MONITORING OF GROUPS II AND V ELEMENTS IN VAPOR
PHASE CRYSTAL GROWTH PROCESSES BY OPTICAL
ABSORPTION SPECTROSCOPY

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Optical absorption spectroscopy was studied as a technique for monitoring vapor phase crystal growth processes involving group II and V elements. Conditions allowing measurement of component partial pressures and component activities in condensed phases were determined for compounds containing Zn, Cd, As and P. Optical densities of these elements and of their gaseous mixtures were measured as a function of spectral wavelength and temperature with a high-temperature, uv-visible spectrophotometer. A linear analysis is presented for interpreting optical absorption spectra of multicomponent, gaseous mixtures. Results of applying the method to reactive and equilibrium processes are presented.

INTRODUCTION

Industrial vapor phase crystal growth processes such as chemical vapor deposition and chemical transport crystal growth can benefit significantly from operationally simple methods for monitoring component partial pressures in the vapor phase. Vapor phase crystal growth processes frequently require high temperatures in the range from 700 - 1200°C, and vapor compositions are not easily measured at such temperatures. In order to industrially monitor or experimentally study vapor phase processes for crystal growth it is necessary to utilize easily controlled, non-destructive methods which do not interfere with chemical reactions or transport processes.

Optical absorption spectroscopic methods are ideally suited for such applications as the optical energy levels are small compared to the enthalpies of chemical reactions in high temperature gaseous mixtures. Furthermore, optical methods do not require the extraction of gaseous samples by probes whose surfaces can react with gas-phase species, nor do such methods require quenching of the gas phase to lower temperatures, a process that frequently produces side reactions. The technique of ultraviolet-visible absorption spectroscopy allows direct, non-destructive measurements of

component partial pressures present in the vapor phase.

Many important compound semiconductors contain high vapor-pressure components and can be grown from the vapor phase. Currently important compound semiconductors containing volatile species are the II-VI compounds (Zn, Cd, Hg) (S, Se, Te), the III-V compounds (Al, Ga, In) (N, P, As, Sb) and the II IV V₂ compounds (Mg, Zn, Cd) (Si, Ge, Sn) (N₂, P₂, As₂)⁽¹⁾. The components in these compounds with significant vapor pressures are the group II and V elements. It is therefore important to identify the conditions under which these elements can be monitored by optical absorption spectroscopy.

Previous studies of the optical densities of zinc vapor at high temperature in equilibrium with zinc alloys have been made by Herbenar⁽²⁾ and by Scatchard and Westlund⁽³⁾. Brebrick and Strauss⁽⁴⁻⁶⁾ have applied this analysis extensively to group II-VI systems. Brebrick⁽⁷⁻¹¹⁾ has studied additional II-VI systems using this method. Measurements of the partial pressures of zinc and arsenic in the Ga-As-Zn system by optical methods have been recently reported by Shih, et.al.,⁽¹²⁾ and by Styer⁽¹³⁾. In this paper the optical absorption spectroscopic method is explored in detail with respect to high-temperature vapors containing cadmium, zinc, arsenic and phosphorous to determine the range of applicability of this method in vapor phase crystal growth processes.

THEORY

In this section the theoretical basis for the use of the optical absorption technique is developed. The simplifying assumptions for this technique are given and a general method is presented for calculating the partial pressure for each of n noninteracting, optically absorbing species present in an arbitrary vapor phase.

TEMPERATURE DEPENDENCE OF OPTICAL DENSITY

The Beer-Lambert Law relates the magnitude of light absorption by a substance to its concentration⁽¹⁴⁾,

$$D_{i, (\lambda, T)} = \log_{10} \frac{I_0(\lambda, T)}{I(\lambda, T)} = \epsilon_{i, \lambda} c_i l \quad (1)$$

where $D_{i, (\lambda, T)}$ represents the optical density of species i measured at wavelength λ and temperature T , $I_0(\lambda, T)$ and $I(\lambda, T)$ represent respectively the intensity of the incident

light and exiting light at the same wavelength and temperature. Here $\epsilon_{i,\lambda}$ is called the extinction coefficient of species i and is dependent upon the wavelength of the measurement, while c_i is the concentration of species i and l is the length of the optical path in which the sample is present. A more convenient quantity for comparison of experimental results, the specific optical density, analogous to the specific absorption coefficient, is

$$d_i \equiv D_i/l \quad (2)$$

so that Eq. (1) can be expressed as

$$d_i = \epsilon_i C_i \quad (3)$$

where the subscript denotes a specific wavelength and temperature.

If the vapor is assumed to be an ideal gas, then $c_i = p_i/RT$ so that with $k_i = \epsilon_i/R$,

$$d_i = k_i \frac{p_i}{T} \quad (4)$$

This restriction to an ideal gas is not essential in the final treatment, but for calibration analysis it serves to simplify the development.

The properties of the liquid and vapor phases of a pure material at equilibrium are related by the Clapeyron Equation⁽¹⁵⁾

$$\frac{dp_i^{\text{sat}}}{dT} = \frac{\Delta H_i^{\text{vap}}}{T\Delta V_i^{\text{vap}}} \quad (5)$$

under conditions where the vapor phase can be considered ideal and where ΔH_i^{vap} is constant. Equation (5) can be integrated with respect to temperature to give the Clausius-Clapeyron Equation,

$$\ln \frac{p_i^{\text{sat}}(T)}{p_i^{\text{sat}}(T_{\text{ref}})} = \frac{\Delta H_i^{\text{vap}}}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \quad (6)$$

This equation can be written in the equivalent form,

$$\log_{10} p_i^{\text{sat}}(T) = A - \frac{B}{T} \quad (7)$$

where

$$A \equiv \log_{10} p_i^{\text{sat}}(T_{\text{ref}}) + \frac{\Delta H_i^{\text{vap}}}{RT_{\text{ref}} \ln 10}$$

$$B \equiv \frac{\Delta H_i^{\text{vap}}}{R \ln 10}$$

Solving Eq. (4) for p_i^{sat} , taking the common logarithm of both sides and using the result of Eq. (7) one obtains the desired relation between specific optical density and absolute temperature,

$$\log_{10} d_i = A' - \frac{B}{T} - \log_{10} T \quad (8)$$

where

$$A' = A + \log_{10} k'$$

Therefore, over small intervals of temperature the magnitude of the change in the value of $\log_{10} T$ will be small relative to that in the B/T term, and a graphical representation of $\log_{10} d_i$ versus inverse absolute temperature should give a nearly linear dependence for a given wavelength, with an intercept of $A' - \log_{10} T$.

DETERMINATION OF PARTIAL VAPOR PRESSURES IN MULTI-COMPONENT SYSTEMS

Partial pressures of a vapor phase containing several species can be determined from optical absorption measurements provided that the optical absorption of the pure component species is known together with the effects of species interactions. For gaseous mixtures of group IIB elements and arsenic, negligible interactions are expected because the valence electrons of the arsenic tetramer, As_4 , are fully paired and not available for bonding. Thus, the spectral dependence of the optical absorption for the pure component species can be used to deduce the partial pressure,

or concentrations for such vapor mixtures.

Consider a mixture of n non-interacting vapor species, each with a partial specific optical density, $d_i \lambda$. The total specific optical density of this mixture at each of n spectral wavelengths λ_j is then

$$d_{m,\lambda_j} = \sum_{i=1}^n d_{i,\lambda_j}; j = 1, 2, \dots, n \quad (9)$$

The relative fugacity or activity⁽¹⁵⁾ can be determined from the values of specific optical density for the pure species together with the corresponding partial specific optical density of the mixture by assuming that d_{i,λ_j} is proportional to d_{i,λ_j}^0 , the value of which is assumed⁽¹⁵⁾ to be known. Thus

$$d_{i,\lambda_j} = a_i d_{i,\lambda_j}^0 \quad (10)$$

Substitution of Eq. (10) into Eq. (9) yields a series of linear equations in the unknown quantities, a_i ,

$$d_{m,\lambda_j} = \sum_{i=1}^n a_i d_{i,\lambda_j}^0 \quad (11)$$

These equations can be solved for a_j by Cramer's Method to give

$$a_i = \frac{\begin{vmatrix} d_{1,\lambda_1}^0 & d_{2,\lambda_1}^0 & \dots & d_{m,\lambda_1} & \dots & d_{n,\lambda_1}^0 \\ d_{1,\lambda_2}^0 & d_{2,\lambda_2}^0 & & & & \\ \dots & \dots & & & & \\ d_{1,\lambda_n}^0 & d_{2,\lambda_n}^0 & \dots & d_{m,\lambda_n} & \dots & d_{n,\lambda_n}^0 \end{vmatrix}}{\Delta} \quad (12)$$

where

$$\Delta = \begin{vmatrix} d_{1,\lambda_1}^{\circ} & d_{2,\lambda_1}^{\circ} & \dots & d_{j,\lambda_1}^{\circ} & \dots & d_{n,\lambda_1}^{\circ} \\ d_{1,\lambda_2}^{\circ} & d_{2,\lambda_2}^{\circ} & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ d_{1,\lambda_n}^{\circ} & d_{2,\lambda_n}^{\circ} & \dots & d_{j,\lambda_n}^{\circ} & \dots & d_{n,\lambda_n}^{\circ} \end{vmatrix}$$

where the column vector $(d_{m,\lambda_1}, \dots, d_{m,\lambda_n})$ replaces the j^{th} column in the numerator of the determinant. If Beer's Law is valid, then

$$a_i = \frac{d_{i,\lambda_j}}{d_{i,\lambda_j}^{\circ}} = \frac{c_i}{c_i^{\circ}} \quad (13)$$

The values of a_i calculated from Eq. (13) should be independent of the chosen wavelengths.

If a virial equation of state in the volume explicit form is assumed

$$\frac{pv}{RT} = 1 + B'p + C'p^2 + D'p^3 + \dots \quad (14)$$

then

$$c_i = \frac{1}{v_i} = \frac{P_i}{RT} \left(\frac{1}{1 + B'p + C'p^2 + D'p^3 + \dots} \right) \quad (15)$$

Where B' , C' and D' are constants independent of the pressure. Substituting Eq. (15) into Eq. (13) one obtains the result,

$$a_i = \frac{P_i}{P_i^{\circ}} \left(\frac{1 + B'p_i^{\circ} + C'p_i^{\circ 2} + \dots}{1 + B'p_i + C'p_i^2 + \dots} \right), \quad (16)$$

-7-

where the term in parenthesis is approximately unity for the species under consideration in this work. Therefore the coefficients a_i have the value

$$a_i = \frac{P_i}{P_i^0} \quad (17)$$

as required to determine component partial pressures.

EFFECT OF A TWO-TEMPERATURE ZONE ON MEASURED PARTIAL PRESSURES

The optical windows through which the optical beam passes must be protected from a supersaturated or reactive gaseous mixture in order to prevent solid deposits from forming. It is feasible to prevent such deposits by maintaining the beam path at an elevated temperature above that of the reactive gas. In this reaction, the possible error in partial pressure measured for a two-temperature cell is examined.

If the experimental cell contains an optical path maintained at a temperature T_{op} which is different from the temperature of the reactive gas, T_r , then the ratio of the concentrations present in the two zones is given by,

$$\frac{c_r}{c_{op}} = \frac{T_{op}}{T_r} \quad (20)$$

where $c_i = P/(RT_i)$. The pressure will be constant throughout the two zones if thermal diffusion effects are absent. The specific optical density is then given by $d_i = \epsilon_i c_i$, and the experimental partial pressures are

$$P_i = \frac{d_i}{d_i^0} P_i^0 \quad (21)$$

Substituting for d_i in terms of c_i , one then obtains

$$P_i = \frac{c_{i,op}}{c_{i,op}^0} P_i^0 \quad (22)$$

where the values of ϵ_i are equal at the same wavelength for all species.

What is really desired in the experimental measurement is the equilibrium vapor pressure in the gas mixture. Using the ideal gas equation, Eq. (21) becomes,

$$P_i = \frac{c_{i,r}(T_r/T_{op})_{mix}}{c_{i,r}(T_r/T_{op})_{cal}} P_i^o, \quad (23)$$

where $(T_r/T_{op})_{mix}$ and $(T_r/T_{op})_{cal}$ are the temperature conditions for the gas-mixture and optical-path zones, respectfully. The error in extrapolated partial pressures for a two-temperature cell is then,

$$P_i = P_i^o \left(\frac{T_{op,mix}}{T_{op,cal}} - 1 \right). \quad (24)$$

Examination of Eq. (24) shows that only if the gas mixture and optical path temperatures are the same for the mixture and calibration measurements, will the temperature effect cancel.

EXPERIMENTAL

MATERIALS

Cadmium and zinc were obtained in 99.9999% purity.* Prior to use, the metals were further purified by vapor transport in vacuum to produce very high-purity crystals. The arsenic used was obtained in 99.9999% purity and was used without further purification.** Ultraviolet-transmitting quartz was used in the construction of T-shaped optical cells having flat and parallel optical windows.

APPARATUS

A high-temperature uv-visible spectrophotometer was built around a Heath Model EU-701 Series Modular Spectroscopy System, using a deuterium lamp source, monochromator

* United Mineral and Chemical Corp., New York, N.Y.

** Alfa Inorganic, Beverly, Mass.

to reduce its radiation effect on the photo multiplier tube. Four Oriel two-inch diameter plano-convex ultra-violet transmitting, silica lenses were used to focus the light beam on the optical cell, contained within the furnace, and on the entrance slit of the monochromator. The output current of the photomultiplier tube was converted to a voltage signal with an electrometric operational amplifier*. The voltage signal was then connected to a log amplifier,** the output of which was recorded on a Leeds and Northrup speedomax strip chart recorder. The system is shown in Fig. 1.

In order to prevent condensation of the vapor contained in the optical cell on the optical window, a two-zone furnace was designed so that the sample cell would have two different temperature zones for the condensed phases and for the optical windows, respectively. The cell geometry is the "T" cell, the cross bar of which served as the high temperature optical path. Since that part of the cell is at a higher temperature than that at which the vapor is generated, there will be no condensation of the vapor in the optical path region.

PROCEDURE

The quartz optical cells were etched in dilute HF, rinsed in de-ionized water, ultrasonically cleaned in methanol, de-ionized water, and vacuum dried at 10^{-5} torr. The cells were filled with condensed phases, vacuum degassed at 200°C for 2-3 hours, then sealed. Each cell was then placed in the two-zone furnace and heated. For each measurement the optical path was maintained at a constant temperature of 936°C , and the stem of the cell, containing condensed phases, was held at a different temperature. A period of one to four hours was allowed for full thermal equilibration, depending on the system studied. Transient reactions were monitored at a fixed wavelength.

RESULTS

ELEMENTAL OPTICAL DENSITIES

The measured specific optical density of arsenic vapor over liquid arsenic is shown in Fig. 2. There was a single absorption line below 2200 \AA , which broadened with increasing temperature. The data indicates that wavelength

* National Semiconductor LH0042.

**Burr-Brown Model 4416.

between 2800 Å and 3800 Å are best suited for arsenic partial pressure measurements. Similar results were obtained for phosphorous vapor in equilibrium with condensed phosphorous, except that the high vapor pressure of this element limited study to low temperatures.

The spectral dependence of the specific optical density of zinc vapor in equilibrium with its own melt is shown in Fig. 3. The absorption line at 2140 Å is the most significant feature of the spectrum, with a minor line at 3076 Å evident at temperatures above 740°C. Wavelengths between 2140 and 2800 Å appear to be best suited for zinc partial pressure measurement by optical absorption.

Figure 4 shows the measured specific optical density of cadmium vapor over pure cadmium, as a function of the spectral wavelength. Cadmium vapor has two salient absorption lines, the stronger of which is centered at 2287 Å and the weaker at 3257 Å. With increasing temperature the 2287 Å line broadens extensively so that above 850°C the vapor absorption band extends to 2900 Å on the red end of the spectrum.

MULTICOMPONENT OPTICAL DENSITIES

Optical densities of multicomponent gas mixtures were examined by the linear theory presented above. The results show that it is necessary to limit the wavelengths chosen for the analysis to the range where all components are known to be partially absorbing. For the As-Cd systems, both elements show absorption in the spectral range from 2800 to 3257 Å. For the As-Zn and P-Zn systems, the usable wavelength range was between 2500 and 8100 Å. When one component was in excess, that component tended to mask the absorption of minor components and prevent a multicomponent analysis of partial pressures.

Several reactive processes studied were found to be partial pressures from the multicomponent analysis:

Synthesis Reactions. - The ability of the optical method to follow gas-phase reactive processes was studied by heating the reactive components to a constant temperature and observing the change in optical density at a fixed wavelength during the reaction. Time transients could be followed readily if the vapor phase equilibrated with reacting components.

Solidification Reactions. - The solidification of Cd-doped GaAs was studied by monitoring the optical density of the vapor phase in equilibrium with the condensed phases. The specific optical density for a cell initially containing GaAs, As and Zn. The liquidus temperature is clearly indicated by the discontinuity at 670°C. Using the calibration spectra for Cd and As, the partial pressures of these components were determined from the linear analysis using a series of wavelength pairs and a statistical evaluation of the results. Figure 6 shows that the melting range extends from 670°C to approximately 160°C. The partial pressure varied more slowly with temperature, with an average error of ~15%.

Chemical Transport Reactions. - When transport agents of the group II elements such as CdI_2 are formed, the uv absorption spectrum is displaced in wavelength. Consequently, it was necessary to obtain a calibration spectrum of the transport agent before applying the multi-component analysis.

DISCUSSION

Of all the groups II and V elements studied, arsenic shows the broadest absorption band. Such a band absorption phenomenon is expected from the fact that most of the arsenic is in the form of As_4 tetramers, which exhibits many closely-spaced molecular vibrational and rotational energy states. The analysis of optical density data for arsenic was best carried out when the optical density was in the range from 0.1 to 1.0 for a cell path length of 2cm.

The high-temperature optical absorption spectrum for cadmium vapor shows extensive line broadening from 2287 to 3000 Å. The apparent enthalpy of vaporization for wavelengths in this range was nearly twice that of the experimental value, which is consistent with the statistical theory of self-broadening in high pressure gases⁽¹⁶⁾. Brebrick has reported that the optical density of the 3257 Å peak is not proportional to the optical path length for absorption⁽¹¹⁾. This behavior is expected when the spectral band-pass is greater than the true half-width of the absorption line.

The error in measured partial pressures arising from temperature instabilities in the two zones of the optical cells was studied by varying the temperature of the optical

path, T_{op} , in the range from 925 to 945°C. The maximum relative error in the partial pressure of the major vapor species in several experimental cells was found to be 0.085% per °C of variation of T_{op} . This deviation is consistent with theory, and demonstrates that the optical path can be maintained at a condensation-free, higher temperature than the sampling zone without error provided that the measurement temperatures are the same for both calibrating and operating conditions.

CONCLUSION

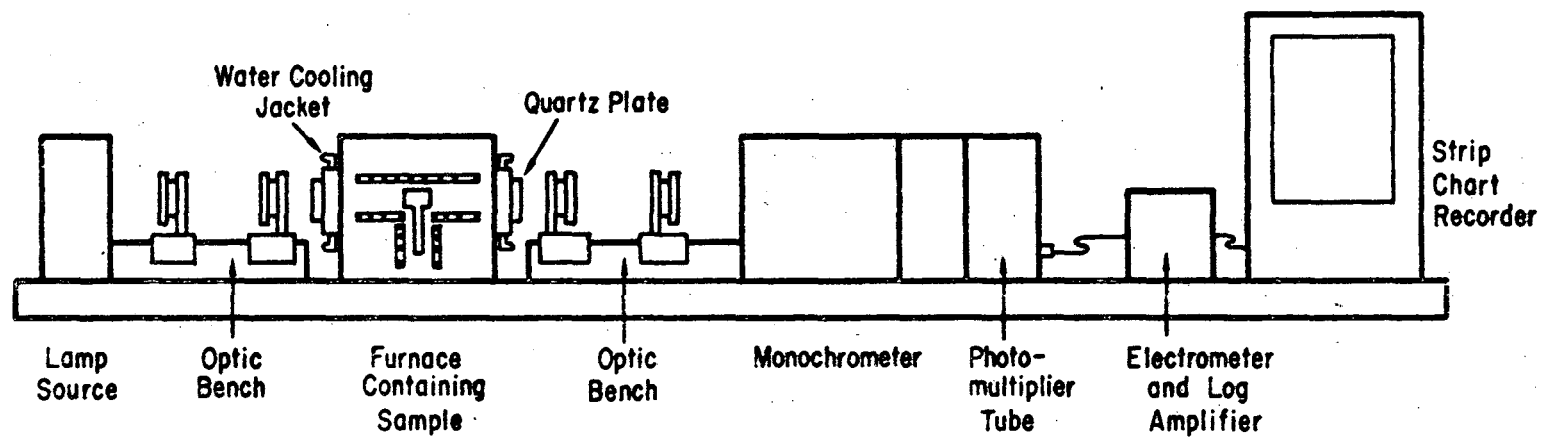
The practical feasibility of using optical absorption spectroscopy for monitoring vapor-solid reactions in compounds containing groups II and VI elements was demonstrated and applied to measure the partial vapor pressures of systems containing phosphorus, arsenic, cadmium and zinc. The method performed well in several studies of condensed phase reactions.

ACKNOWLEDGEMENT

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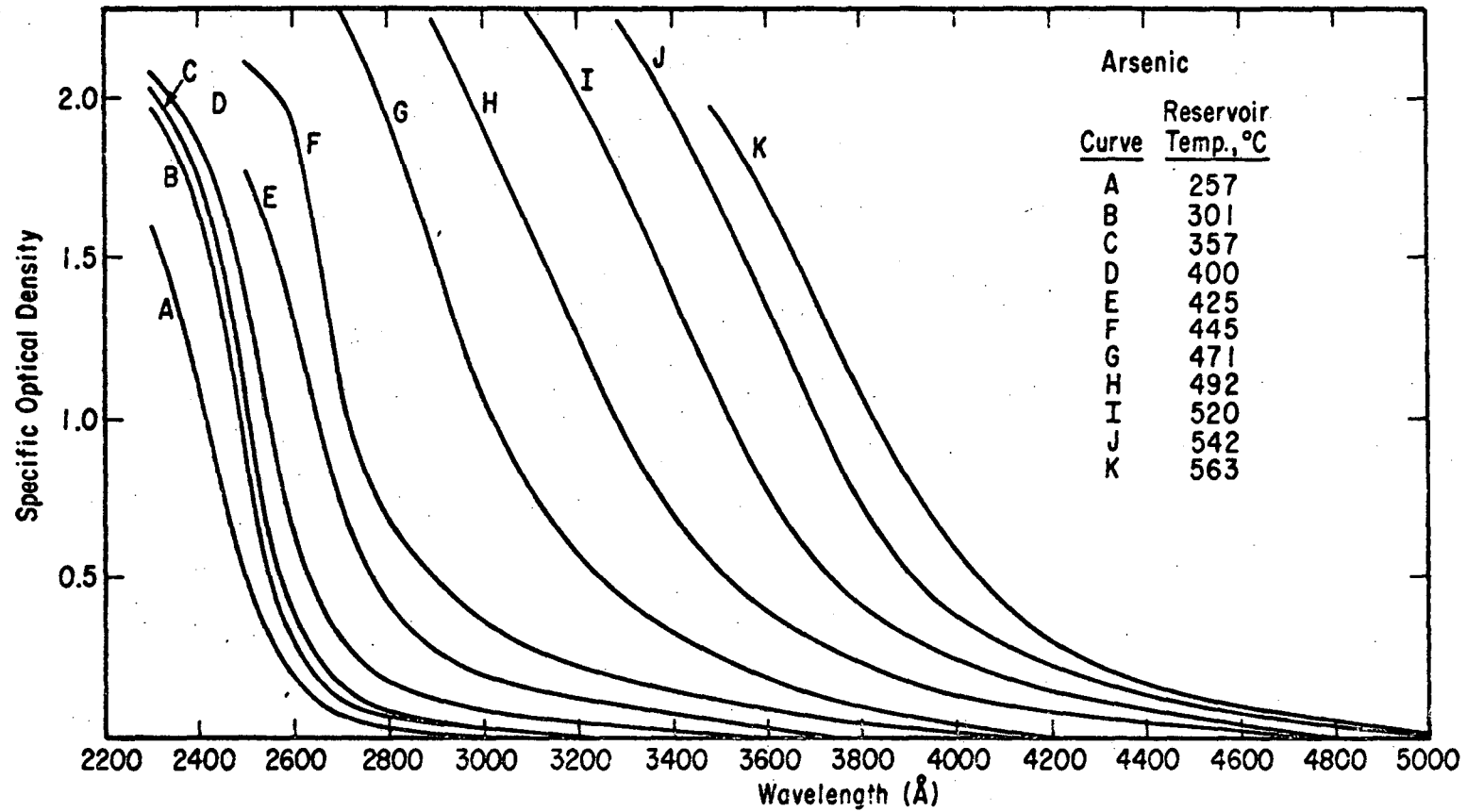


-13-

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Fig. 1. Schematic of experimental system.

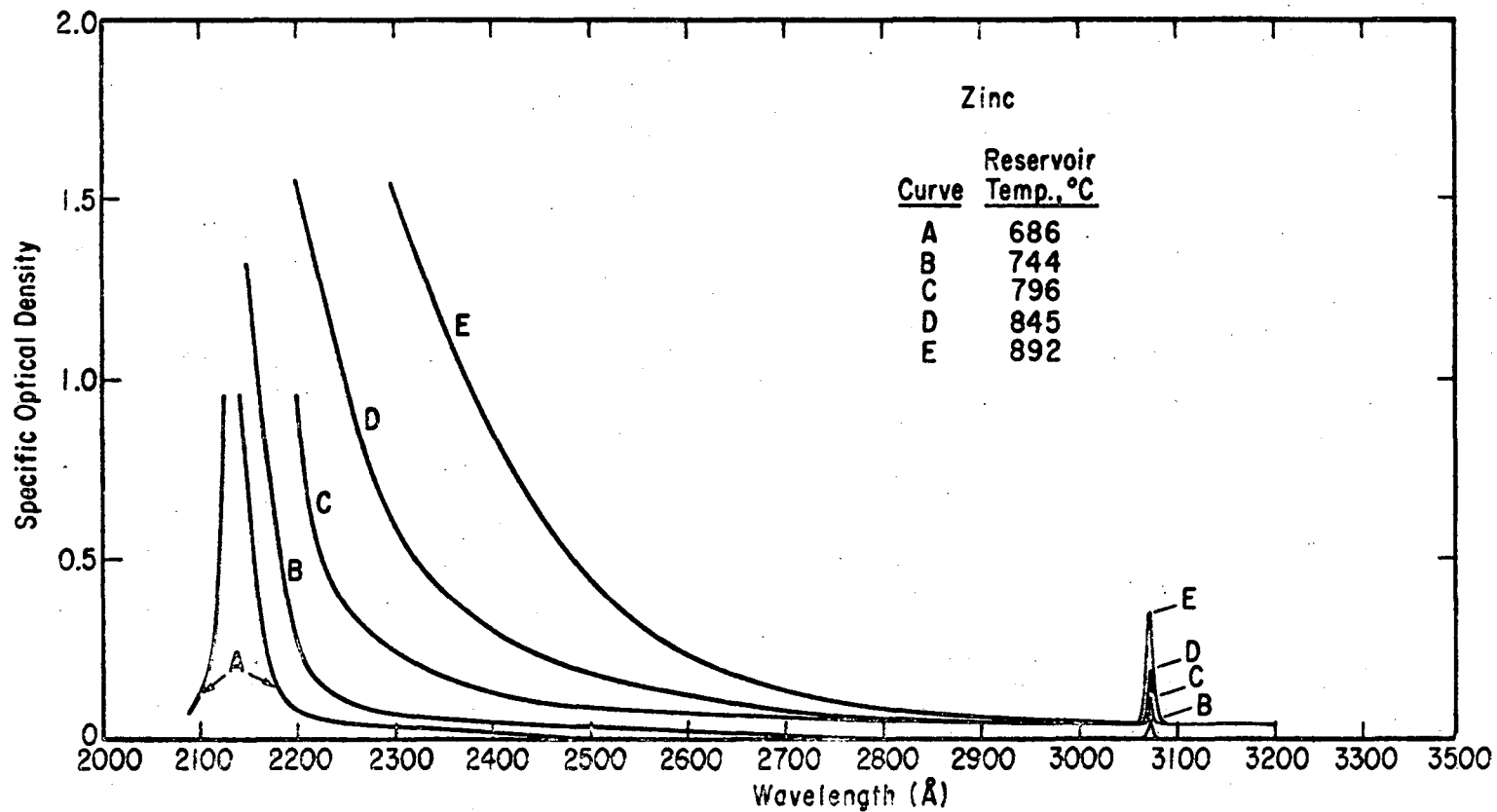
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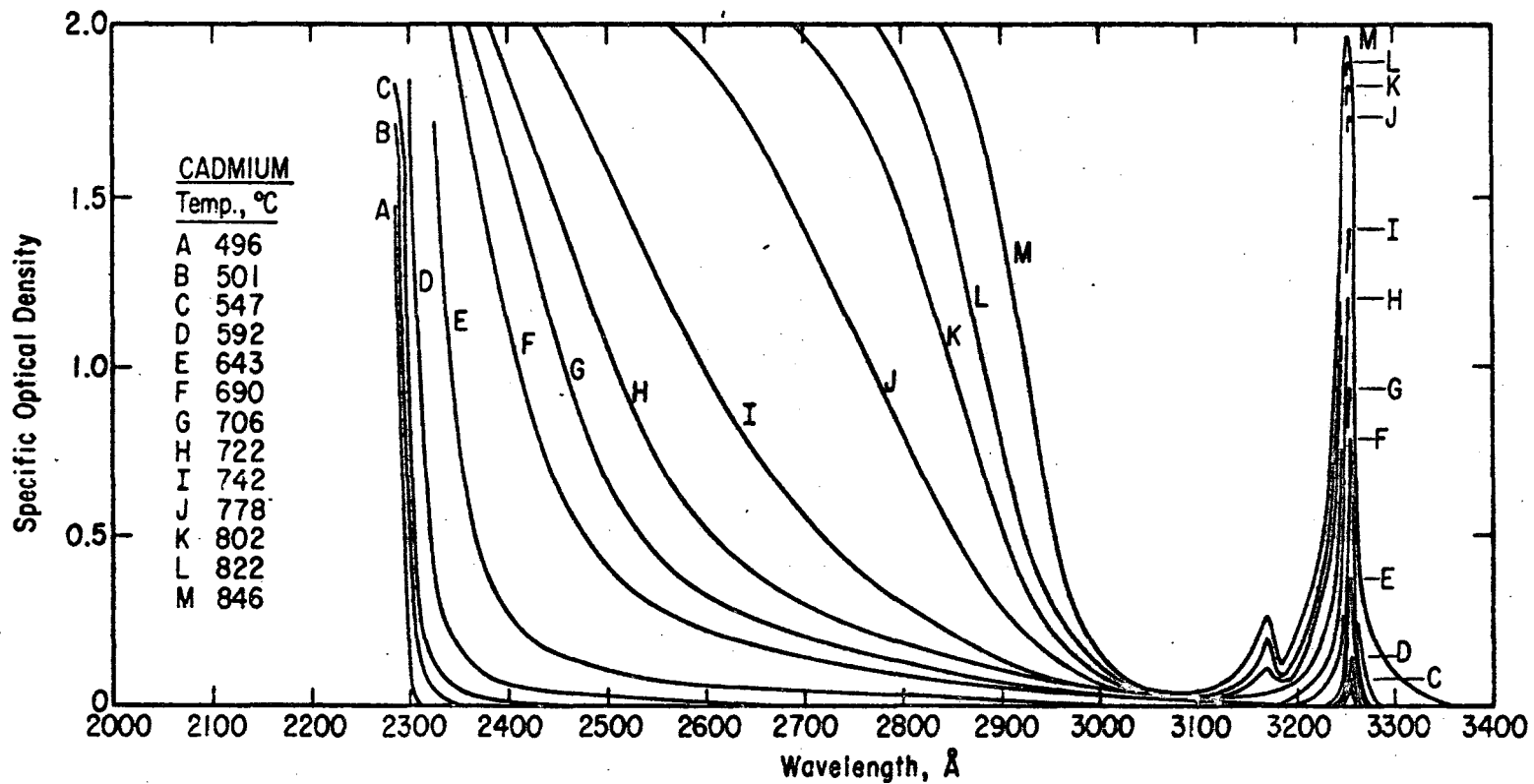
Fig. 2. Specific optical density of pure arsenic vapor vs. wavelength at different temperatures of phase equilibrium in the cell reservoir.



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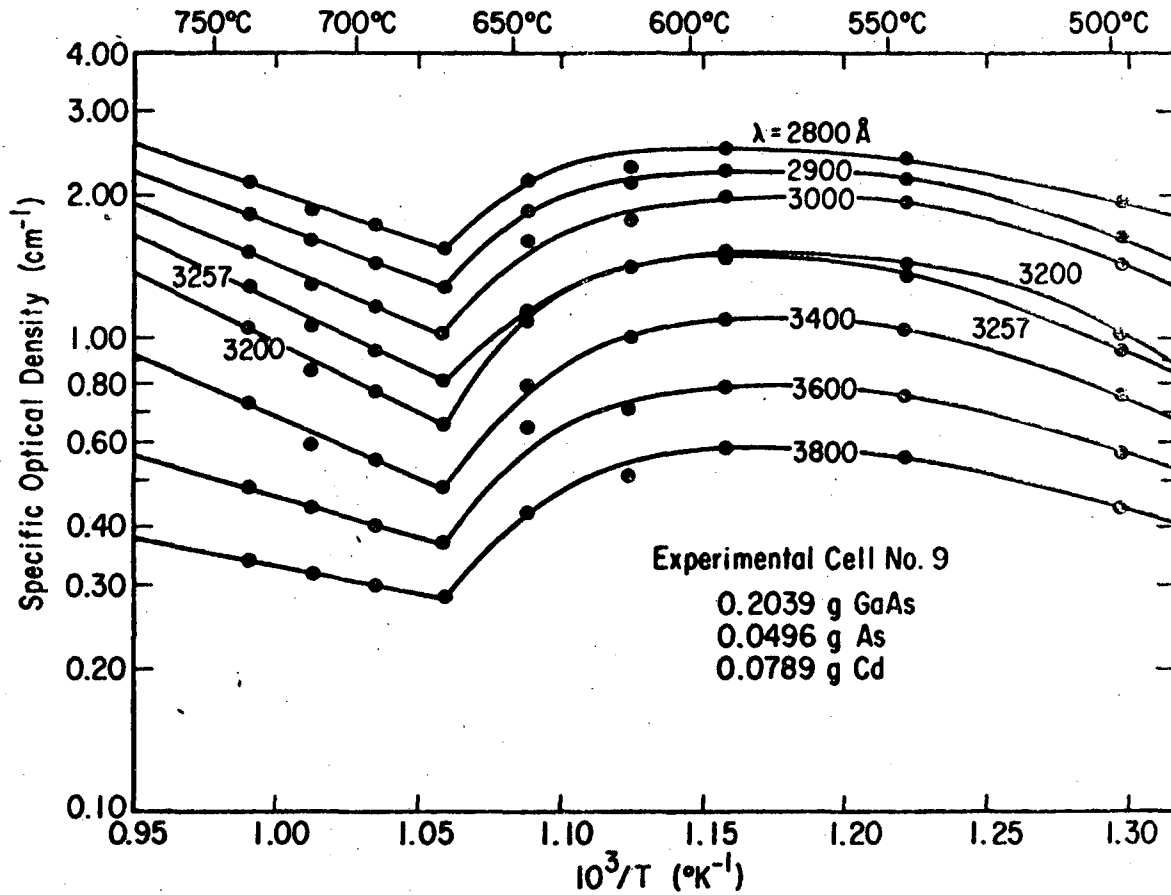
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Fig. 3. Specific optical density of pure zinc vapor vs. wavelength at different temperatures of phase equilibrium in the cell reservoir.



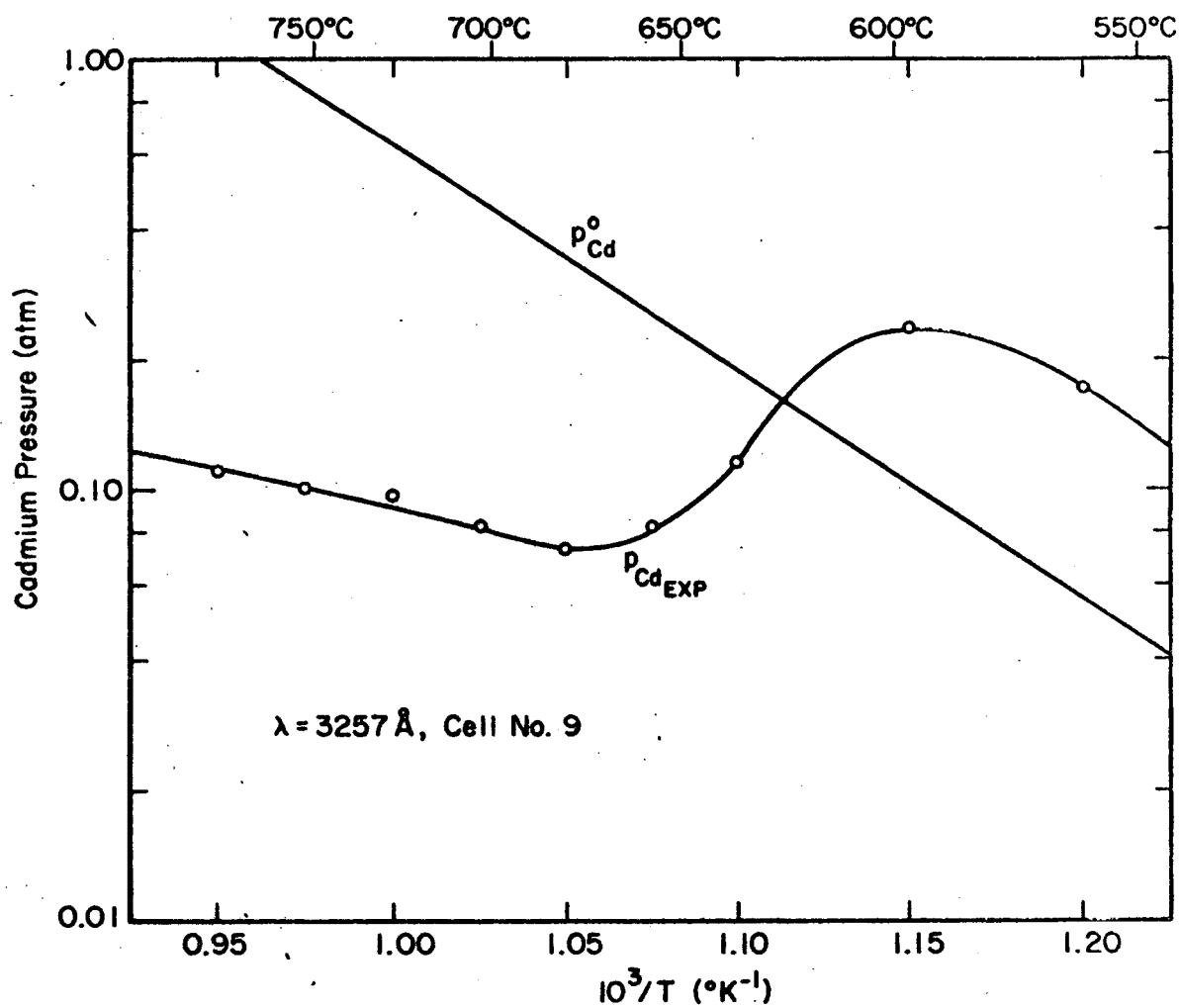
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Fig. 4. Specific optical density of pure cadmium vapor vs. wavelength at different temperatures of phase equilibrium in the cell reservoir.



XBL 755-6251

Fig. 5. Log specific optical density vs. inverse absolute temperature for experimental cell No. 9.



XBL 755-6252

Fig. 6. Partial pressure of cadmium for cell No. 9.

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