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ACTIVITIES of GOLD-TELLURIUM ALLOYS

By

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Metallurgical Engineering.

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## ABSTRACT

The binary alloy system, gold-tellurium, was investigated in the temperature range 615°C to 750°C by equilibration of alloy samples with tellurium vapor using a multi-sample equilibration apparatus. The experimentally determined parameters were alloy temperature, tellurium temperature, and alloy composition. The activities and activity coefficients of tellurium were determined from the experimental data, and the activities and activity coefficients of gold were determined by use of the Gibbs-Duhem relation. The system shows severe deviations from ideality.

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## INTRODUCTION

Thermodynamic activities in an alloy are influenced by the forces of repulsion and attraction that are present within the alloy. These forces are, at least to some extent, controlled by the atomic arrangement in the alloy, so that activity data may give indications of this atomic arrangement. Further, activity data aid in predicting how a material will react in both chemical and physical reactions.

Electrical measurements are currently in progress on this campus on single crystals of the intermetallic compound  $\text{AuTe}_2$ . The activity data of this investigation were obtained in hopes that it would aid in the preparation of these single crystals. Also, in combination with these electrical measurement, the data may give indications of the atomic structure present in both the solid and liquid alloys of the system.

## THEORETICAL DISCUSSION

The activity of a component in an alloy is related to its partial molar free energy,  $\Delta\bar{G}$ , as follows:

$$\Delta\bar{G}_i = RT \ln a_i$$

The integral free energy of a particular system can be calculated if all the partial free energies are known:

$$\Delta G = \sum N_i \Delta\bar{G}_i$$

Where  $N_i$  is the atom fraction of component  $i$ .

All the rest of the thermodynamic variables can be calculated if the partial free energies are known as a function of temperature.

$$\begin{aligned} \Delta\bar{H}_i &= \Delta\bar{G}_i + T \Delta\bar{S}_i \\ \Delta\bar{S}_i &= \frac{\Delta\bar{H}_i - \Delta\bar{G}_i}{T} \\ \Delta\bar{H}_i &= \frac{\partial(\Delta\bar{G}_i/RT)}{\partial(1/T)} \end{aligned}$$

and again the integral quantities are calculated as before.

$$\Delta S = \sum N_i \overline{\Delta S}_i \quad \Delta H = \sum N_i \overline{\Delta H}_i$$

The activity,  $a_i$ , of component  $i$  in an alloy system is defined as the ratio of the fugacity of  $i$  in the alloy,  $f_i$ , to the fugacity in the standard state,  $f_i^\circ$ .

$$a_i = f_i / f_i^\circ$$

If the vapor over the alloy acts as an ideal gas, the fugacity can be replaced by the vapor pressure. At the high temperatures and low pressures encountered in most alloy studies the vapors are very close to ideal. Hence, activity is defined as:

$$a_i = P_i / P_i^\circ$$

where  $P_i$  is the vapor pressure over the alloy and  $P_i^\circ$  is the vapor pressure in the standard state. Thus, the activity can be thought of as the escaping tendency of a component from the alloy.

The standard state for a condensed phase is the pure material at one atmosphere pressure and at the temperature in question. Experimentally, however, the pure material at its equilibrium vapor pressure is a state which is relatively easy to obtain, convenient to use as a reference, and hence generally employed. The difference between the two is negligible as a pressure of one atmosphere does not affect the

vapor pressure. If it is more convenient to use another standard state, it is simple to convert from one standard state to another.

An alloy may be regarded as a solution so that its behavior may be compared with an ideal solution. An ideal solution is defined as one in which the components have no effect on each other. In this case, the vapor pressure of each component over the solution is proportional to the amount of the component present. Put into the form of Raoult's law, the partial pressure over the solution is equal to the atom fraction times the vapor pressure of the pure material.

$$P_i = P_i^\circ N_i$$

Thus the activity is equal to the atom fraction.

Since very few alloy systems exhibit ideal behavior, it is convenient to introduce a new quantity, the activity coefficient,  $\gamma_i$ . The activity coefficient is defined as the ratio of activity to mole fraction, so that the activity coefficient for an ideal solution is one.

$$\gamma_i = a_i / N_i$$

Then the partial molar free energy will be given by:

$$\Delta \bar{G}_i = RT \ln N_i + RT \ln \gamma_i$$

If the activity of one component in a binary solution

is determined experimentally, then the activity of the other component can be calculated by using the Gibbs-Duhem equation. For a two-component system the equation is (Darken and Gurry, 1953, p. 258):

$$N_1 d \ln a_1 + N_2 d \ln a_2 = 0$$

where the 1 refers to component 1 and the 2 refers to component 2.

If  $a_2$  is known as a function of mole fraction, then:

$$\ln a_1 = \int_{N_1=1}^{N_1=N_1} - \frac{N_2}{N_1} d \ln a_2$$

Since it is difficult to express the experimental data for  $a_2$  in analytic form, this integral is usually evaluated graphically. As  $N_1$  approaches 1,  $N_2$  approaches 0 and their ratio approaches infinity, which makes the graphical integration impossible. To overcome this problem, Darken and Gurry proposed the following substitution:

$$\alpha_2 = \frac{\ln \gamma_2}{N_1^2} \quad \alpha_1 = \frac{\ln \gamma_1}{N_2^2}$$

Substituting  $\alpha$  into the Gibbs-Duhem equation, it becomes:

$$\ln \gamma_1 = \alpha_2 N_1 \frac{dN_1}{N_1^2} - \int_{N_1=1}^{N_1=N_1} \alpha_2 dN_1$$

By constructing a curve of  $\alpha_2$  vs. composition, the above integration can be performed graphically as  $\alpha$  remains finite at all values of  $N$ .

## HISTORICAL DISCUSSION

There are a number of ways to measure activities experimentally; the two most common for alloy systems are the measurement of vapor pressures or the measurement of electromotive forces of electrochemical cells. The electrochemical cell method has two severe conditions that must be met. The cell reactions must be completely reversible and the cell reactions must be known with certainty. The method gives good results when done properly, but the entire procedure requires great care.

The vapor pressure method of activity measurement is a very direct way of obtaining activities. There are two general techniques used, the equilibrium or static methods and the kinetic methods. In general, the kinetic methods pass a known amount of inert gas over the alloy, condense out the volatile component from the inert gas and analyze the condensate. By varying the gas flow rate, the metal content as a function of flow rate can be determined and extrapolated to

zero flow rate which should be the equilibrium value. This method has several complicating features. The gas must be very pure, or it may affect the surface of the samples. The surface of the samples may become depleted in one alloy component, resulting in concentration gradients within the sample. Diffusion of the metal vapors through the system may cause the gas sample to become depleted or enriched with the metal vapor relative to the amount of material vaporized when the gas was passed over the sample.

The equilibrium methods are generally more reliable than the kinetic methods as they involve fewer variables. The pressure of the vapor over the alloy can be measured directly with one of the many types of pressure gauges available. Care must be taken to avoid any cold spots in the system, and any interferences between the gauge mechanism and the vapor must be avoided or corrected for. For example, many low pressure gauges are affected by the molecular weight of the vapor. If more than one component is present in the vapor, some method must be found to obtain the partial pressures.

When only one component in the alloy is volatile, some specific methods are available. One of these methods is the dew point method of Hargraves (1939, p. 115). Here the alloy is sealed in the end of an evacuated transparent tube. The alloy end of the tube is set at some appropriate temperature, while the temperature of the other end of the tube is lowered

until a fine deposit or "dew" of the volatile component is condensed at the cold end. The vapor pressure over the alloy at the higher temperature must equal the vapor pressure of the pure component at the lower temperature. The dew point method is convenient to use experimentally, but it has limitations which may prevent its use. The amount of the deposit must be kept small, or the composition of the alloy will be changed. If the condensation coefficient for the vapor species on the alloy is quite low, the evaporation rate will be small, thus the dew will cause the vapor pressure in the tube to be lowered below the equilibrium value, as fresh material cannot leave the alloy at sufficient rate to maintain the pressure. A situation like this will give a dew point temperature below the true value. Supercooling of the vapor may be necessary to cause nucleation of the fine droplets. If this occurs, again the dew point temperature will be below the true value. Also the vapor pressure of the volatile component as a function of temperature must be known.

Another method first used by Seith and Kraus (1938, p.98) is applicable when only one component is volatile. Here an alloy at an appropriate temperature is equilibrated with the volatile vapor from a sample of pure material at a lower temperature. The alloy will either gain or lose the volatile component until the partial pressure over the alloy equals the vapor pressure over the pure material at the lower

temperature. The time necessary to obtain equilibrium must be known, as the alloy composition will be incorrect if equilibrium is not obtained. There must be no areas in the system which have a lower temperature than the temperature of the pure component, as the component will condense in these cold areas and give a lower vapor pressure than desired throughout the system. It is necessary that the alloy samples remain in their equilibrium composition when the equilibration is complete, thus some method of rapid cooling should be devised. Again, the vapor pressure of the volatile component as a function of temperature must be known. A modification of this method was used in this study.

It is necessary to know the vapor pressure of tellurium as a function of temperature in order to calculate the desired activity values. There are a number of published studies in the literature concerning the vapor pressure of tellurium: Brooks (1952, p. 227), Gattow and Schneider (1959, p. 189, Kudryantsev and Ustyugov (1961, p. 2421), Machol and Westrum (1958, p. 2950), Kelley (1935, p. 102). After careful consideration of the data given in each, it was decided that the data of Machol and Westrum would be used. The work, as reported in the publication, appears to have been done with great care, and it is thought to be the best data available. The vapor pressure as a function of temperature is given by the following equation.

$$\log P_{\text{mm Hg}} = \frac{-10,663.14}{T} + 64.73140 - 18.61687 \log T + 0.00341783 T$$

The equation is valid over the temperature range 449°C to 855°C. The equation covers completely the temperature range of this investigation.

By analogy with sulfur and selenium (Kelley, 1935, p.102), it was thought that tellurium might have more than one vapor species. It should be noted that the above expression for the vapor pressure is for total pressure and therefore the question of vapor species does not affect the activity calculations, but it is an interesting point that seems worth discussing. Yost and Russell (1944, p. 285) state "electron-diffraction experiments on tellurium vapor at approximately 600°C show that mainly  $\text{Te}_2$  molecules are present." Georgi (1957) has measured the vapor density of tellurium from 512°C to 880°C and has concluded that there is only a single vapor species of tellurium present in this temperature range. Thus, it is thought that tellurium vapor is made up of essentially  $\text{Te}_2$  molecules.

There has been very little information published about the gold-tellurium system. The phase diagram has been investigated by several workers and is reproduced in Hansen (1958, p. 234). This work was done quite some time ago and may not be entirely correct.

Tunnel and Pauling (1952, p. 375) have studied the structure of calaverite ( $\text{AuTe}_2$ ) and Krennerite ( $\text{AgTe}_2$ ) and have reported the space groups for the two compounds. In  $\text{AuTe}_2$  they conclude that the gold atoms are surrounded by six tellurium atoms and that the tellurium atoms are surrounded by three gold atoms and three tellurium atoms.

Markham (1960, p. 1460) has studied the phases present in the ternary system Au-Ag-Te in the temperature range  $150^\circ\text{C}$  to  $450^\circ\text{C}$ .

Kuznetsov and co-workers (1960, p. 1077) have studied electrocapillary phenomena in gold-tellurium alloys from 0-44% Au at  $485^\circ\text{C}$ . From this work they have been able to calculate activities. The activity data were presented only in the form of a graph. Values from their curve are shown in Figure 15.

## EXPERIMENTAL APPARATUS

When this study was begun, it was thought that the dew point method would be the most desirable method to use. Results as discussed later proved this method was not suitable and a vapor equilibration method was used.

The cells for the dew point method were made from 9mm pyrex tubing 8 inches long. A sidearm was sealed on the center of the tube to allow for sample insertion and evacuation. Circular pieces of pyrex plate were sealed on each end of the cells. A schematic diagram of the cells is shown in Figure 1.

The lower temperature end of the tube needed to be varied over a wide range of temperature. To accomplish this, a small nichrome heater was made up as is shown in Figure 2. The inner core of the heater was constructed of aluminum. The core was wound with 20 gauge nichrome wire. To prevent shorting, the wire was insulated with fish spine insulator. The insulated wire was wound on the core and coated with

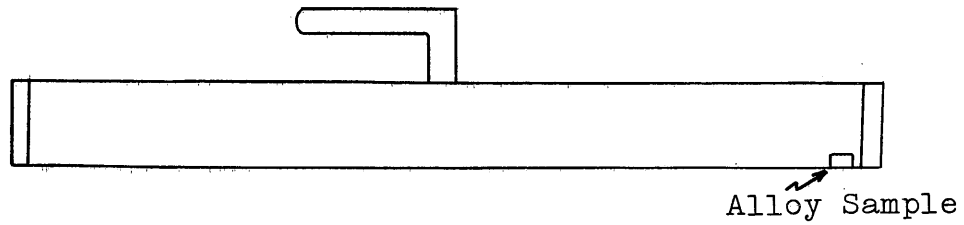
Sauereisen zirconium base cement. A small hole was placed in the end of the heater to allow access for a thermocouple and a larger hole to allow the end of the tube to be viewed.

The furnace used to obtain the desired temperatures was a Heavy Duty resistance furnace, Model No. M-5024-S. The furnace had an inside diameter of 5 inches and was 28 inches long. It was equipped with three elements each with a separate tap for individual regulation.

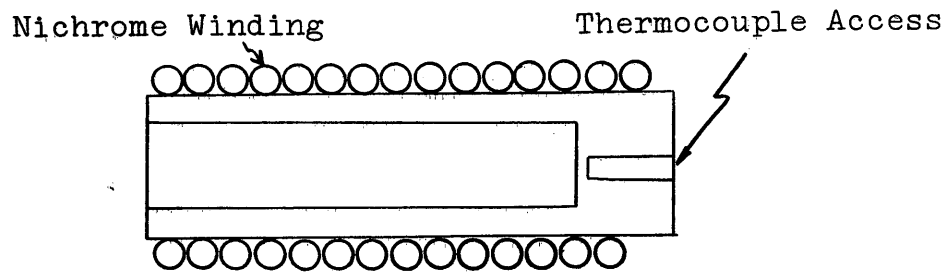
An Inconel block 4 inches in diameter and 3 inches long was placed in the furnace. Four holes were drilled in the block at equally spaced intervals, to accommodate the higher temperature end of the cells. A light was placed at the back of the furnace to illuminate the cells.

Since the dew point method was not satisfactory as discussed later, it was decided to use a vapor equilibration method. For this method it was necessary to know the time required to reach equilibrium. To determine the time, cells were made up similar to the dew point cells. Here the cells were made from 9mm vycor tubing, and were evacuated by gettering as described later. The same furnace arrangement was used as above.

The equilibrium time studies indicated that at least three weeks would be required to obtain equilibrium. It would have taken an extremely long time to collect the necessary data running a maximum of four samples at a time. To



Dew Point Cell  
Figure 1.



Nichrome Heater  
Figure 2.

Figure 2.

overcome this problem, a furnace was set up to run as many as 25 samples at one time.

Cells such as are shown in Figure 3 were made to run several samples per cell. Here the cells were 24 inches long, again made from 9mm Vycor tubing. Small indentations were placed in the tube to hold the alloy samples in place.

The same furnace described earlier was used in the equilibration but with some modification. Since each winding could be controlled individually, a temperature gradient could be maintained along the length of the furnace. Stainless steel blocks 1 inch thick and 5 inches in diameter were placed along the length of the furnace. A diagram of the blocks is shown in Figure 4. The equilibration cells passed through the larger holes and the thermocouples thru the smaller holes. The blocks were located along the length of the furnace so that the alloy samples were located in the center of each block. Thermocouples were located in the center of each block to measure its temperature. Thus the blocks served three purposes: 1) smoothed out the temperature gradient at the sample location; 2) provided a convenient method to measure sample temperatures; 3) held the sample tubes in the proper location.

Since both the tellurium in the reservoir and the alloy samples were liquid at the temperatures involved, some method of keeping the materials in place was required.

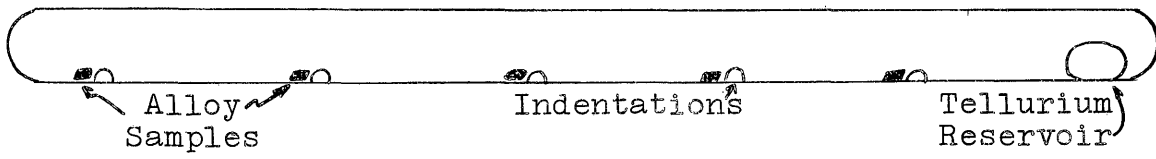


Figure 3. Equilibration Cell

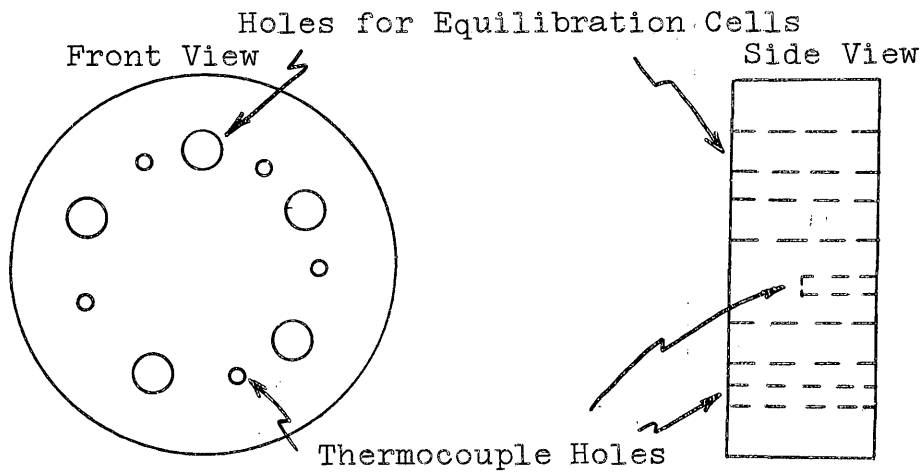


Figure 4. Stainless Steel Block

The furnace was inclined at a slight angle from the horizontal with the tellurium reservoirs being located at the lower end, so that the tellurium was kept in that end of the cell. The alloy samples were small, and the small indentations were sufficient to keep the alloys in place.

The temperature of the tellurium reservoirs was maintained by using small heaters such as were described earlier, except that here the inner core was made of stainless steel. The lower melting point of the aluminum prevented its use.

A diagram of the completed furnace arrangement is shown in Figure 5. The convection block was a piece of 1/4 inch thick transite. It prevented air from circulating around the cells between the heaters and the last stainless steel block.

The temperatures in the furnace were controlled by using a General Electric controller, Model No. 8HP. The controller operated on the high-low principle, i.e., if the temperature dropped below the set point, the controller operated in the high voltage position. If the temperature rose above the set point, the controller switched to the low voltage position. The controller thermocouple was placed in the highest temperature in the furnace. The controller output was fed into three variable transformers, one for each winding. By stepping down the controller voltage to the windings, a temperature gradient could be set up and controlled in the furnace. Control was  $\pm 3/4^\circ\text{C}$  of the highest temperature block and  $\pm 1\ 1/4^\circ\text{C}$  in the

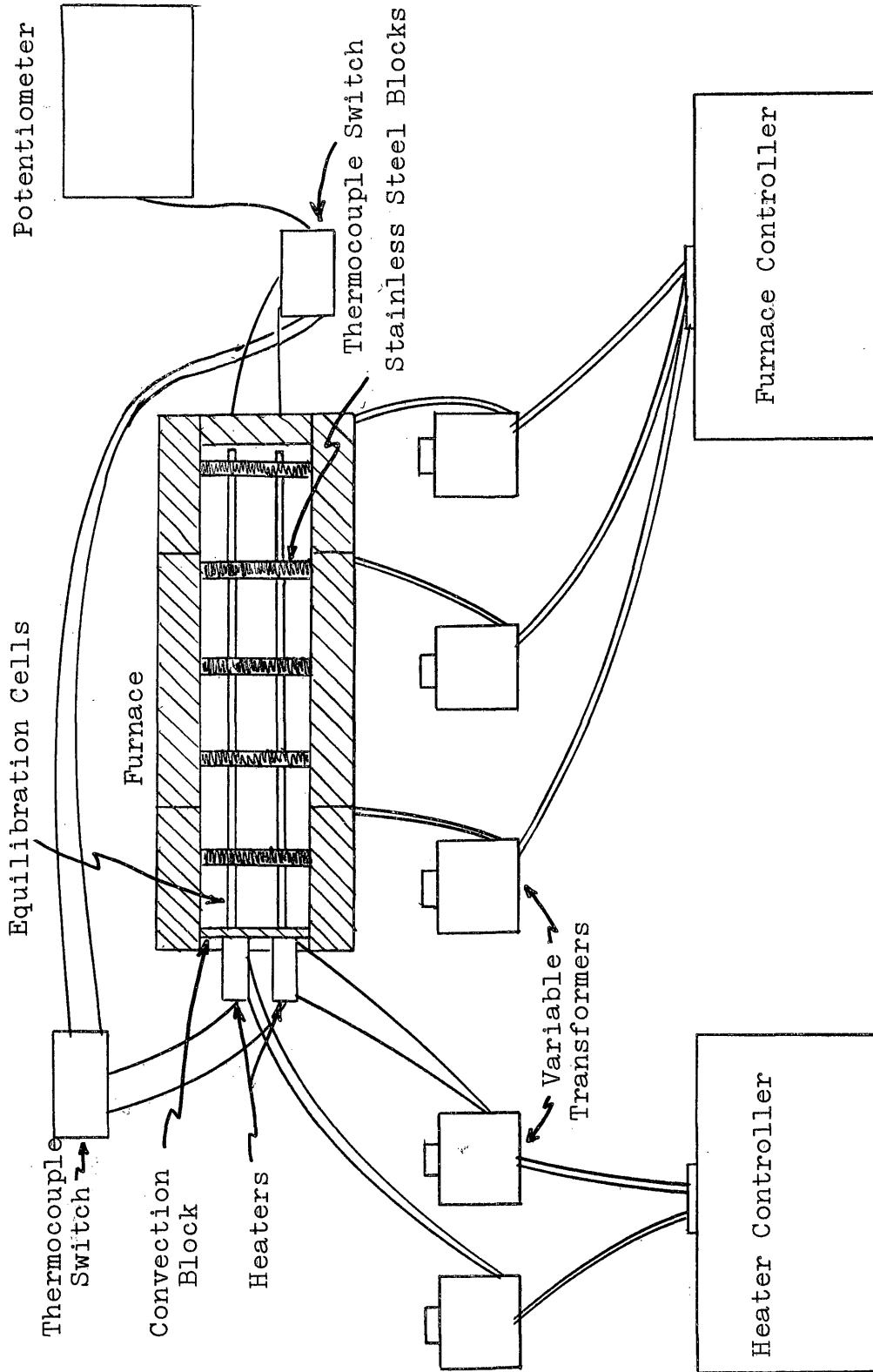


Figure 5. Schematic of Furnace Arrangement

lowest temperature block.

Temperature control for the heaters was maintained by use of a Foxboro Potentiometric Controller. This controller also operated on the high-low principle. A galvanometer was built into the controller which was used to read the control thermocouple voltage. The position of the galvanometer needle determined whether the controller was in the high or low position. The control thermocouple was inserted into the highest temperature heater, so that again the highest temperature was used as a control point. The controller output was fed into variable transformers, one for each heater. Again by cutting the controller voltage down, the desired temperature could be maintained. On the highest temperature heater, the temperature was held to  $\pm 1\frac{1}{2}^{\circ}\text{C}$ , while on the others the temperature variation was  $\pm 2^{\circ}\text{C}$ .

All temperature measurements were made with platinum-platinum rhodium thermocouples. The wire used in the thermocouples was from Engelhard Industries and was calibrated at their factories (Appendix No. I). The wires were C.P. platinum and C.P. platinum (87%) - C.P. rhodium (13%). The calibration was reliable to within 0.25% up to  $1300^{\circ}\text{C}$  for extended periods of time. The thermocouple wires were encased in ceramic insulators  $\frac{1}{8}$  inch in diameter and passed through the blocks as shown in Figure 5. The thermocouple voltages were measured using a Leeds and Northrup Portable Precision

Potentiometer Model 8662. This instrument was calibrated against a Leeds and Northrup K-3 Potentiometer and was accurate to  $\pm 3$  microvolts.

## EXPERIMENTAL PROCEDURE

In the dew point method, the cells were prepared as explained, the alloy sample inserted, and the cell evacuated with a diffusion pump to  $1 \times 10^{-6}$  mm Hg pressure. The cells were then placed in the Inconel block and brought to temperature. The window of the cell was observed through the hole in the heater. The temperature of the heater was slowly lowered until a deposit was formed on the window, raised until the deposit disappeared, lowered again, and so forth until the actual dew point was determined. Due to difficulties explained later, the method was abandoned.

The cells used in the equilibrium time determinations were evacuated in a different manner. The tube was sealed off at one end, the alloy sample was placed in the tube, and a neck was placed 8 inches from the sealed end. Several pieces of titanium sponge were placed behind the neck, and another neck was placed in the tube about three inches from the first. Thus the titanium was restricted to a three inch section of

the tube. The tube was then connected to a mechanical vacuum pump and evacuated for 30 minutes. During this time, the walls of the tube were flamed several times in an attempt to remove some of the absorbed water vapor from the tube walls. At the end of the evacuation period, the cell was sealed off at the second neck, leaving the section containing the titanium sponge attached to the cell. The section containing the sponge was then placed in a resistance furnace for 24 hours at approximately 700°C. At this temperature, the titanium acted as a getter, reacting with the oxygen, nitrogen, carbon dioxide, and water vapor present in the cell, but not with hydrogen which is not expected to cause trouble. After gettering the cell was sealed off at the first neck and was ready for equilibration.

The cells were placed in the Inconel block used in the dew point studies to provide a constant temperature for the alloy samples. The temperatures of the other end of the cells were maintained by using the heaters as before. The starting material was all of the same composition, approximately  $\text{AuTe}_2$ . Cells were taken out of the block at periodic intervals and analyzed. Equilibrium was considered to have been reached when the alloy composition became constant. Studies were carried out at alloy temperatures of 600°C and heater temperatures of 500°C. Equilibrium was attained within three weeks, but not in two weeks, so the multi-sample method described

earlier was employed.

The alloys used in this study were all initially of the nominal composition  $\text{AuTe}_2$ . The alloy was prepared by melting under vacuum. The materials used in making the alloy were supplied by the American Smelting and Refining Company and were 99.999% pure. The company analyses are given in Appendix II. The prepared alloy was analyzed spectroscopically and was found to contain essentially the same impurities as given in the company analyses. In the first few runs, all samples were approximately 200 mg., but later runs smaller samples were used. At high tellurium pressures, the large samples took up so much tellurium that they ran around the indentations in the cells. The smaller samples stopped this problem.

After the alloy samples were placed in the cells, tellurium was added at the reservoir end of the cells. A neck was placed 5 inches from the first indentation. The cells were then evacuated in exactly the same manner as the equilibration time cells. The cells were then ready for equilibration.

The equilibration was a relatively simple matter. The cells were loaded into the furnace and the temperatures were set at the desired levels. The samples were allowed to equilibrate for a period of four weeks. This longer period was chosen to eliminate any complications that might be caused

by the longer cells. Further, the sample temperatures were higher than the temperatures in the equilibration time runs so it is felt that equilibration was reached in all runs. During the equilibration period, temperature measurements were taken at least once a day. After the period was up, the furnace was shut off and the furnace was opened to the air. The cells could not be removed immediately. The alloys were liquid and removing them before they solidified would have caused them to run out from behind the indentations. Cool air was blown across the cells and blocks to hasten cooling. Even with the cooling air, there was still some tellurium loss from the samples. The tellurium lost from the samples condensed in the cells just outside the blocks. By scraping the condensed material out of the cells and weighing it, the loss was estimated to be no more than 2 to 3 mg. from a 200 mg. sample. The cells were broken open by scratching the outside of the tube with a file and then breaking the tube. The samples were removed and were then ready for analysis.

As can be seen from the phase diagram for the system in Figure 6, there is a two-phase liquid-solid region on the gold side of the diagram. With an equilibration method as was used here, samples whose composition is in this region will not be obtained unless the tellurium vapor pressure in the cells corresponds exactly to the equilibrium pressure in that region. The chance of setting the temperature of the reservoir to

exactly the proper value to give the equilibrium pressure are very slight. Thus, the samples fell into two definite composition regions, those in the single phase liquid region and those in the solid solution region near the gold axis.

The samples from the liquid phase region were analyzed by a method described by Seath and Beamish (1937, p. 373).

The samples were put into solution by dissolving them in hot aqua regia. The aqua regia solution was then evaporated to near dryness; 50 ml of 5 N HCl were added to the solution and again evaporated to near dryness. This procedure was repeated one more time. The evaporations were necessary to remove all the nitrate from the solution. The resulting solution was diluted with 50 ml of 1 N HCl and the solution heated. 10 ml of a 1 weight percent solution of hydroquinone were added to the solution containing the sample. The gold was precipitated quantitatively by the hydroquinone. The precipitate was filtered out using fritted glass filter, dried at 85°C, and weighed. The amount of tellurium present was found by difference. The method was checked by using known amount of gold and was found to be accurate to 0.25 mg. out of 50 mg. sample.

The samples containing very low percentages of tellurium were analyzed spectroscopically. Standards were made up by distributing small amounts of  $\text{TeO}_2$  in a carbon matrix. The standards were vaporized in a carbon arc and their spectra

were recorded photographically using a Baird three meter spectrograph. The alloy samples were analyzed with the same equipment. The samples were approximately 10 mg. in size, and were in the form of a small piece of alloy. The piece was tamped into a carbon electrode containing loose carbon. Both the standards and samples were arced for 20 seconds. The tellurium present was determined by measuring the transmittency of the tellurium lines in the standards and comparing them to the transmittency for the samples. The standards and the samples were run on the same photographic plate so that no problems would arise from developing. This is a quantitative method without a matrix correction and is estimated to be accurate to within a third of an order of magnitude.

## EXPERIMENTAL RESULTS

With the experimental apparatus used in this investigation, there were two independent variables, the sample temperature and the reservoir temperature. When these two variables were set, the value of the third variable, the alloy composition was fixed. The value of these variables are summarized in Table 1, along with the calculated activity values for tellurium.

## CALCULATIONS and DISCUSSIONS

In this investigation the activities of both tellurium and gold were calculated. The tellurium values were calculated from the experimental data and the gold values were obtained from the Gibbs-Duhem relation.

A consideration of the phase diagram for the system, Figure 6, shows two regions of interest: A single-phase, liquid region, and a two-phase, liquid solid region. A single-phase, solid solution region is present near the gold axis. The solid solution region has a very narrow range of composition and does not show on the diagram. Applying Gibbs' Phase Rule,

$$F = C - P + 2$$

to the single condensed phase region,  $F = 2$ . Then, if the temperature and pressure are fixed, the equilibrium composition is fixed. Thus varying pressures along an isotherm will cause the composition to vary. In the two-condensed phase region,  $F = 1$ . At a particular temperature there is only one

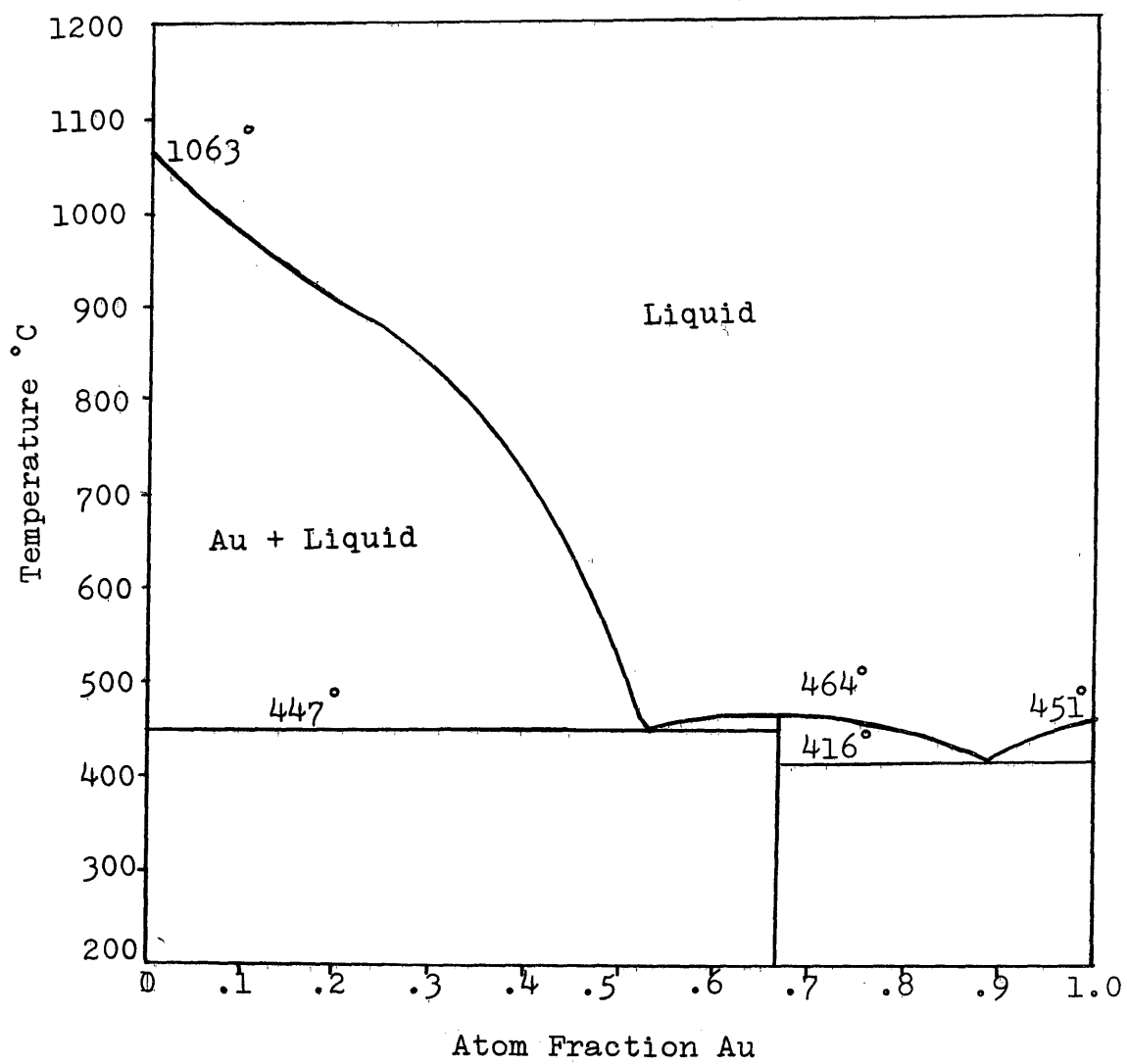


Figure 6. Phase Diagram

equilibrium pressure in that region. This single equilibrium pressure requires that the activity remain constant.

When the dew point method was applied to this system, it was found that several of the necessary conditions were not met. It was not possible to condense a fine dew on the window. The only observable deposit that was condensed consisted of discrete droplets that had to grow to a fairly large size before they could be seen. These droplets were large enough that the composition of the sample may have been changed to a significant degree. Further, the cell may have been displaced from equilibrium by this large deposit.

In order to determine whether the method was consistent, measurements were made on pure tellurium. Here the dew should form at the same temperature as the tellurium in the other end of the tube. It was found that approximately 10°C of supercooling were necessary to form an observable deposit. A sensitive photocell was attached to the cell window in hopes that it would detect the deposit before it could be seen visually. The photocell indicated approximately the same amount of supercooling to detect the deposit. The long equilibrium times necessary in this system cast further doubt on the applicability of the dew point method. The tellurium loss from the alloy is so very slow that an equilibrium would be very difficult to obtain. Thus, the dew point method was abandoned in favor of the vapor equilibration method.

The activities and the activity coefficients of tellurium are given in Table 1. The corresponding values for gold are given in Table 2. Figures 7 through 11 are plots of activity vs. composition for the indicated temperatures. Before these figures could be drawn, several facts had to be used. The activity of pure tellurium has to be 1, thus one point on the curve is defined. The experimental activities define the curve throughout the liquid region. The activity continues to decrease in the liquid region until the composition of the two-phase region is reached. At this point the activity must become constant. There was not sufficient experimental data to define the two-phase region boundary. The composition of the phase boundary was obtained from the phase diagram. The constant activity portion of the curve was drawn until it intersected the phase boundary, then the rest of the curve was drawn as indicated by the experimental points. The composition of the solid solution region was so narrow that it shows up as essentially a vertical line on the gold axis.

As discussed above, the activity in the two-phase region is constant. It was not possible to obtain points in this region; however, it was possible to bracket the activity in this region to a narrow range. Alloys whose compositions were in the solid solution region did not have activities exceeding 0.045. In the liquid region, activities as low as

TABLE 1. Experimental and Calculated Results for Tellurium

Sample Wt. (mg)	Gold Wt. (mg)	Sample Temp °C	Reservoir Temp °C	P <sub>T</sub> mm Hg	A <sub>T</sub> e	N <sub>T</sub> e	Y <sub>T</sub> e
RUN 1							
94.71	94.554	608	420	0.06	0.0103	0.00254	4.07
91.74	91.601	644	420	0.06	0.0055	0.00233	2.35
89.60	89.599	677	420	0.06	0.0032	0.00001	268.11
88.45	88.447	748	420	0.06	0.0011	0.00003	31.99
94.57	94.569	800	420	0.06	0.0006	0.00001	41.67
155.52	94.720	608	475	0.34	0.0520	0.4977	0.1046
94.68	94.276	644	475	0.34	0.0276	0.00657	4.213
74.87	74.816	677	475	0.34	0.0162	0.0011	14.728
87.27	87.267	748	475	0.34	0.0059	0.00005	111.204
93.05	93.024	800	475	0.34	0.0030	0.00042	7.255
221.77	92.59	608	552	2.19	0.3296	0.682	0.483
153.50	92.74	677	552	2.19	0.1029	0.503	0.204
131.66	92.95	748	552	2.19	0.0373	0.391	0.0954
87.20	87.117	800	552	2.19	0.0195	0.00145	13.38
RUN 2							
150.67	88.52	615	528	1.29	0.1706	0.5201	0.3281
137.19	91.46	650	528	1.29	0.0932	0.4356	0.2141
125.21	90.34	661	528	1.29	0.0779	0.3733	0.2087
94.19	94.174	711	528	1.29	0.0365	0.00026	137.54
98.00	97.972	746	528	1.29	0.0222	0.00044	51.144

Table 1. (Contd.)

Sample Wt. (mg)	Gold Wt. (mg)	Sample Temp °C	Reservoir Temp °C	P <sub>T<sub>e</sub></sub> mm Hg	A <sub>T<sub>e</sub></sub>	N <sub>T<sub>e</sub></sub>	Y <sub>T<sub>e</sub></sub>
203.86	96.03	615	553	2.24	.2964	.6342	.4675
146.44	86.73	650	553	2.24	.1620	.5152	.3144
144.97	84.29	661	553	2.24	.1354	.5264	.2572
139.33	90.07	711	553	2.24	.0634	.4578	.1385
93.07	92.91	746	553	2.24	.0391	.0025	15.453
RUN 3							
170.04	101.77	624	517	1.00	.1125	.5087	.2212
120.64	82.13	644	517	1.00	.0797	.4199	.1900
144.29	96.74	664	517	1.00	.0575	.4314	.1333
99.42	99.39	726	517	1.00	.0228	.00045	50.32
103.70	103.68	745	517	1.00	.0176	.00026	66.04
586.55	73.16	624	607	6.55	.736	.915	.804
212.06	83.84	644	607	6.55	.522	.702	.743
137.47	63.75	664	607	6.55	.376	.641	.587
RUN 4							
159.88	103.73	726	607	6.55	.150	.455	.329
179.22	130.16	745	607	6.55	.116	.368	.315
183.04	59.87	671	597	5.43	.279	.760	.367
96.85	56.94	697	597	5.43	.188	.520	.362
113.73	66.96	710	597	5.43	.156	.519	.300
122.00	83.19	747	597	5.43	.0935	.419	.223
122.68	84.20	768	597	5.43	.0712	.414	.172

Table 1. (contd.)

	Sample Wt. (mg)	Gold Wt. (mg)	Sample Temp °C	Reservoir Temp °C	P <sub>Te</sub> mm Hg	A <sub>Te</sub>	N <sub>Te</sub>	X <sub>Te</sub>
Run 4 (contd)	131.25	36.97	671	628	9.54	.491	.797	.615
	103.13	53.36	697	628	9.54	.330	.590	.560
	78.63	45.34	710	628	9.54	.273	.531	.514
	89.36	60.17	747	628	9.54	.164	.428	.383
	109.84	77.74	768	628	9.54	.125	.389	.322
	317.52	55.10	671	653	14.57	.749	.880	.851
	90.92	50.17	697	653	14.57	.504	.556	.906
	129.40	73.24	710	653	14.57	.417	.542	.769
	76.43	54.27	747	653	14.57	.250	.387	.648
	78.63	60.13	768	653	14.57	.191	.322	.593
	311.64	63.21	697	671	19.44	.673	.859	.784
	163.27	45.86	710	671	19.44	.557	.798	.700
	192.27	75.00	747	671	19.44	.335	.707	.473
	125.52	59.90	768	671	19.44	.255	.628	.406
	197.72	74.17	747	710	34.91	.601	.720	.834
	164.28	88.19	768	710	34.91	.458	.571	.802
RUN 5	103.85	30.73	612	588	4.57	.637	.786	.811
	86.91	34.23	630	588	4.57	.463	.704	.658
	73.45	35.54	648	588	4.57	.341	.622	.548
	38.00	23.69	708	588	4.57	.135	.482	.279
	37.76	27.44	745	588	4.57	.081	.367	.220

Table 1. (contd.)

Sample Wt (mg)	Gold Wt. (mg)	Sample Temp °C	Reservoir Temp. °C	P <sub>T</sub> mm Hg	A <sub>T</sub> e	N <sub>T</sub> e	Y <sub>T</sub> e
72.92	30.24	612	573	3.40	.474	.685	.691
58.94	25.75	630	573	3.40	.344	.665	.517
46.19	25.24	648	573	3.40	.253	.562	.451
60.78	39.17	705	573	3.40	.105	.459	.228
9.56	9.515	745	573	3.40	.060	.0072	8.29
98.82	43.09	630	542	1.77	.179	.666	.269
92.49	46.29	650	542	1.77	.128	.606	.210
67.80	27.44	745	708	33.92	.599	.694	.863
129.54	34.94	648	630	9.88	.737	.807	.913
35.11	23.10	708	630	9.88	.291	.445	.654
153.61	73.45	708	648	13.41	.395	.627	.630
55.36	37.32	745	648	13.41	.237	.427	.555
137.18	79.31	612	507	.78	.110	.530	.207
84.05	74.36	630	507	.78	.080	.167	.476

RUN 5  
(contd)

(contd)

**TABLE 2. Activity and Activity Coefficients of Gold Calculated from Gibbs-Duhem Relation**

Temp	Activity	Activity Coefficient	Atom Fraction Gold
615°C	.0032	.032	.1
	.0174	.087	.2
	.0666	.222	.3
	.190	.475	.4
	.460	.920	.5
	.924	1.54	.6
	.917	1.31	.7
	.920	1.15	.8
	.927	1.03	.9
650°C	.00495	.055	.1
	.0984	.123	.2
	.163	.234	.3
	.257	.429	.4
	.415	.831	.5
	.924	1.54	.6
	.917	1.31	.7
	.920	1.15	.8
	.927	1.03	.9
670°C	.00468	.052	.1
	.0968	.121	.2
	.1645	.235	.3
	.268	.447	.4
	.419	.839	.5
	.924	1.54	.6
	.917	1.31	.7
	.920	1.15	.8
	.927	1.03	.9

Table 2. (Contd.)

Temp	Activity	Activity Coefficient	Atom Fraction Gold
705°C	.00909	.101	.1
	.137	.171	.2
	.180	.257	.3
	.230	.383	.4
	.313	.626	.5
	.924	1.54	.6
	.917	1.31	.7
	.920	1.15	.8
	.927	1.03	.9
750°C	.0182	.202	.1
	.218	.237	.2
	.232	.331	.3
	.241	.401	.4
	.267	.535	.5
	.400	1.00	.6
	.917	1.31	.7
	.920	1.15	.8
	.927	1.03	.9

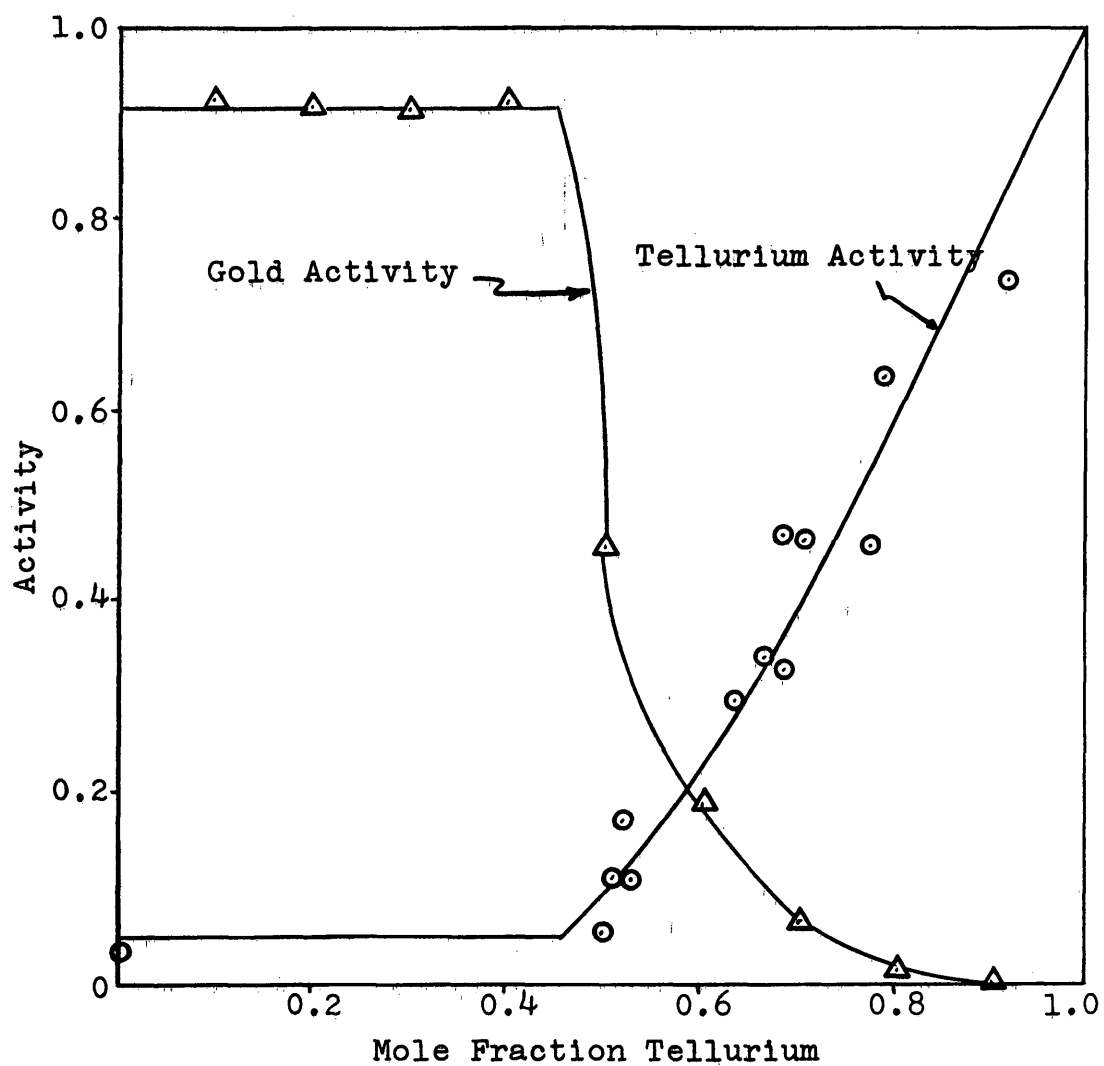


Figure 7. Activity vs. Mole Fraction Tellurium 615°C

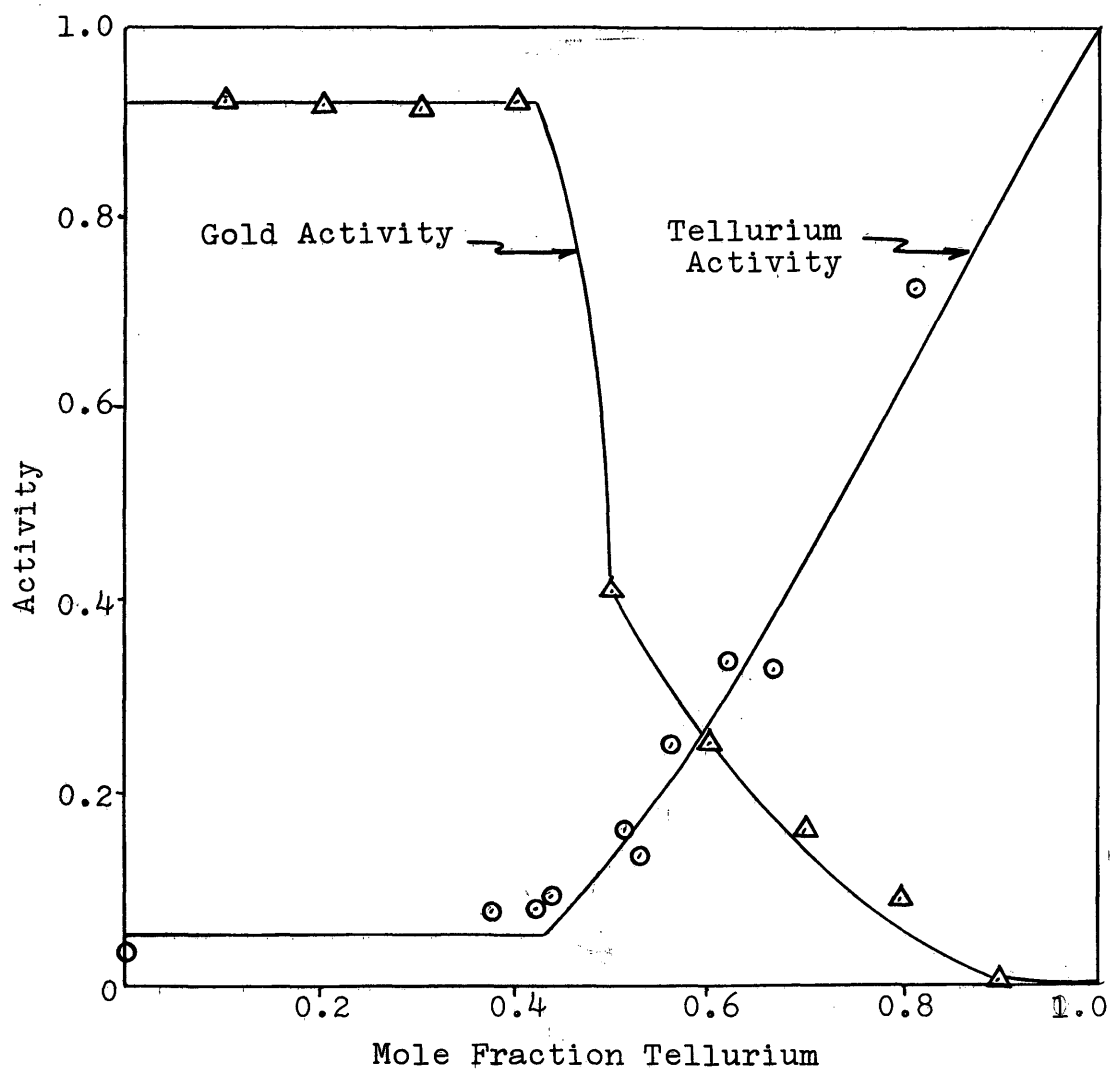


Figure 8. Activity vs. Mole Fraction Tellurium 650°C

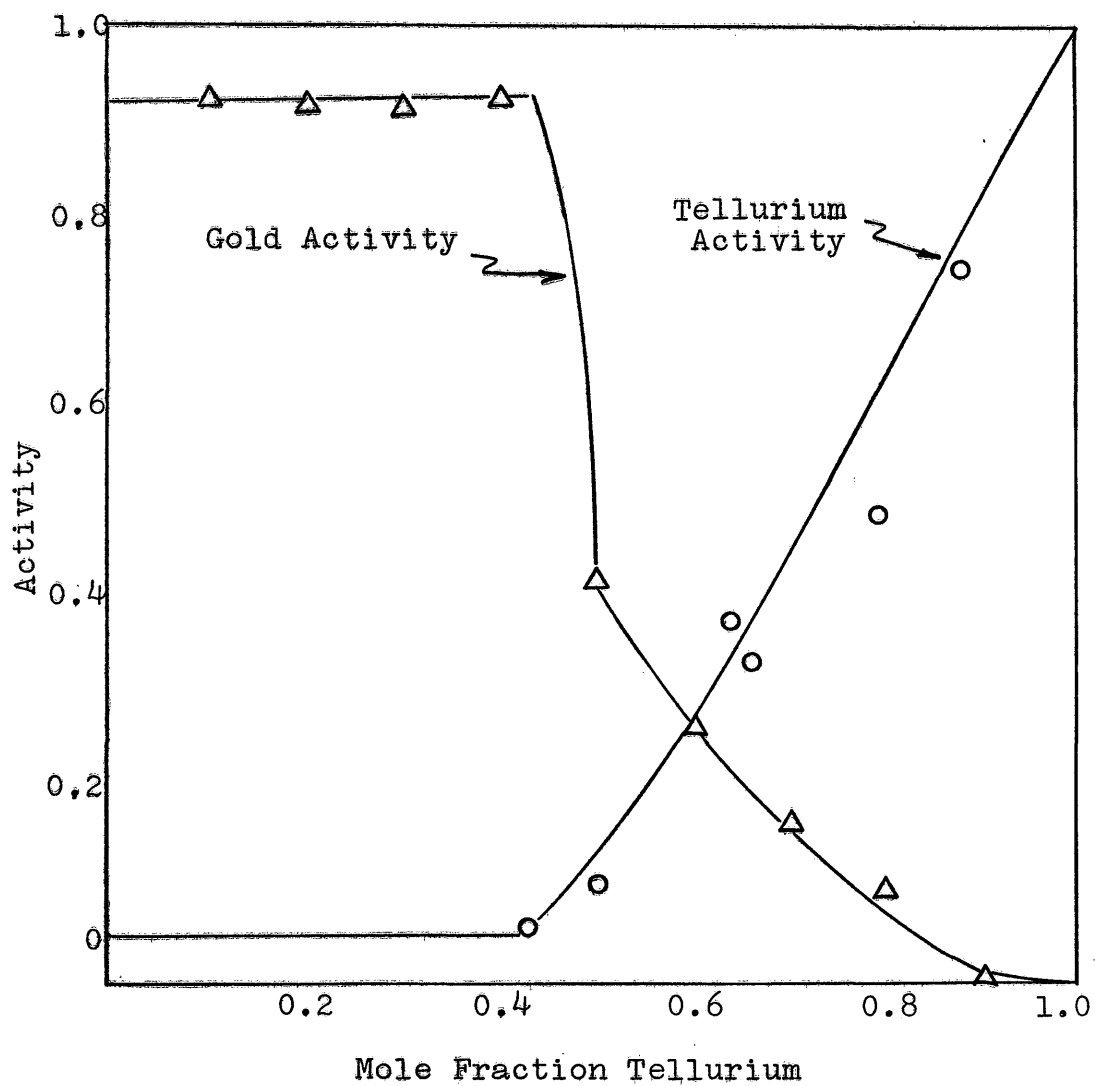


Figure 9. Activity vs. Mole Fraction Tellurium 670°C.

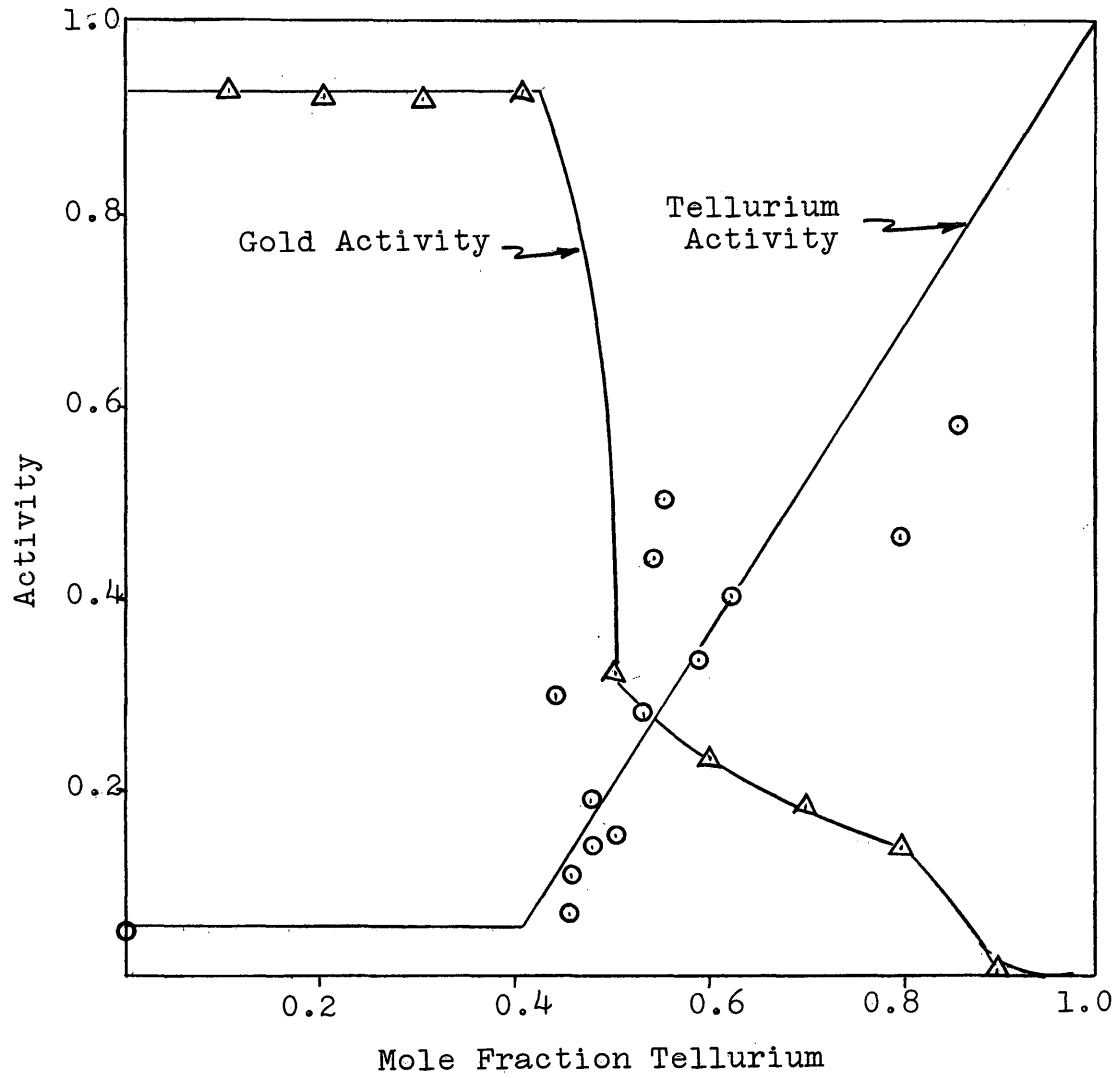


Figure 10. Activity vs. Mole Fraction Tellurium 705°C.

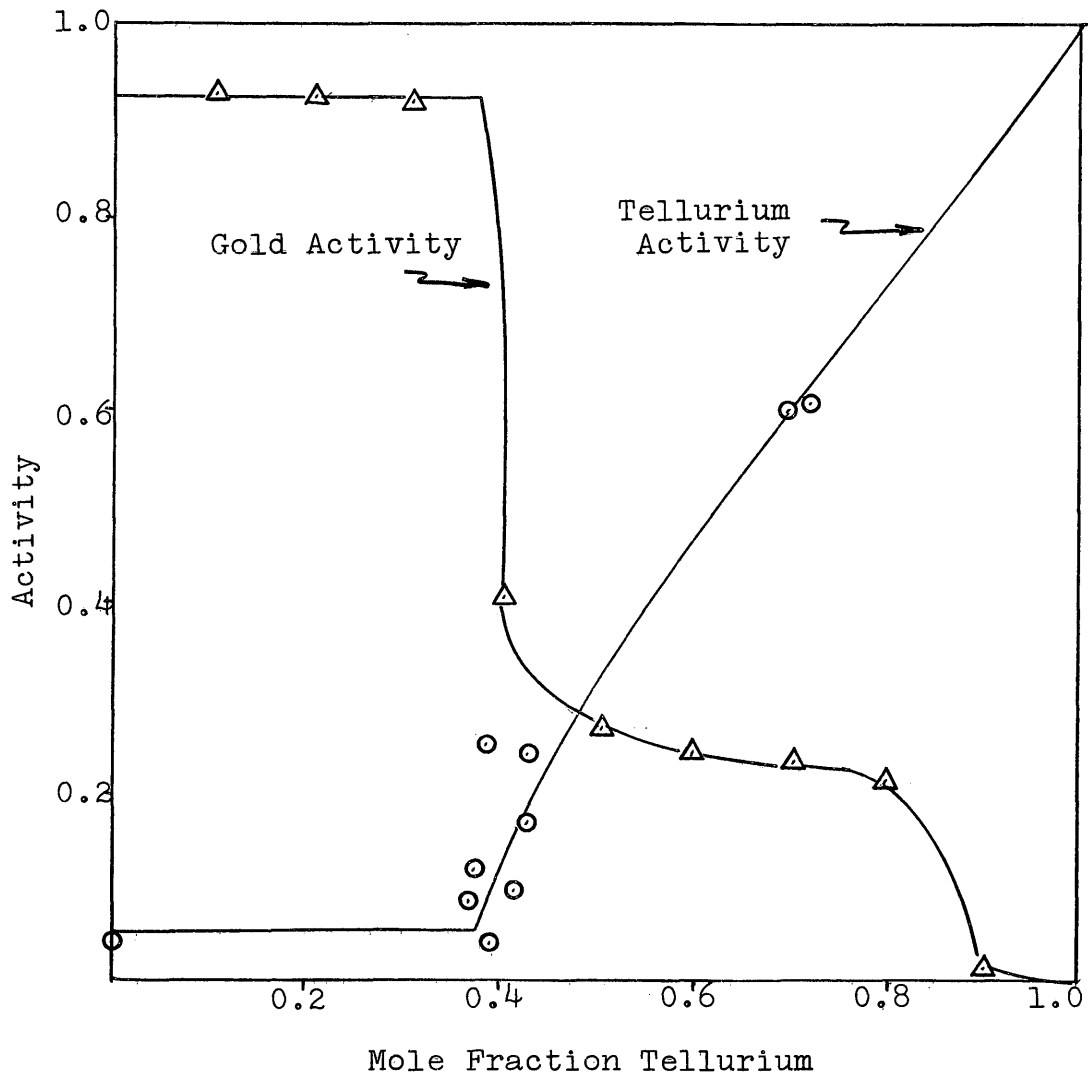


Figure 11. Activity vs. Mole Fraction Tellurium 750°C.

0.055 were obtained. Thus the activity in the two-phase region is bounded by 0.045 and 0.055. The data indicate negligible change in activity with temperature, but it is expected that there would be some small change. If there is any change, it is less than the experimental uncertainties. The experimental points for the 650°C isotherm indicate a higher activity in the two-phase region than the range stated above. The curves for 615°C and for 670°C bracket the activity quite well. It is not expected that the activity would increase at 650°C and then decrease at 670°C, so it was assumed that the activity was the same at 650°C. When the temperature is such that the tellurium pressure in the cell is very close to the equilibrium pressure over the two phase mixture, temperature fluctuations can shift the pressure so that the equilibrium composition may wander from one side of the two-phase region to the other. In this case, equilibrium is never reached and compositions can fall anywhere in the two phase region. It is thought that this is the cause of the apparently high activities in the two phase region for the 650°C isotherm.

Experimental difficulties were encountered in the 750°C isotherm when 750°C was the highest temperature in the furnace. The samples in the last block could not be cooled fast enough to prevent excessive tellurium loss from the samples. This loss shifted the compositions toward the pure gold axis, thus giving points of apparent high activity. On

later runs, cooling air was focused directly on the last block. Points obtained with this type cooling lie close to the curve.

The 705°C isotherm is not entirely satisfactory. The experimental points show considerable scatter that cannot be explained. The maximum error in activity due to temperature control is approximately  $\pm 5\%$  and the error in composition is estimated to be  $\pm 3\%$ . These errors are not sufficient to account for the scatter. The curve was to some extent drawn by utilizing the general shape of the other curves.

The sample temperatures from various runs for a particular isotherm differed from the average temperature by as much as 10°C. The necessity of correcting the activities to the average temperature was studied and the corrections were found to be so small that they were negligible.

It is thought that the equilibrium is affected by the presence of oxygen. Tellurium oxide is a definite white color and is easily detected if present in the equilibration cells. When the oxide could be seen in the cells, the results differed considerably from the results where oxygen contamination could not be detected. The results of contaminated cells were discarded. Occasionally a dark film was found on the samples, apparently a thin oxide film. These samples gave essentially the same activity as samples with no film.

In the single phase, liquid region the tellurium activities show substantial deviation from ideality. The negative

deviation from ideality indicates that there are substantial attractive forces present in the alloy tending to keep the tellurium in solution. Further, the deviation indicates a tendency toward compound formation in the solid state.

In the single phase, solid solution region near the gold axis, the tellurium activity shows severe deviations from ideality, only here the deviations are positive rather than negative. The tellurium activity increases very rapidly with a very small change in composition. This very strong deviation indicates that tellurium is repelled by the solid gold, as would be expected from the very narrow range of solid solution.

During the course of this investigation, several samples were obtained whose composition was in the solid solution region. Since the extent of solid solution has not been reported in the literature, the solid solution samples were analyzed spectroscopically to get some idea of the extent of solution. Figure 12 is a plot of activity vs. atom fraction tellurium in the solid solution region at 750°C. Assuming the activity in the two phase region is 0.045 to 0.055, then the boundary of the solution region lies between 0.0035 and 0.0060 atom fraction tellurium. The boundary was not determined at any other temperatures, as there were not sufficient points available to construct another isotherm.

In the two phase region, there is very little meaning

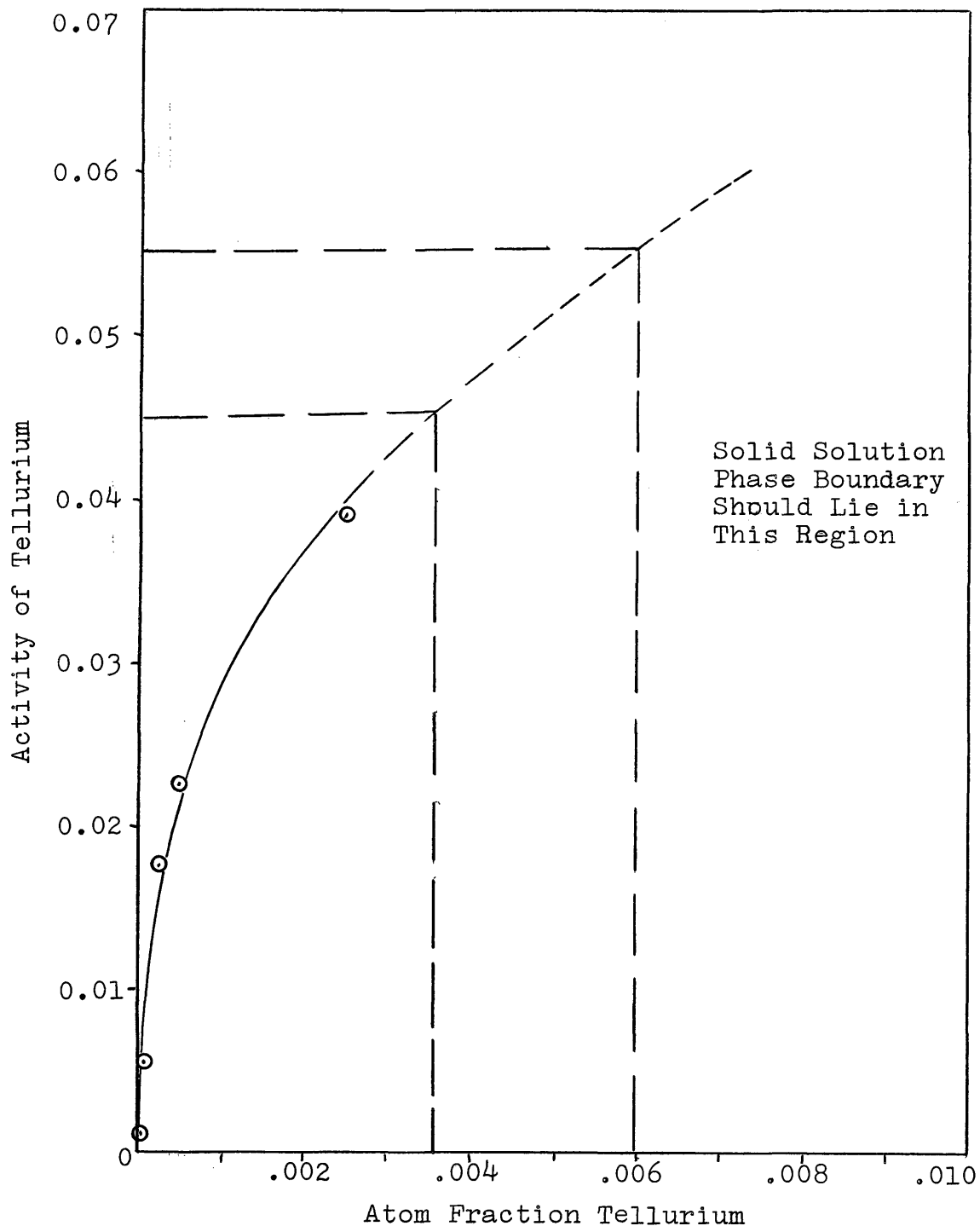


Figure 12. Activity vs. Atom Fraction Tellurium in Solid Solution Region at 750°C.

in talking about deviations from ideality. The extent of the deviation in such a region is a measure of the sum of the attractive and repulsive forces present. This sum is dependent on the amount of each phase present.

One method to check the consistency of the data is to plot  $\ln P_{Te}$  vs.  $1/T$  for a particular composition. This is an application of the Clausius-Clapeyron equation.

$$\Delta H_V = RT^2 \frac{d(\ln P)}{dT}$$

$\Delta H_V$  should change only slightly with temperature over a 100 degree change, so that the plot should be very close to a straight line.  $\Delta H_V$  is the average partial heat of vaporization over the temperature range in question of the volatile component (Kubaschewski and Evans, 1958, p. 11).

A plot of this type is shown in Figure 13. The values used in the figure were taken off the smoothed activity curves. The activity values were used to calculate the tellurium pressure over the alloy. As can be seen from the plot, the points for a single composition fall on a reasonably good straight line. The slopes of these lines are equal to  $\Delta H_V/R$ . The  $\Delta H_V$ 's were evaluated and are given in Table 3.

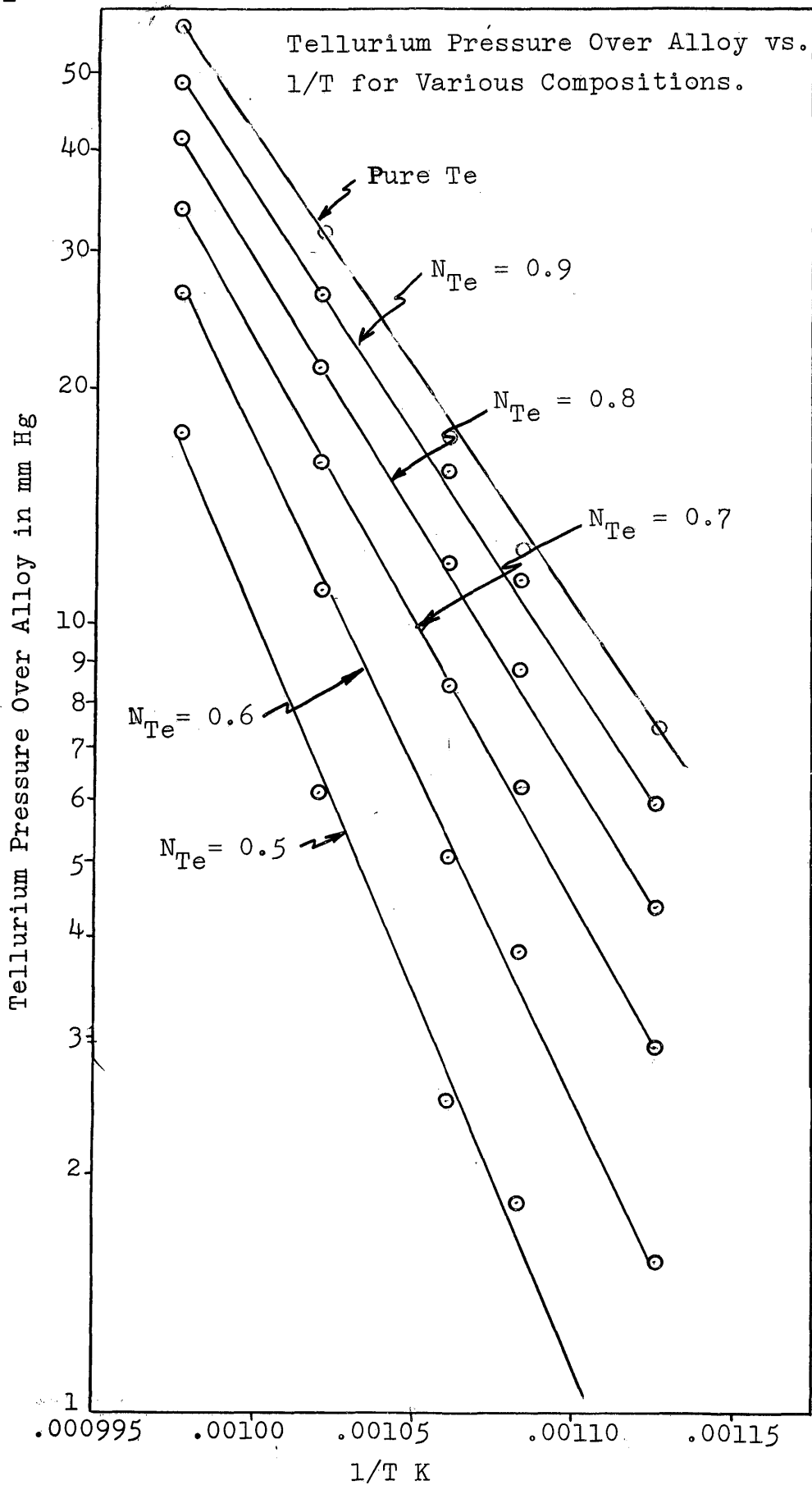


Figure 13.

TABLE 3. Partial Molar Heat of Vaporization vs Atom Fraction.

Composition Atom Fraction Tellurium	$\Delta H_V$ (cal/mole)
.9	28.1
.8	29.5
.7	32.1
.6	32.6
.5	38.9

The heat of vaporization of tellurium at 680°C, the average temperature of this study, is 25.5 kcal/mole (Machol and Westrum, 1958, p. 2950). As can be seen in Table 3, the partial heat of vaporization is approaching the heat of vaporization of pure tellurium as the atom fraction of tellurium increases. The data is plotted in Figure 14. No significance is attached to the shape of the curve, but it does extrapolate close to the heat of vaporization of pure tellurium. The change in the partial heat of vaporization with composition again indicates that the attractive forces present in the liquid phase increase with decreasing tellurium content, as was indicated by the increasing negative deviation from ideality of the activity with decreasing tellurium content.

Figure 15 compares the activity data of Kuznetsov at 485°C with the 615° and 750° isotherms of this study. As can

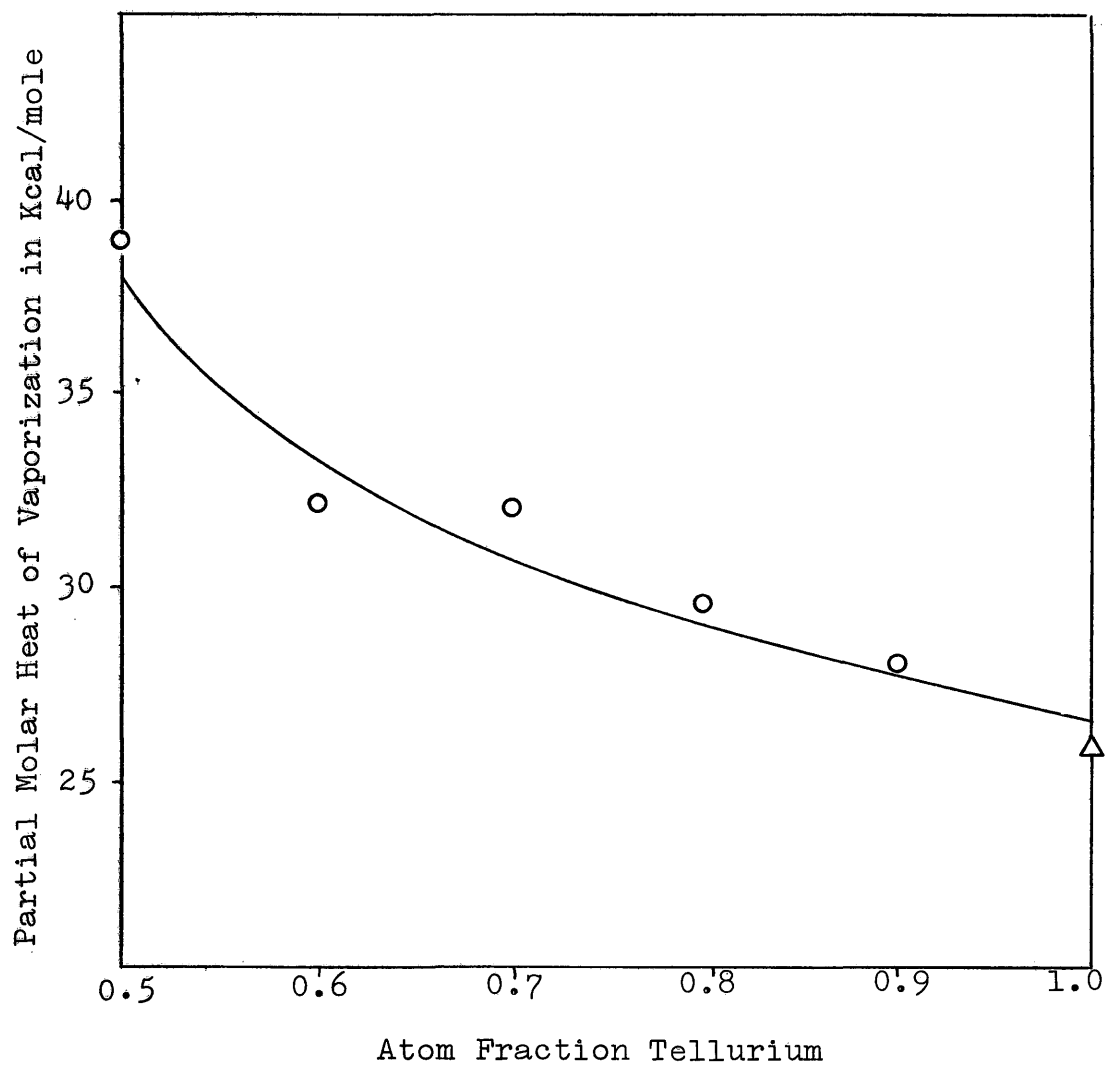


Figure 14. Partial Molar Heat of Vaporization of Tellurium vs Atom Fraction.

Figure 14. Atom Fraction Tellurium

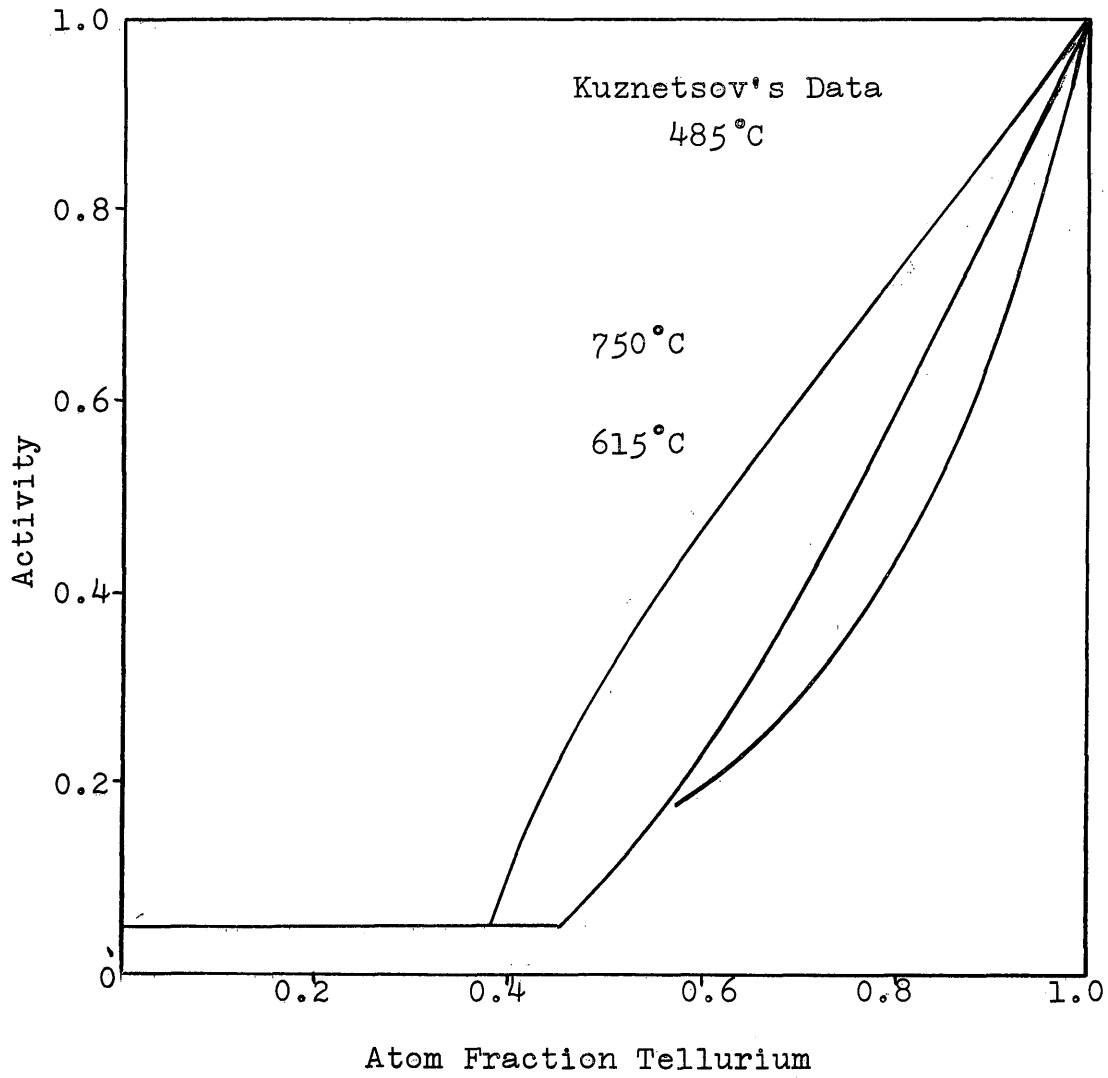


Figure 15. Comparison of Data of This Study with that of Kuznetsov at 485°C.

Figure 15. Atom Fraction Tellurium

be seen from the figure, the three activity curves show the same general type of behavior. Further, as would be expected, the activity increases with increasing temperature.

## CONCLUSIONS

The activities of tellurium and gold in their alloys were determined as a function of temperature and composition as given earlier.

The activity of tellurium in the alloys shows strong negative deviations from ideality in the liquid region from 615°C to 750°C.

The phase boundary of the gold-rich solid solution was found to lie between 0.0035 to 0.0060 atom fraction tellurium at 750°C.

APPENDIX I. Calibration data for platinum-platinum-rhodium  
Thermocouples

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<u>Millivolts</u>	<u>Degrees C</u>	<u>Millivolts</u>	<u>Degrees C</u>
3.404	400	10.477	1000
4.464	500	11.819	1100
5.570	600	13.196	1200
6.728	700	14.583	1300
7.934	800	15.967	1400
9.184	900		

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The calibration of thermocouple may change during use. The magnitude of the change depends upon the temperature, the length of time, and the conditions under which it is used. Thermocouples of the type covered by this certificate are reliable within about 1/4% up to 1300°C if used in a clean oxidizing atmosphere and not used for extended periods above 1300°C.

APPENDIX II. Analyses from American Smelting and Refining  
Company of Gold and Tellurium Used.

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99.999 + % Au - Grade A-60

Lot No. 62-7

Impurities Detected

Mg	1 ppm
Pb	2 ppm
Si	1 ppm
Fe	1 ppm
Cu	2 ppm
Ag	1 ppm

99.999 + % Te - Grade A-58

Lot No. 466 B

Impurities Detected

Mg	1 ppm
Si	1 ppm
Fe	1 ppm
Cu	1 ppm

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