

The Design of a Solution Calorimeter and its
application to Liquid Metal Thermodynamics
by

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Abstract

A liquid metal solution calorimeter has been constructed capable of measuring heats of solution of various metals in liquid metal solvents.

The calorimeter is described in detail and the techniques employed in its operation are fully explained.

The performance of the equipment, and the results obtained are critically evaluated. The results indicate that the calorimeter is capable of very high sensitivity and precision suitable for studies of stored energies of deformation, irradiation and atomic bonding in alloys.

Results for the partial heats of solution of gold, silver and copper in tin are presented together with a comparison of recently published data.

Further work has been directed towards critically testing a theory of ternary liquid metal systems, and to this end, partial heats of solution of gold and silver in tin, bismuth and tin bismuth alloys have been measured.

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Introduction

The values of free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) changes that accompany intermetallic reactions are parameters of importance in the economic aspects of extraction metallurgy, for formulating optimum conditions in various reactions. In the field of alloy theory it is necessary to know these parameters to formulate and check new and existing theories.

Ideally these three parameters can all be derived from measurements of the variation with temperature of the free energy changes. In practice it is found that although the free energy changes can often be determined from equilibrium measurements (ref 1); the accuracy with which the other two parameters can be deduced from the equilibrium measurements is unsatisfactory, particularly in the case of solid state reactions.

Galvanic cells are used to measure the difference in emf between an alloy and its pure constituents. This gives the value of the free energy change and hence enthalpy changes. There is difficulty in finding reversible cells (ref 2) and relatively small errors in the e.m.f. measurements can result in large errors in the derived values of enthalpy changes.

Vapour pressure measurements lead to a determination of enthalpy changes via Claperyon's equation. The vapour

pressure method used, depends on the material under investigation (ref 3). The limitation is in the actual interpretation of the vapour pressure measurements, even though these may be precise, the experimental conditions may be such as to render their accurate interpretation difficult.

Equilibrium and e.m.f. measurements lead to accurate data for Gibbs free energies, but there remains the problem of determining precise values for the enthalpy changes.

Calorimetry provides an independent method for the determination of enthalpy changes, and produces data which can be interpreted directly. A suitably chosen calorimetric technique has the additional advantage of 'precise' measurement, in that both the change in energy and the reaction producing this change can be clearly defined. However, not all calorimetric techniques will define the reaction clearly, and these methods are unsuitable for precise measurement.

Calorimetry developed comparatively late as a science owing to misunderstandings as to the nature of heat. The work of Joseph Black (1759) had led to some clarification of the difference between heat capacity and temperature, but he amongst others (Lavoisier, Leibnitz, Lord Bacon, Robert Hooke); did not understand the nature of heat.

Progress towards understanding the nature of heat was made through the works of Joule, William Thomson (Kelvin), James Thomson, and Carnot. In 1850 Clausius laid down the principles which now are called the 1st and 2nd laws of thermodynamics.

Since that time calorimetry has been widely used for determining energy changes. Routine investigations employing calorimetry determine such things as the heating value of coal, oil, gas and foods. In chemistry equilibrium constants are determined, many results have been tabulated (ref 4) and are useful in industrial processes. Calorimetry is also used for measuring the energy changes involved in radioactive decay, binding energy between atoms in metals and between ions in solution.

Early calorimetric methods are in essence the same as those employed today. In 1760 Joseph Black introduced the ice calorimeter which consisted simply of a hollowed out block of ice in which the reactions proceeded. The amount of water resulting was a direct measure of the energy changes involved in the reaction. This idea was later modified by Bunsen into his well known 'ice' calorimeter which is now used in improved forms (refs 5 and 6). In 1856 Henri Regnault (ref 7) produced a simple 'mixing' calorimeter, samples of known mass being added to a known mass of water at a given temperature. This equipment was

suitable for determining heat capacities of various substances. James Prescott Joule whose experimental work extended from 1840 to 1878 was interested in the mechanical equivalent of heat and for this purpose he produced a calorimeter which measured mechanical work in terms of the energy change in a calorimeter filled with water (ref 8).

The theoretical understanding of heat and experimental demonstrations of its effect in calorimetry etc. have subsequently led to experimental studies of metallurgical interest. The study undertaken here was to test experimentally a theory of ternary solutions.

The theoretical progress in the field of liquid metal solutions has been slow owing to the many variables that have to be taken into account. In this work a simple solution model has been applied to the tin-bismuth-gold and the tin-bismuth-silver system to see if it can explain the thermodynamic facts; and if not, to discover how deviations from this model might arise.

For the present investigation, therefore, precise data for the heats of mixing and transformation in metallic systems is required.

A calorimetric method was considered essential as other methods for measuring enthalpy changes are indirect and somewhat inaccurate.

Previous Calorimetric Work

For the precise definition of an energy change associated with some transformation it is necessary to measure not only the energy change, but also to define the exact transformation taking place.

The combination of precise measurement and definition of process or reaction is difficult where the measurement is made during the reaction. This is particularly true of solid state reactions and has, as a result, led to indirect methods.

In an indirect method samples in the unreacted and fully reacted states, e.g. the solid components of an alloy and the solid alloy, are brought to some accurately defined state e.g. a liquid solution. The difference in the energy required to achieve this end state being equated to the difference in energy of the initial samples. In this way heats of formation of solid alloys can be determined which could not be determined directly.

The most sensitive calorimeters that have been developed for determining precisely, heats of transformation in solid metals are probably those of Borelius (ref 9) and of Clareborough (ref 10). With these instruments, however, there has always been some doubt concerning the nature of the reaction under investigation.

On the other hand solution calorimeters can, by the indirect method, define the reaction very clearly, but in general, the precision of the energy measurement is not very high. The indirect method is, however, very suitable for many reactions, and there seemed to be a greater possibility of improving the measuring techniques than the definition of a reaction; and this factor was indicative in the choice of an indirect method.

The interest in liquid metals and alloys themselves further directed the choice of technique so that this review deals almost exclusively with liquid metal solution calorimeters.

Previous investigators employing the calorimetric technique for this application have used the following types of calorimeter method:

1. Combustion calorimetry
2. Direct mixing calorimetry
3. Acid solution calorimetry
4. Metallic solution calorimetry

Combustion calorimetry is limited in application as in many cases side reactions can lead to uncertainty in the end state (ref 11). The method is further limited by the magnitude of the measured heat effect as compared with the desired value of the enthalpy change.

Direct Mixing calorimetry (ref 12, 13) as its

name implies simply consists of the mixing of two or more liquid metals; and measuring the heat of mixing in the calorimeter in which the reaction vessel is immersed. The method has certain practical difficulties which affect the final accuracies, such as an inexact knowledge of the temperature of the added melts, slight oxidation, imperfect mixing, and finally the method uses large quantities of pure material which is uneconomic in many cases.

Acid Solution calorimetry (ref 14) is limited to finding suitable solvents. With oxidizing acids it is possible to get irreproducible oxidation states. However, the main drawback is basically the same as that in combustion calorimetry; that being the large heat of solution of metals in inorganic solvents, as compared with the heats of formation of alloys.

The use of liquid metal solvents eliminates many disadvantages of acid solution calorimetry. End states are well defined and are reproducible. Further, the heats of solution in liquid metals are of the same order as the heats of formation to be determined. It is this last consideration that has made metallic solution calorimetry most valuable for the accurate determination of changes in enthalpies in metallic systems.

The operational difficulties and limits of precision encountered in the calorimeters that are reviewed,

are imposed by some or all of the following factors:

1. The temperature control; which must be at least as precise as:
2. The temperature measurement
3. The calibration of the calorimeter; which depends on:
4. The heat transfer calculation.

With reference to equation (10)^{Page 32}, the final precision of a calorimeter is set by the ultimate precision with which temperature can be measured and by the uncertainty in the evaluated energy equivalent of the calorimeter cell, C_p .

Systematic errors in integrated heat capacities of sample materials can be referred to as 'standard' and will be changed should subsequent knowledge improve the quality of present data.

The lower limit on C_p is set by the requirement that dilute solutions must be maintained, so that enthalpy changes are a simple function of composition of the solvent.

The lower limit of temperature measurement is set by the stability of the environment, as measurement to a greater precision than this would have little meaning.

The ultimate accuracy, as distinct from the precision or sensitivity of the equipment, will depend on the calibration of the calorimeter cell, which is a function of

the heat transfer coefficient (see equations (7) and (8)). The heat transfer coefficient must be known with some precision, otherwise the remaining precautions (measurement, and stability of environment) are of no use.

To evaluate the heat transfer coefficient various approximations to Newton's law have been made which fit experimentally observed data. The Newtonian equation itself is insufficient as there is a considerable portion of heat transferred by means other than radiation away from the calorimeter. Such is the case in all calorimeters so far constructed. The calorimeter on which this investigation has been based shows a large measure of improvement in this direction, thereby increasing the overall accuracy of the results.

Work in this field has been channelled into solution calorimetry, and in particular metallic solution rather than acid solution; the metallic solution method provides not only precise data for heats of formation, mixing, and transformation in metallic systems (by virtue of the small heats of solution in liquid metals as compared with those in acid solution); but apart from this important consideration, the reaction producing the change is clearly defined.

The biggest single factor influencing a choice of calorimetric technique is the precision of data obtainable.

In acid solution, the heats of solution of metals are large, due to chemical combination, whereas metallic solution produces smaller effects comparable with the magnitude of heats of formation of alloys.

The problem of selecting a suitable metallic solvent has been studied extensively. At room temperatures mercury has been used on the solvent (refs 15, 16, 17) and at higher temperatures other metals have been used; cadmium, lead, bismuth, tin, zinc, copper and iron have been tried. It is to be noted, that as work in this field has developed, liquid tin has become the most used solvent; as it has a long liquid range combined with low vapour pressure, and excellent solvency properties. It does not attack stainless steel and molybdenum at temperatures below 800°C , which is useful, as these materials are suitable for fabrication of the crucible and tin stirrer.

In designing a calorimetric system various criteria have to be considered.

(a) A calorimeter cell contained in a thermal environment must only transfer heat between itself and the environment according to a known law.

(b) There must be a way of measuring the energy equivalent of the calorimeter cell and changes of energy produced in it during a reaction.

Metallic solution calorimeters so far developed, attempt to comply with these criteria. The first criterion can be eliminated by use of 'adiabatic' calorimetry, but this advantage is usually outweighed by the stringent experimental requirements if heat transfer between the calorimeter and its environment is to be entirely eliminated.

In the metal solution calorimeter described by B.W. Howlett, J.S.Ll. Leach, L.B. Ticknor and M.B. Bever (ref 18, diagram 1) a design was developed which satisfies to some extent the above criteria.

Their equipment consists of a Dewar flask which acts as the calorimeter cell containing the liquid metal solvent. The Dewar flask is completely immersed in a salt bath composed of molten sodium, lithium and potassium nitrates. Samples are added down the long neck of the Dewar flask through an air lock from temperatures of 0°C or -195°C . A stirrer shaft and paddle made of glass also enter the Dewar flask through a vacuum seal at its top end.

The salt bath constitutes an isothermal environment to which the heat transferred can in theory be calculated. The temperature of the salt bath is maintained constant by means of a stabilised power supply coupled with a proportional control system (ref 19). The thermostat is also vigorously stirred with a central paddle at the base of the bath, the gears involved being mounted

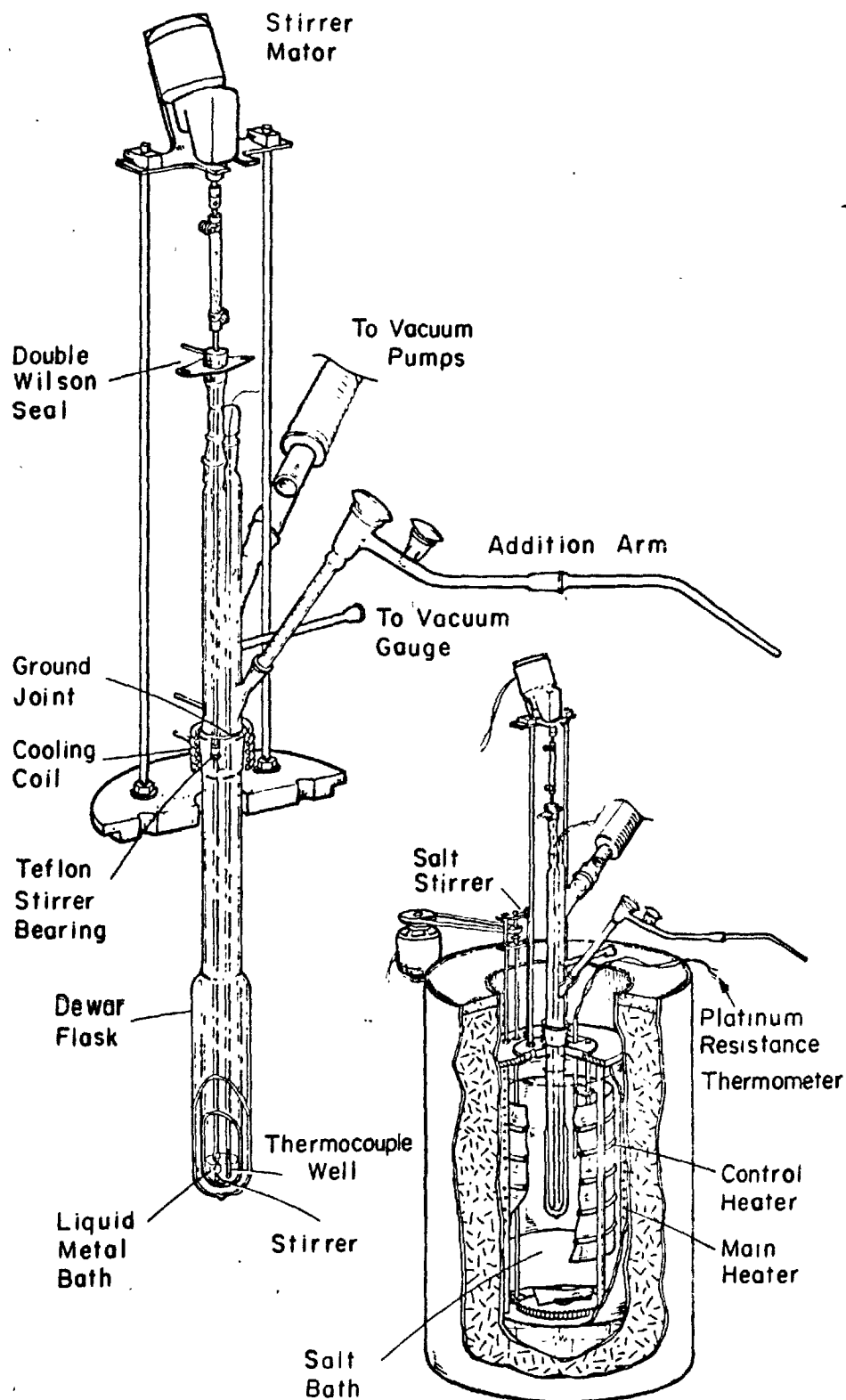


DIAGRAM I. THE LIQUID METAL SOLUTION CALORIMETER AND THERMOSTAT EMPLOYED BY BEVER.

on stainless steel ball races. With the room temperature constant to $\pm 1^{\circ}\text{C}$, the temperature of the salt bath is controlled to $\pm 0.002^{\circ}\text{C}$ and the tin bath to $\pm 0.001^{\circ}\text{C}$.

Temperatures within the salt bath and tin bath are measured with iron-constantan thermocouples connected to a sensitive potentiometer and galvanometer (sensitivity $0.5\mu\text{V}/\text{mm.}$). The operating temperature extends to about 375°C with a pyrex Dewar flask and to 450°C with a quartz flask, the limit here is set by the decomposition temperature of the salt melt.

The calorimeter is calibrated by addition of tin. The calculation of a heat effect of an addition is made in two parts: 1. An observed temperature change, (at a given time after completion of reaction), is noted; and the heat effect corresponding to this temperature change evaluated. 2. During this time not all the heat of a reaction has remained in the calorimeter and a correction, depending on the heat transfer coefficient of the system, has to be evaluated.

It is this feature of calorimetric work that has proved the most difficult. In this equipment the heat transfer coefficient varies during the period of an addition. This problem was fully investigated, and deviations from Newton's law are ascribed to heat flow along the walls of the Dewar flask and down the thermocouple tube and stirrer rod. An analysis of this

mechanism (ref 20) permits calculation of the variation in the heat transfer coefficient, k , with time in the post reaction period. There is also a deviation during the initial stages of a calibrating addition. Experiments with tin samples indicated that the value of k in the initial stages of a reaction was greater by 6%, and a factor of $1.06k$ is employed to correct for this difference.

In general, the overall accuracy of the equipment is dependent on the uncertainty in k and consequently for slow reactions the error is greatest.

A variation in the experimental equipment is incorporated in the calorimeter developed by R. Orr, A. Goldberg, and R. Hultgren (ref 21, diagram 2). Here the thermal environment is constructed out of a metal block rather than a molten salt environment. This calorimeter is also an example of a heating or isothermal calorimeter. In their equipment the crucible is fabricated out of molybdenum. It rests on an insulator which is supported on a copper block, part of the copper jacket which surrounds the whole crucible. The assembly is enclosed in a vacuum chamber, as is a sample dispenser unit which preheats samples to any given temperature prior to an addition.

The thermal environment is stabilized with a proportional controller and a stabilized power supply delivering a power of 30 W to maintain the calorimeter

unit at 250°C. Constancy of temperature to $\pm 0.002^\circ\text{C}$ is observed for periods of 30 to 60 minutes, sufficient for complete solution in most cases.

Temperatures within the copper jacket and calorimeter cell are measured with copper-constantan thermocouples connected to a sensitive potentiometer and galvanometer. The scale is located about 7 meters from the galvanometer to obtain high sensitivity ($0.17\mu\text{V/mm.}$).

The energy equivalent of the calorimeter and its heat transfer coefficient are determined two or three times during a series of additions, by additions of solid tin to the tin bath.

Calculations of any particular heat effect are based on Newtonian conditions as in the previous description. The deviation from 'linear' Newtonian conditions in the value of k is dealt with by ascribing a time dependence of the form: $t(1 - \frac{a}{2}t - \frac{b}{2}t^2)$. This reduces k to linearity, and enables heat losses to be evaluated.

A similar calorimeter has been built by J.N. Pratt and A.W.H. Morris (ref 22).

In R. Hultgren's calorimeter, no overall accuracy is given; the rate of any particular solution determines the final accuracies. For alloys with slow solution rates, the limits of error may be ± 50 calories/g atom. or $\pm 1\%$.

Another worker in the field of metallic solution

LEGEND

A Copper Cooling Coils	N 18 Gage Nichrome Heating Element	Z Layite Cup Insulator
B Steel Rod	O Aluminum Stirrer Shaft	a Molybdenum Crucible
C Copper Rod Dispenser Shaft	P Copper Preheat (Dispenser) Unit	b Molybdenum Impeller
D Ball Bearing	Q Ejector	c Tin Solution Bath
E Bushing	R Radiation Shield	d Molybdenum Sleeve Connector
F O-Ring	S Nickel Deflector	e Lavite Crucible Support
G Split Ring Connector	T Lavite Dish	f Thermocouple Well
H Lavite Terminal Post Support	U Lavite Heater Plate	g Copper Jacket
I Terminal Post	V Aluminum Furnace Tube	h Steel Ring To Support Radiation Shield
J Steel Brace	W 9/16" Vycor Feeder Tube	i Vacuum Outlet (4" Dia. Steel Elbow)
K Lavite Washer	X Platinum Resistance	j Seamless Tube Steel Shell
L Steel Ring Support	Y Thermometer Winding	k Specimens In Preheat (Dispenser) Chamber
M Lavite Ring Insulator	Y Lavite Disk	l 1" Pipe Legs

NOTE Thermocouple & Power Circuits And Outlets Through Shell Are Omitted From Drawing.
Some Of The Supports Are Rotated Into The Plane Of Section.

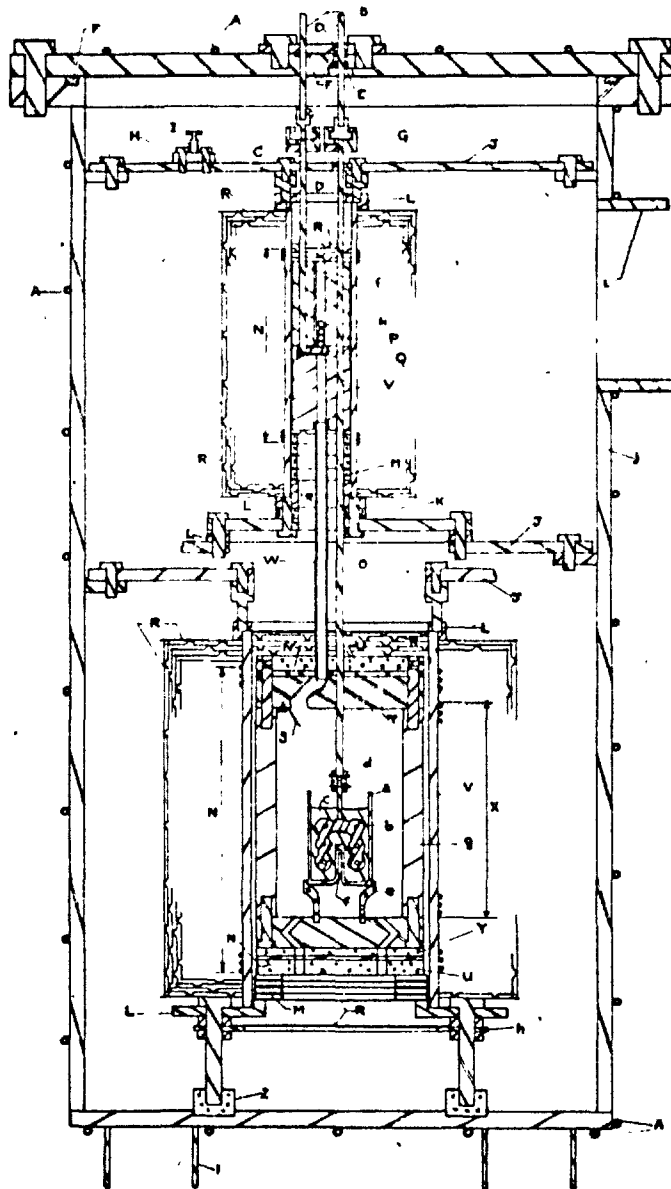


DIAGRAM 2. VERTICAL SECTION THROUGH CALORIMETER AND DISPENSER UNITS.

calorimetry is O.J. Kleppa who has developed a calorimeter (ref 23, diagram 3) which is of the metal enclosure type described above. This equipment is also an example of a 'heating' calorimeter and relies for accurate data on evaluation of the heat losses from the calorimeter.

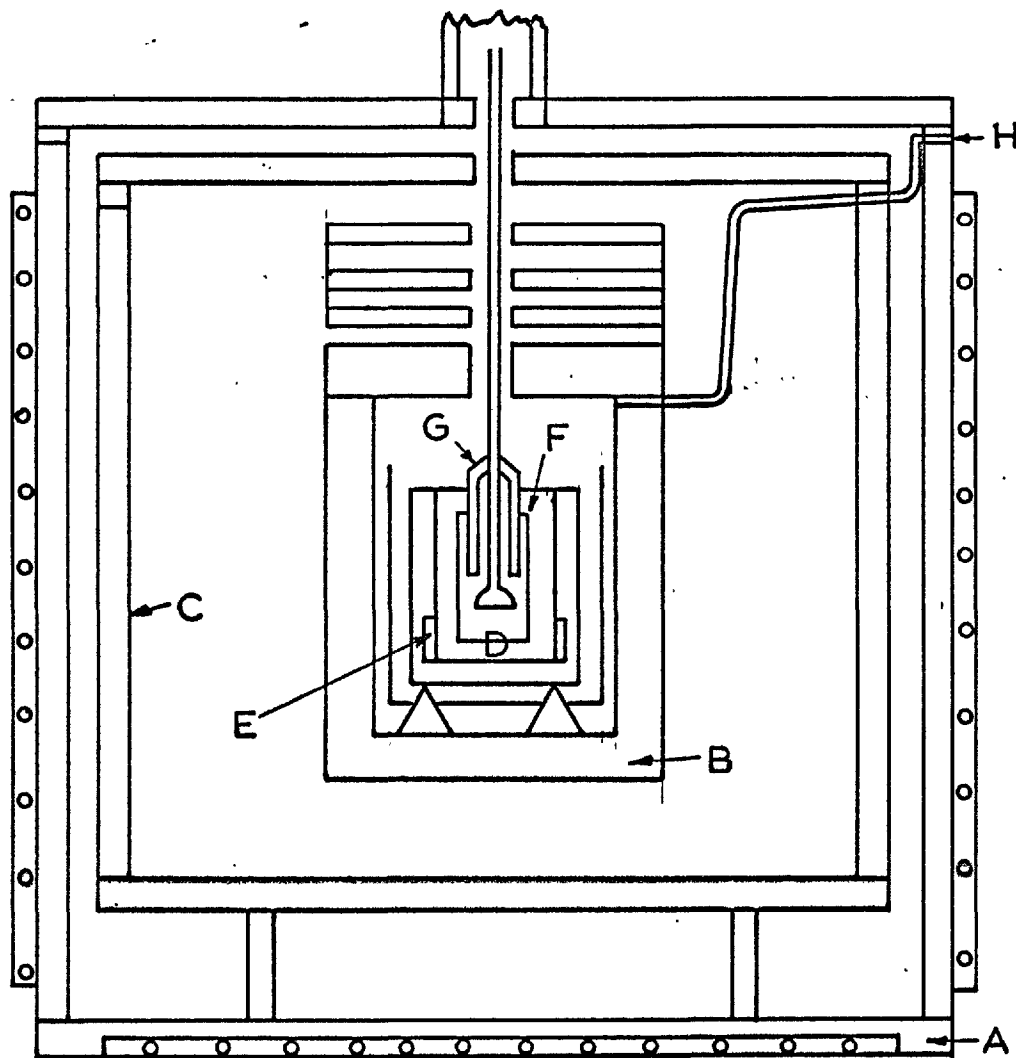
The calorimeter was originally calibrated electrically, but more recently molybdenum (which is insoluble in molten tin below 800°C) is added to give a more accurate determination. The design of the calorimeter is such that samples are in the same enclosure as the calorimeter before addition.

The errors that arise in Kleppa's equipment are due to the following causes:

- (a) Calibration errors; due to variation in the electrical power input estimated at 0.2% to 0.3%.
- (b) Measurement; the temperature of the calorimeter is measured in its wall rather than in the tin bath.
- (c) Variation in the temperature of the 'isothermal' jacket.
- (d) Unequal heat losses between the sides and top of the calorimeter.

The overall accuracy of the equipment is estimated at $\pm 1\%$. This equipment has been used to measure the heats of formation of solid and liquid alloys.

R.A. Oriani and W.K. Murphy (ref 24) had in operation

KLEPPA) CALORIMETER

A furnace core and main heater.

B constant temperature jacket.

C heavy shield.

F crucible.

D calorimeter block.

G charging and stirring device.

E calibration heater.

H thermocouple.

DIAGRAM 3. CALORIMETER EMPLOYED BY KLEPPA.

a twin, differential metal solution calorimeter to which two samples are added simultaneously. The difference in temperature of the two molten tin baths was then recorded as a function of time. Although other methods of obtaining the desired information can be used in this calorimeter design, the differential method was its intended mode of operation. From the results obtained, heat transfer to the environment was assumed to follow a relationship of the form:

$$\frac{d\Delta T}{dt} = -k(1 - at) \Delta T$$

where ΔT is the difference in temperature between the calorimeter and its environment at any time t ; k is the heat transfer coefficient.

Errors arise if this does not hold; there were also errors in the calibration, which was made electrically; and difficulties in the initial part of the temperature difference - time curves, where interpretation is awkward as solutions may take place at different rates.

The overall accuracy of the equipment is estimated at $\pm 2\%$.

Of the calorimeters constructed, using liquid metal solvents, none have been of the adiabatic type as this presents very stringent experimental requirements. Those constructed on an 'isothermal' pattern have differences in experimental detail, which enables them

to operate over different temperature ranges and also exhibit varying degrees of overall accuracy. The isothermal calorimeters can be classified into two distinct categories:

1. Metal block environment
2. Fluid environment

1. Metal block environment calorimeters have a long operational temperature range. They do not have, however, the precise conditions needed to satisfy criteria (a), which stipulates that heat transfer between the calorimeter and its environment must be in accordance with a known law. Heat transfer can be evaluated by approximation of a known law as is the case with all calorimeters of the metal block type, e.g. R. Hultgren uses the modified Newtonian relationship $\log \Delta T = -k(t - \frac{a}{2}t^2 - \frac{b}{3}t^3)$. This type of calorimeter is also used by O.J. Kleppa.

2. Fluid environment calorimeters fulfil both the criteria (a) above and (b) which stipulates that there must be a way of measuring the energy equivalent of the calorimeter cell and changes of energy produced in it. Experimentally, however, the range of operation is limited to the decomposition temperature of the environmental fluid. Normally a eutectic of sodium and potassium nitrates is used which decomposes at about 550°C.

For this work very precise data is required,

and it was decided to forego the long temperature range in favour of satisfying the criteria.

Basic Calorimetry

A. The heat transfer coefficient

The main difficulty in producing accurate data from 'heating' metallic solution calorimeters is the uncertainty in the heat exchanged with the environment during a reaction. For this reason calorimeters are evacuated to reduce heat transfer by conduction and convection. On the other hand radiative heat losses are reduced by silvering and polishing the radiating surfaces within the calorimeter.

The rates of heat loss by conduction and convection through the gas surrounding the calorimeter are dependent on the temperature difference, ΔT , between the calorimeter and its environment and also on the number of molecules of gas in this space. Evacuation to a point where the mean free path of gas molecules exceeds the internal dimensions in the calorimeter system reduces conduction and eliminates convection by gas molecules.

In the design described in the next section, it can be seen that the calorimeter can be regarded as a small body, of emissivity E and absorptivity A , situated at the centre of a hollow sphere at temperature T_2 . A list of symbols used in this section will be found in Appendix I.

The energy absorbed by the calorimeter per unit area is given by Stefan-Boltzmann's Law

$$\dot{q}_A = \sigma A T_2^4$$

where σ is known as Stefan's constant,

$$5.67 \times 10^{-5} \text{ erg cm}^{-2} \text{ sec}^{-1} \text{ deg}^{-4} \text{ K.}$$

The energy radiated by the calorimeter at a temperature T_1 is

$$\dot{q}_r = \sigma E T_1^4$$

For grey bodies, as is the calorimeter $E = A$, so the net energy radiated by the calorimeter, per unit area is

$$\dot{q} = \sigma E (T_1^4 - T_2^4) \text{ erg cms}^{-2} \text{ sec}^{-1} \dots \dots \dots (1)$$

Normally T_1 is never 1% greater or smaller than T_2 and we can write $T_1 - T_2 = \Delta T$; hence,

$$\begin{aligned} \dot{q} &= \sigma E [(T_2 + \Delta T)^4 - T_2^4] \\ &= \sigma E T_2^4 \left[\left(1 + \frac{\Delta T}{T_2}\right)^4 - 1 \right] \\ \dot{q} &= \sigma E T_2^4 \left[\left(1 + \frac{4\Delta T}{T_2} + 6\left(\frac{\Delta T}{T_2}\right)^2 + \dots \right) - 1 \right] \end{aligned}$$

and where $\Delta T \ll T_2$

$$\dot{q} = 4\sigma E T_2^3 \Delta T \dots \dots \dots (2)$$

Since the environment has been silvered, the radiative losses are slightly less than this, but since the enclosure in this calorimeter is large, not much radiation is reflected back to the calorimeter from it. A smaller system would need a more rigorous treatment to correct for successive reflections (ref 25).

If the energy equivalent of the calorimeter is C_p cals, then the heat lost from unit area per second is

$$= \frac{J.C_p \frac{dT_1}{dt}}{S} \text{ erg cms}^{-2} \text{ sec}^{-1}$$

where S is the Surface area of the calorimeter, and J = 4.184 ergs cal⁻¹. This must be equivalent to (2), hence:

$$-\frac{dT_1}{dt} = \frac{4\sigma T_2^3 \cdot E \cdot S}{J \cdot C_p} (T_1 - T_2) = k(T_1 - T_2) \dots \dots \dots (3)$$

Since all the variables are known a theoretical value of k, the heat transfer coefficient due to radiation, can be obtained:

$$k = \frac{4\sigma T_2^3 \cdot E \cdot S}{J \cdot C_p} \dots \dots \dots (4)$$

From the point of view of design, equation (4) enables the experimental variables E, S and C_p to be chosen so as to reduce the final value of k. The emissivity, E, is reduced by polishing the surface of the crucible. The value of S/C_p, for a given C_p, is minimum for a spherical body, but can also be reduced by increasing the size of the calorimeter.

The system described in the next section has been designed with these factors in mind and it is evident from the data obtained that the design has proved successful, reducing the value of k and, over small temperature intervals reducing the loss by heat transfer to the form given in equation (3)

$$-\frac{dT_1}{dt} = k(T_1 - T_2)$$

Experimentally T₂ is the constant environment temperature

Integrating this equation,

$$\int \frac{dT_1}{(T_1 - T_2)} = -k \int dt$$

$$\log(T_1 - T_2) = -kt + \text{constant} \dots \dots \dots (5)$$

A plot of $\log (T_1 - T_2)$ against time gives a straight line of slope $-k$. The rigorous integration of equation (1) is discussed later and is used to estimate the heat losses due to conduction and convection, see app. II. The plot also serves to determine when a reaction is complete; as prior to completion of a reaction, the plot is not linear.

The temperature correction that is applied to an observed temperature, after completion of a reaction in the calorimeter is also obtained by consideration of equation (3). The correction is that amount of the temperature drop or rise which is not realised, due to heat exchanged with the surroundings.

The correction is:

$$\int_{t_0}^{t_f} -dT_1 = \int_{t_0}^{t_f} -d(T_1 - T_2) = k \int_{t_0}^{t_f} (T_1 - T_2) dt \dots \dots \dots (6)$$

where t_0 is the time at which a specimen is dropped into the bath and t_f is some time after the reaction has been completed..

A consideration of diagram 4 will show that the value of $\int_{t_0}^{t_f} \Delta T dt$ represents the area ABCD. This area is evaluated numerically by the trapezium rule. The corresponding value of the calorimeter temperature drop

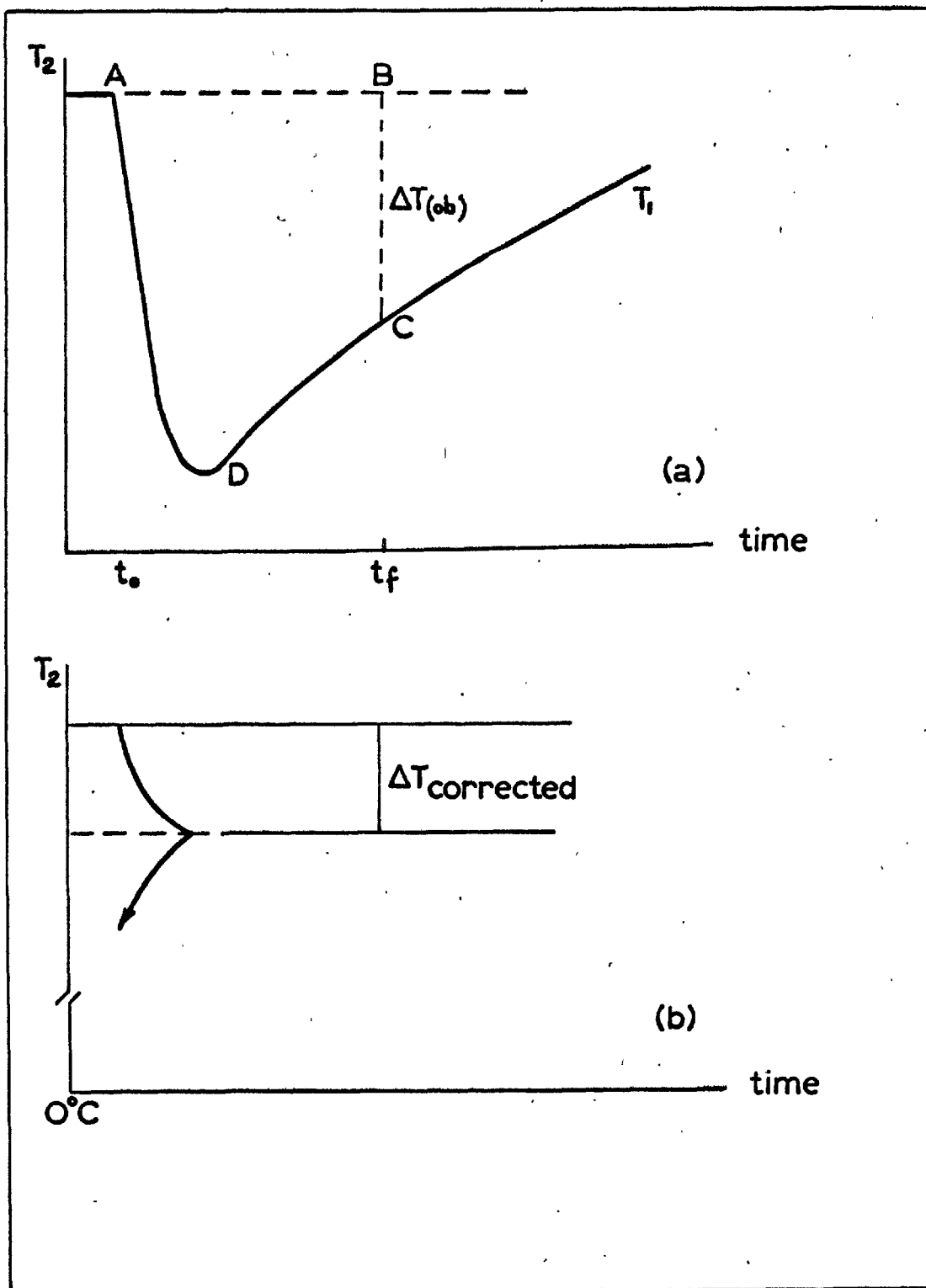


DIAGRAM 4. SCHEMATIC CALIBRATION ADDITION.

that would have been observed had the same reaction been carried out adiabatically is given by

$$\Delta T_{(\text{corrected})} = \Delta T_{(\text{observed})} + k \int_{t_0}^{t_f} \Delta T dt \dots \dots \dots (7)$$

The Calibration addition

The energy equivalent of the calorimeter is determined by addition of a sample of tin from the same source as the solvent. Sufficient is added to alter the calorimeter temperature by about 1°C, the sample being added from 0°C.

The type of temperature-time relationship obtained is similar to that shown in diagram 4(a) with a very rapid solution time. The corrected temperature changes have been represented in a diagrammatic form by 4(b), $\Delta T_{(\text{corrected})}$ being the theoretical adiabatic drop experienced in a similar experiment under adiabatic conditions.

The energy gained by the sample specific heat C_s , mass m , at the expense of the calorimeter, is:

$$m \int_0^{T_2 - \Delta T_{(\text{corr})}} C_s dT$$

and the energy lost by the calorimeter is :

$$\text{hence } C_p = \frac{m \int_0^{T_2 - \Delta T_{(\text{corr})}} C_s dT}{\Delta T_{(\text{corrected})}} \dots \dots \dots (8)$$

where 'integrated' heat capacities have been taken from known data (ref 26). It is evident that with each sample addition, the value of C_p increases, and for any particular mass of tin and sample material in the calorimeter there is a specific value of C_p . In all the experimental results given this feature has been allowed for; two calibration additions of tin are made at the beginning of each run, and one (or two) at the end. The value of C_p prior to the addition of a sample, is obtained by interpolating the value from these calibration additions, allowing for the equivalent heat capacity of the samples in solution.

As an example of how the heat capacity in solution is found for a sample, consider the case of gold. From the results, values of heats of solution of the first sample after a calibration addition has been made are found. It is noted that heats of solution are not independent of temperature and hence, from Kirchoff's equation

$$\frac{\Delta H(T_1) - \Delta H(T_2)}{(T_1 - T_2)} = C_{p_{\text{solid}}} - C_{p_{\text{solution}}}$$

where $\Delta H(T)$ is the heat of solution in tin at a given temperature T and $C_{p_{\text{solid}}} - C_{p_{\text{solution}}}$ is the difference in heat capacities per g mole of the solute species in the solid and dissolved solution form. For gold it was found experimentally that

$$\frac{\Delta H(T_1) - \Delta H(T_2)}{T_1 - T_2} = -7\frac{1}{3} \text{ calories } ^\circ\text{C}^{-1} \text{ mole}^{-1}$$

in the range 240°C to 310°C .

$$\text{and } C_{p_{\text{solid}}} = 5\frac{2}{3} \text{ cal } \text{mole}^{-1} \text{ } ^\circ\text{C}^{-1}$$

Hence

$$C_{p_{\text{solution}}} = 13 \text{ cal } \text{mole}^{-1} \text{ } ^\circ\text{C}^{-1}$$

From published data (ref 26), the heat capacity of tin in this temperature range is known to be $7.15 \text{ cal } \text{mole}^{-1} \text{ } ^\circ\text{C}^{-1}$ approximately. The heat capacity of gold compared to tin on a weight for weight basis is therefore

$$C_p \text{ of } 1 \text{ grm of gold} = C_p \text{ of } 1.09 \text{ grm of tin}$$

This type of factor is used in the interpretation, with the additional information of the quantity of gold in solution prior to an addition.

Other systems have been used to calibrate calorimeters; O.J. Kleppa (ref 23) used an electrical method, but errors were introduced from variations in the power input. Another factor which makes this method unsuitable is the losses to the surroundings by the heater windings; before the electrical energy is used to raise the calorimeter temperature. An indirect method which can be used to calibrate the calorimeter, is by addition of a reacting sample, whose heat effect has been thoroughly investigated. Such a substance is gold. The difficulty is fundamental, as values of the heat effect of gold are dependent on previous calibrations of calorimetric systems. A useful method which has been employed by M.B. Bever (ref 18) is the addition of a non-reacting species to the liquid metal. Provided that heat content data for the species are well known, the method is reliable. However, pieces of solid

metal will upset the overall sensitivity of the calorimeter to subsequent additions, as the solid will not equilibrate rapidly to the liquid metal changes. Another disadvantage of this technique is the possibility that solid specimens remaining in the liquid tin might jam a lightweight stirring mechanism. For these reasons calibration by tin addition was chosen.

It is to be noted that calibration by tin is only valid when tin is added to pure tin. In non-dilute solutions of gold tin, for example, a non reacting sample or an electrical calibration has to be used. In the studies of the tin-bismuth-gold system tungsten was added to calibrate the system. Calibration by tin addition was also made, but the partial heat of solution of the tin in the alloy was taken into account.

The Sample Addition

In the case of the calibrating addition the use of a sign convention to describe the heat 'lost' or 'gained' was unnecessary. For a more complicated case such as an exothermic reaction a sign convention is adopted.

Consider diagram 5 which represents the solution of gold in tin. Initially the calorimeter temperature drops as the cold sample comes in contact with the tin. The exothermic reaction then rapidly increases the energy of the calorimeter and the temperature follows a curve

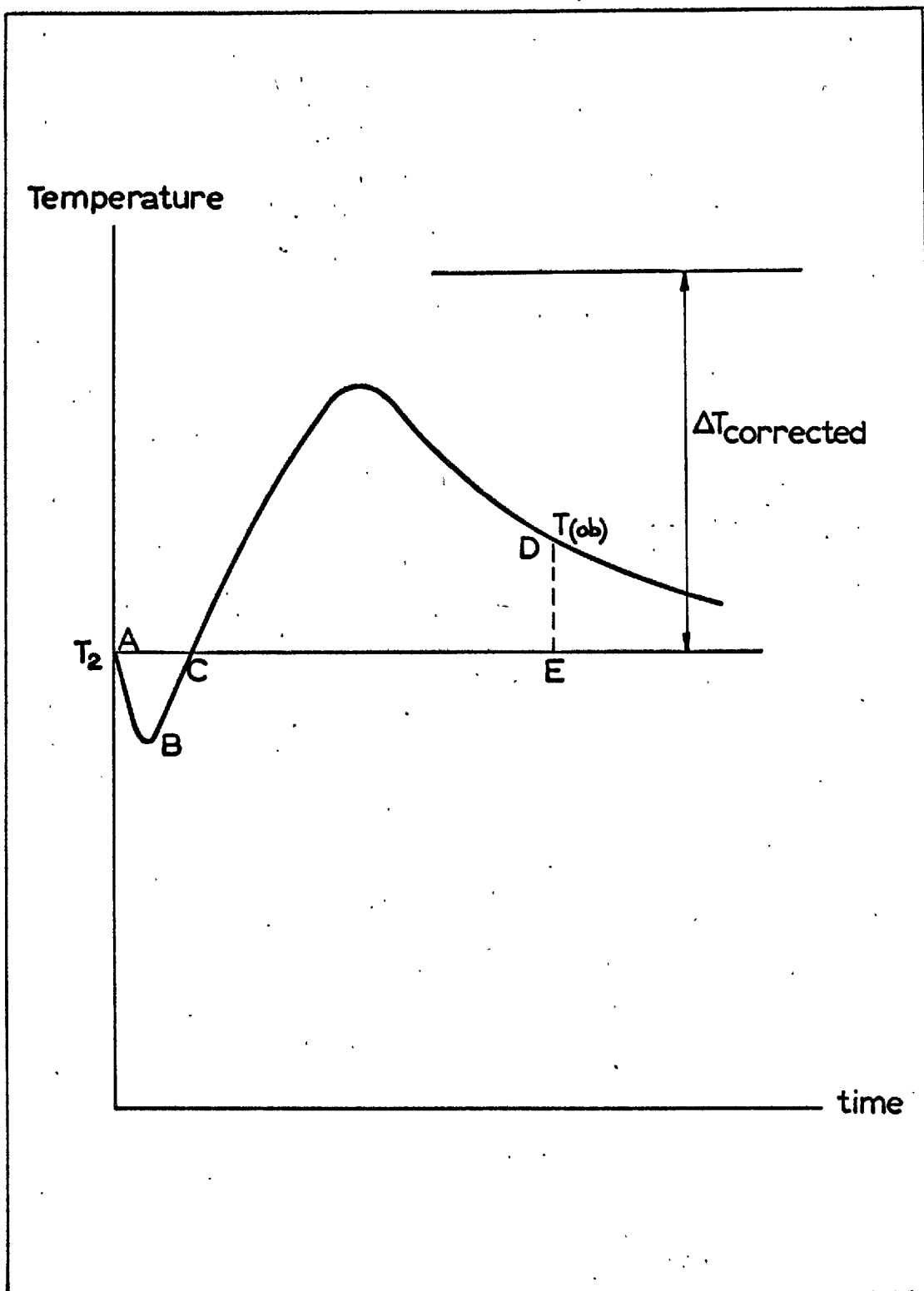


DIAGRAM 5. SCHEMATIC EXOTHERMIC REACTION.

similar to that indicated. To do this the sample on solution must be giving up energy, hence exothermic heat effects are designated negative.

The value of $\Delta T_{(\text{corrected})}$ in this case is given by

$$\Delta T_{(\text{corrected})} = \Delta T_{(\text{observed})} + k \left[\int_A^C \Delta T dt + \int_C^E \Delta T dt \right] \dots (9)$$

In this convention temperature differences are given their natural sign and since ΔT at any time t is given by $(T_1 - T_2)$, $\Delta T_{(\text{observed})}$ is positive for an exothermic reaction, as is the second term in equation (9) (for the conditions existing when gold is added from 0°C to the calorimeter).

The complete heat balance of the calorimeter is given by

$$-\Delta H n = C_p \Delta T_{(\text{corr})} + n \int_0^{T_2 + \Delta T_{(\text{corr})}} C_s dT \dots \dots \dots (10)$$

where the energy required to raise the temperature of the calorimeter by $\Delta T_{(\text{corr})}$ is $C_p \Delta T_{(\text{corr})}$; and the energy gained by the sample is evaluated from heat content data (ref 27). This energy is supplied by the heat (exothermic in this case) of solution of the sample ΔH per gram mole, where n is the number of g moles added.

The equation applies also for an endothermic reaction, as here $C_p \Delta T_{(\text{corr})}$ becomes a negative quantity and hence ΔH is now positive as expected.

Equations (5), (7), (8) and (10) are the general equations on which 'heating' calorimetry depends, and

through them any heat effect can be evaluated.

Previous approaches to the structure of liquid metal solutions, with particular reference to bismuth and tin.

There are various experimental techniques available for the study of liquid metal structures. Similarly various theoretical approaches have been developed which contribute to the understanding of the liquid state. A powerful method used to investigate liquid structure is the X-ray diffraction technique; the thermodynamic approach adopted in this work provides additional information useful for interpreting structure in the liquid state.

I. X-ray diffraction studies. Since the density of a liquid metal is not very different from that of the solid it is to be expected that the average distance of nearest neighbours in the two states will not alter by large amounts. In the liquid state there is no long range order, so observed diffraction patterns are different from those of the solid but similarities arising from nearest neighbours might be present.

Zernike and Prins (ref 28) introduced a radial distribution function $p(r)$ so defined that $4\pi r^2 p(r)$ represents the number of atoms, lying at any instant, at distances between r and $r+dr$ from the centre of a specified atom. Difficulties have arisen in evaluating $4\pi r^2 p(r)$ from given experimental data. Debye and Menke (ref 29)

developed a formula for this evaluation. A similar type of formula was later introduced by Gingrich (ref 30).

The radial distribution curves give two sets of information:

(1) The nearest neighbour distance

(2) The area under the first peak $\int_{r_1}^{r_2} 4\pi r p(r) dr$,

where r_1 and r_2 define the limits of the first peak; is the number of nearest neighbours to a specific atom. This is normally termed the coordination number z .

Although nearest neighbour distances are well defined by the radial distribution curves, the areas evaluated are somewhat variable depending on the summation technique.

With particular reference to bismuth and tin the following data has been obtained (Table 1).

From such data it is possible to derive an equivalent structure in the liquid state. For bismuth a sodium chloride structure is postulated. This is not too surprising as the structure of the solid is also related to the sodium chloride structure. The structure of liquid tin proposed by Furukawa, Orton, Hamor and Williams (ref 31) is one of grey tin tetrahedra floating in a matrix of metallic tin; with continuous interchange of atoms between the two states.

Table 1

Reproduced in part from Phil. Mag., 8, p. 141, 1963.

Reference	Temp. (°C)	Position of 1st Peak(Å)	Area under 1st Peak		$\int_{r_1}^{r_2} 4\pi r p(r) dr$		
			Peak made symmetrical	R.H.S. extrapolated to abscissa	r_1	r_2	
Furukawa, Orton, Hamor and Williams (ref. 31)	232	3.27	7.6	8.9	8.8	2.5	3.9
	245	3.27	7.7	8.9	8.6	2.5	3.9
	300	3.27	7.8	8.3	8.3	2.5	3.9
	400	3.27	7.5	8.3	8.3	2.5	3.9
	495	3.27	7.4	8.2	8.2	2.5	3.9
Richter (ref. 32)	-	3.38	10.9				
Bublik (ref. 33)	300	3.6	11.5				
	350	3.38	10.0				
	390	3.36	8.9				
Danilov (ref. 34)	232	3.2	10.0				
Hendus (ref. 35)	280	3.2	10.0				
Gammertsfelder (ref. 36)	250	3.38	10.0				
	390	3.36	8.9				
Winkler (ref. 37)	226	3.17 - 3.58	7.9				
	240	3.21 - 3.66	8.4				
	300	3.19 - 3.62	7.7				
	450	3.19 - 3.66	8.4				
	680	3.22 - 3.74	8.5				
	930	3.22 - 3.76	8.3				
	1140	3.22 - 3.78	8.4				
Krebs; (ref. 38)	320	3.35	6 calculated from the Debye and Menke equation				
Hendus (ref. 35)	340	3.32	7 to 8				
Sharrah and Smith (ref. 39)	300	3.35	7.7				

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Studies on liquid alloys have not been extensive. Hendus (ref 35) studied gold-tin alloys and concluded that the alloy was in part like a compound and in part random, the randomness increasing with temperature.

Thermodynamic activity data by Kleppa (ref 40) from emf measurements on a $\text{Sn(l)}/\text{Sn}^{++}/(\text{Sn+Au})(\text{l})$ cell indicated from entropy measurements, that there is short range order in the gold-tin alloy.

II Thermodynamic studies The quasi-chemical approach of Alcock and Richardson (ref 41), involves a knowledge of the coordination number, of the non dilute species. The results obtained by X-ray diffraction studies provide this information; although the values given show sufficient scatter to make the value uncertain.

In their paper, Alcock and Richardson derive equations which can be directly applied to results obtained from calorimetric measurements.

They considered the case of a dilute solute S in a mixture of X and Y, and assumed that each atom interacts with the same number of nearest neighbours z . The number of S-S bonds is small and it may be assumed that the distribution of X and Y atoms is random except in the coordination shells round an S atom. In this coordination shell there will be more bonds of the Y-S variety provided that the Y-S bond is stronger than the X-S bond. The ratio of their numbers being a function of the exchange energy W ,

where:

$$\frac{n(Y-S)}{n(X-S)} = \frac{N_Y}{N_X} \exp \frac{W}{zRT} \dots\dots\dots(11)$$

and

$n(X-S)$ is the number of X-S bonds

$n(Y-S)$ is the number of Y-S bonds

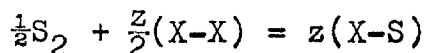
N_Y is the mole fraction of Y

N_X is the mole fraction of X

W/z is the energy change that occurs when one mole of Y-S bonds are changed to X-S bonds

$$W = \bar{\Delta H}_S(X) - \bar{\Delta H}_S(Y) - \bar{\Delta H}_{X(X+Y)} + \bar{\Delta H}_{Y(X+Y)} \dots\dots\dots(12)$$

where $\bar{\Delta H}_S(X)$ represents the change in energy associated with the formation of z (X-S) bonds in accordance with the equation:



The other terms correspond to the making and breaking of the other bonds.

Since this investigation was concerned with the ternaries of gold-tin-bismuth and silver-tin-bismuth with gold and silver present in dilute concentrations, the knowledge that the bismuth-tin form a nearly ideal solution ($\Delta H_M = .25$ cal), is useful in that the last two terms in equation (12) can be neglected, that is

$$\bar{\Delta H}_{X(X+Y)} = \bar{\Delta H}_{Y(X+Y)} = 0$$

hence,
$$W = \bar{\Delta H}_S(X) - \bar{\Delta H}_S(Y) \dots\dots\dots(13)$$

If the exponential term in equation (11) is put equal to K

$$\text{then, } \frac{n(Y-S)}{n(X-S)} = \frac{N_Y}{N_X} K$$

$$\text{or } \frac{N_Y^0}{N_X^0} = \frac{N_Y}{N_X} K$$

where N^0 represents the mole fractions in the coordination shells round the solute atoms.

$$\text{Since, } N_X^0 + N_Y^0 = 1$$

$$\text{we have } N_X^0 = \frac{N_X}{KN_Y + N_X} \dots\dots\dots(14)$$

$$N_Y^0 = \frac{KN_Y}{KN_Y + N_X}$$

The heat change associated with the addition of n_S atoms of S to a large volume of X + Y is then given by the equation:

$$\begin{aligned} \Delta H = & \frac{1}{2}D \cdot n_S + n_S z N_X^0 E_{XS} + n_S z N_Y^0 E_{YS} \\ & - n_S \frac{z}{2} [N_X^0 N_X E_{XX} + (N_X^0 N_Y + N_Y^0 N_X) E_{XY} + N_Y^0 N_Y E_{YY}] \end{aligned}$$

where D is the dissociation energy of the solute and E_{XX} etc are the pairwise energies of interaction.

$$\text{Since } \bar{\Delta H}_{S(X)} = \frac{1}{2}D_S + zE_{XS} - \frac{z}{2}E_{XX}$$

$$\bar{\Delta H}_{S(Y)} = \frac{1}{2}D_S + zE_{YS} - \frac{z}{2}E_{YY}$$

it follows that:

$$\Delta H = n_S [\bar{\Delta H}_{S(X)} + \bar{\Delta H}_{S(Y)} - N_X^0 \bar{\Delta H}_{X(X+Y)} - N_Y^0 \bar{\Delta H}_{Y(X+Y)}]$$

where $\overline{\Delta H}_{X(X+Y)}$ and $\overline{\Delta H}_{Y(X+Y)}$ hold for composition N_X and N_Y , and are both nearly zero.

With this assumption we have

$$\overline{\Delta H}_{S(X+Y)} = N_X^0 \overline{\Delta H}_{S(X)} + N_Y^0 \overline{\Delta H}_{S(Y)} \dots\dots\dots(15)$$

Calorimetric techniques are easily adapted to these equations as $\overline{\Delta H}_{S(X)}$, $\overline{\Delta H}_{S(Y)}$, W and T are well defined. The approach adopted in this work is to compare values of $\overline{\Delta H}_{S(X+Y)}$ which are found experimentally with those calculated for a given value of z .

The systems chosen for this work have certain advantages. The near ideality of the 'major' component system, tin-bismuth, allows the basic equations to be substantially simplified; also experimental data can be obtained from the two solute species, gold and silver, giving a comparison of data for different values of W .

In applying their theory Alcock and Richardson chose the systems $[\text{Fe}, \text{Ni}, \text{O}]$; $[\text{Fe}, \text{Al}, \text{O}]$ and $[\text{Cu}, \text{Fe}, \text{S}]$ and measured the distribution ratio of the dilute solute species in the alloy. This particular measurement results in values for the ratio of activity coefficients of the solute in the alloy and pure metals. In order to interpret these results further equations were derived which express $\gamma_{S(X+Y)}$, i.e. the activity coefficient of the dilute species in X and Y , in terms of $\gamma_{S(X)}$, $\gamma_{S(Y)}$, and K . For obvious reasons $\gamma_{X(X+Y)}$ and $\gamma_{Y(X+Y)}$ cannot be neglected in the systems chosen and these too enter into the final

equations. For the present application, this theory can be taken at its most simple level, namely in terms of $\bar{\Delta H}_S(X+Y)$ as shown by equations (11), (13), (14), and (15). These equations, however, are in no way less precise than those involving activity coefficients, and in addition possess the advantage that the parameters required are directly obtainable from calorimetric data.

In order to interpret the results of Alcock and Richardson in terms of the quasi-chemical theory, it was found necessary to use values of z which were two or one e.g. the Fe,Ni,O system. There are several possible reasons for this; one is that the systems chosen do not represent random mixtures as clustering or chemical bonding may take place; and there is also the large size difference between the solute and metal molecules.

If the quasi-chemical theory is to be successful it is necessary to choose systems in which only the chemical contribution to the energetics is important, i.e. the formation and breakage of bonds of different energies, not including compound formation. Further, only nearest neighbour interactions should be considered, hence size effects are of great importance. For this reason the systems studied are of a type which would yield a reasonable solution if interpreted by the quasi-chemical theory.

Experimental Equipment and Design

In designing the equipment, criteria formulating the best calorimetric system were considered. It is obvious that to achieve results which are 100% accurate would be impossible; but by qualifying these criteria and by consideration of expected heat effects a suitably accurate system can be designed. The following features were considered.

1. Solute concentration must be low, as heat effects are dependent on this parameter.
2. Heat effects must be measurable to $\pm 0.1\%$
3. Heat transfer between the calorimeter and environment must be in accordance with equation (5).

It was decided that samples weighing about a gram would be added to the solvent. To ensure that the solute concentration would be low, the mass of the crucible and tin load was fixed at about 750 grams (50 cal). Samples of a gram produce heat effects of about 1°C as can be ascertained from the parameters in equation (10) (using approximate values). To measure heat effects to $\pm 0.1\%$ therefore necessitates measuring temperature changes to about $\pm 0.001^{\circ}\text{C}$. This in turn fixes the control system limits to $\pm 0.001^{\circ}\text{C}$, which requires the size of the furnace and complexity of the control system.

To reduce heat transfer to Newtonian conditions,

the calorimeter is surrounded by a vacuum system. The size of the vacuum system is fixed by the mean free path of gas molecules which must be greater than the internal dimensions of the vacuum system. The calorimeter is mounted in a manner which reduces heat transfer along its supports. The overall effect of these considerations is to reduce heat transfer to a good approximation to Newtonian conditions.

The description is divided into the following sections:-

1. The Thermostat
2. The Vacuum System
3. The Calorimetric Unit
4. The Temperature Control System
5. The Temperature Measuring System

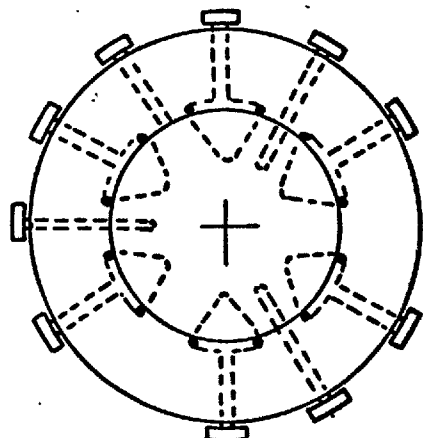
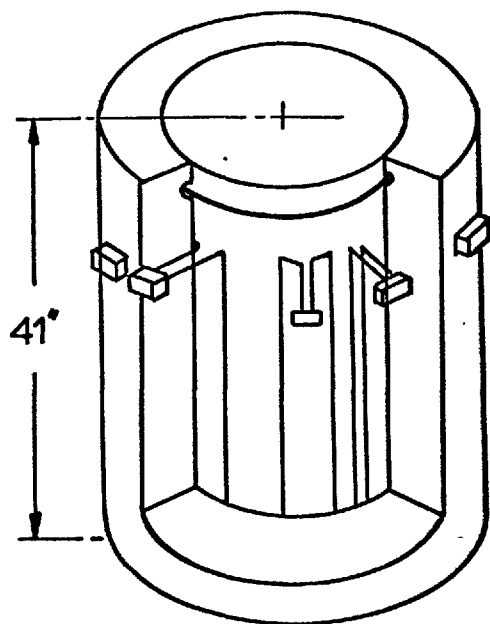
The Thermostat

The basis of the thermostat is a stirred salt bath contained in a steel container, 26" in diameter, 33" deep with a wall thickness of $\frac{1}{2}$ ". This bath is heated by seven coaxial mineral-insulated heaters clamped to the outside of the container. The thermal insulation is provided by 8" of Selfrac lightweight firebrick (thermal conductivity 5×10^{-4} cal/sec/cm²/cm¹/°C at 300°C); which is enclosed in an outer container of galvanised iron 42" in diameter, 41" deep with a wall thickness of $\frac{1}{8}$ ".

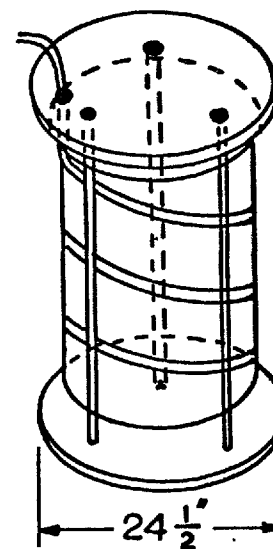
The seven heaters each have a maximum power rating of 1KW, and are placed as follows; six with their bars vertical and equispaced round the walls of the salt container, and the seventh wound into a ring round the top of the furnace to counter thermal losses in this direction. These seven heaters are wired in parallel and derive their power from a 20 amp variac, powered by the stabilised supply. Provision has also been made to change the furnace temperature rapidly by incorporating three more heaters of the same rating, powered directly by the 230 V mains, and wired in parallel in a similar manner to the 'stabilised' heaters. A schematic diagram 6 shows the arrangement of the heaters and their wiring.

The thermostat heat transfer medium is a 55/45 app. mole ratio, mixture of sodium nitrate and potassium nitrate, the phase diagram of which is shown in diagram 7. This mixture is completely fluid at approximately 225°C, and is held inside the inner mild steel container. A mild steel plate covers the molten salt bath and on top of this is placed 4" of glass wool, the insulation is completed by a Sindanyo sheet resting across the top of the thermostat.

The power-temperature characteristic of the furnace is shown over the range 200°C to 350°C, a power of 1.65 KW being sufficient to maintain a temperature of 300°C, as shown in the diagram 8, this being in accordance with the theoretical losses expected from a thermostat of the above



(a)



(b)

DIAGRAMS

6(a) MAIN HEATER ARRANGEMENT.

6(b) CONTROL HEATER ARRANGEMENT.

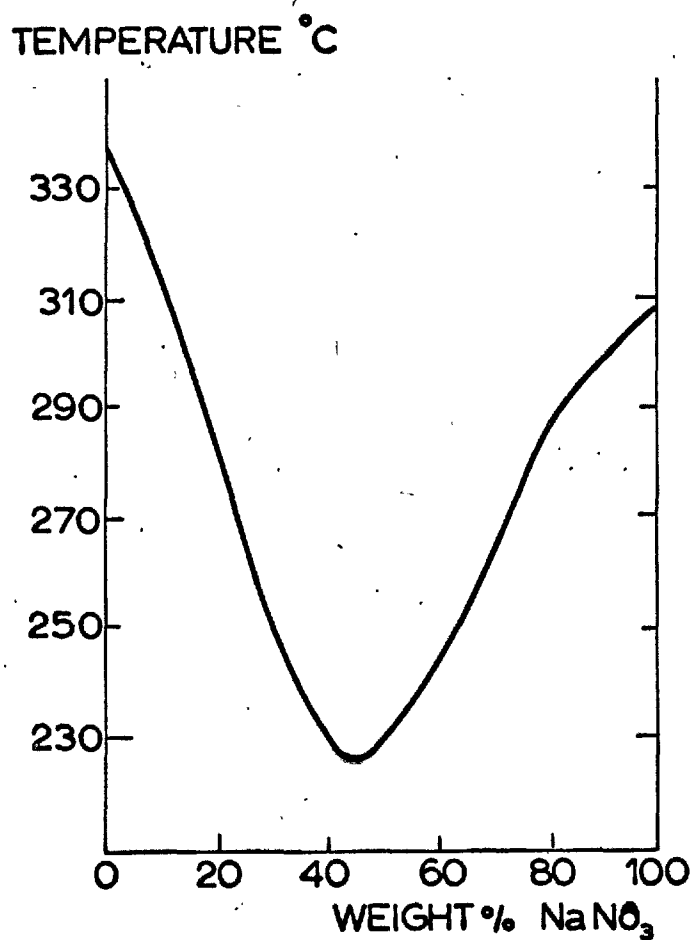
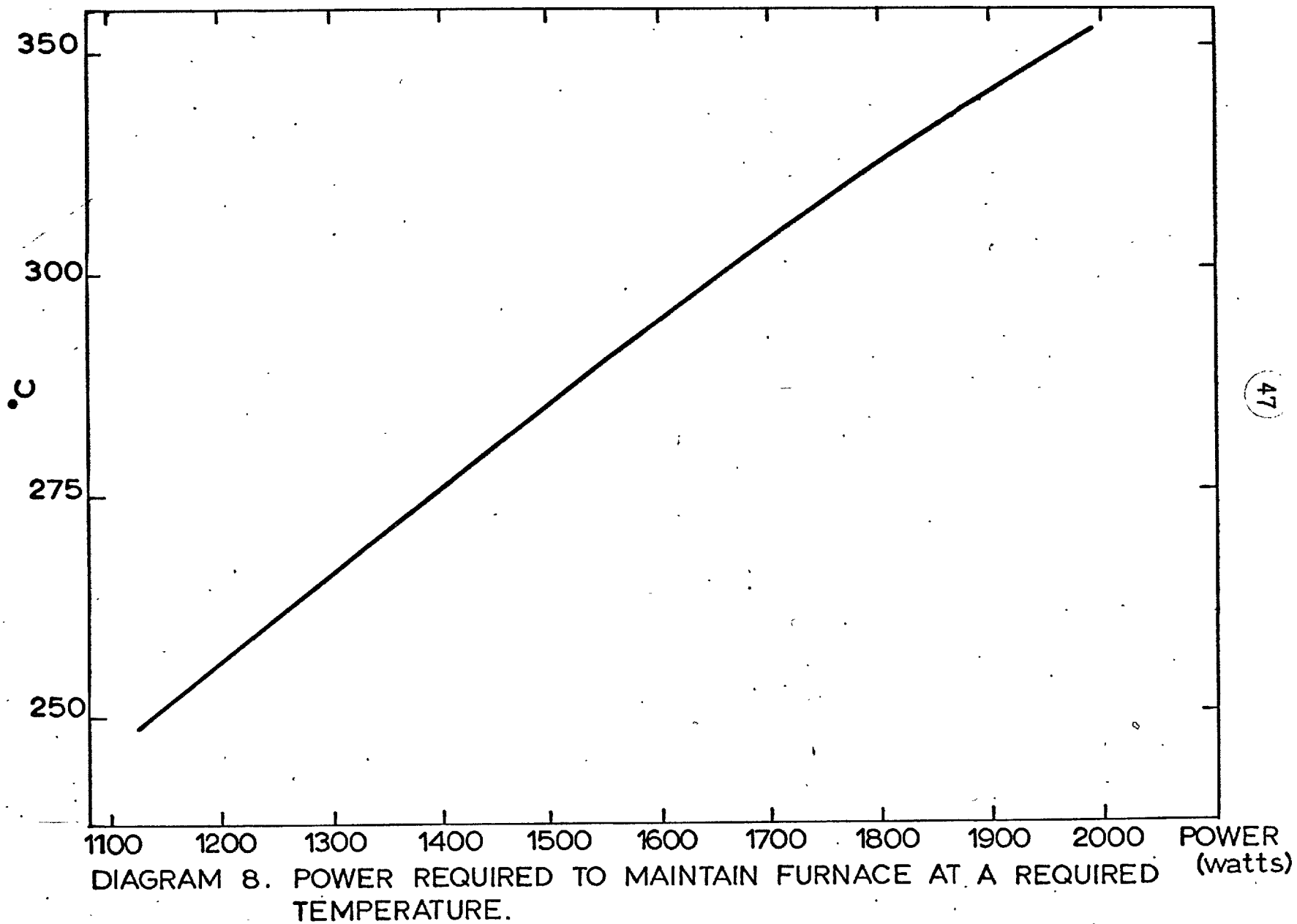


DIAGRAM 7. FREEZING POINT CURVE FOR THE
 $\text{NaNO}_3 - \text{KNO}_3$ SYSTEM.



dimensions and insulation, see appendix II.

The Vacuum System

There are two reasons for enclosing the calorimeter in a vacuum system, one is to avoid convection and conduction through the air or gas surrounding the calorimeter; the other is to reduce oxidation of the metals in the calorimeter. Below 5×10^{-5} mm Hg, the mean free path of argon molecules, with which the vacuum system is filled before evacuation, is large (approximately 25") compared with the internal dimensions of the vacuum chamber, eliminating convection across the vacuum space and reducing conduction through lack of a transfer medium. The oxidation of tin within the calorimeter is reduced by the low pressure of oxygen, but any oxide originally present cannot be removed as its vapour pressure at the operating temperature is below the best vacuum obtainable.

The vacuum in the system is maintained by combination of a backing pump and a diffusion pump. The system to be evacuated is shown in diagram 9, together with its position relative to the salt bath. The system is evacuated first with an Edwards ISC50 backing pump to a pressure of about 50 microns before the 2" oil diffusion pump is introduced into the system, this reduces the pressure to 5×10^{-4} mm Hg in a total time of five minutes. Pumping for a further hour reduces the pressure to better than 10^{-5} mm Hg, as measured by a Penning vacuum gauge unit at the

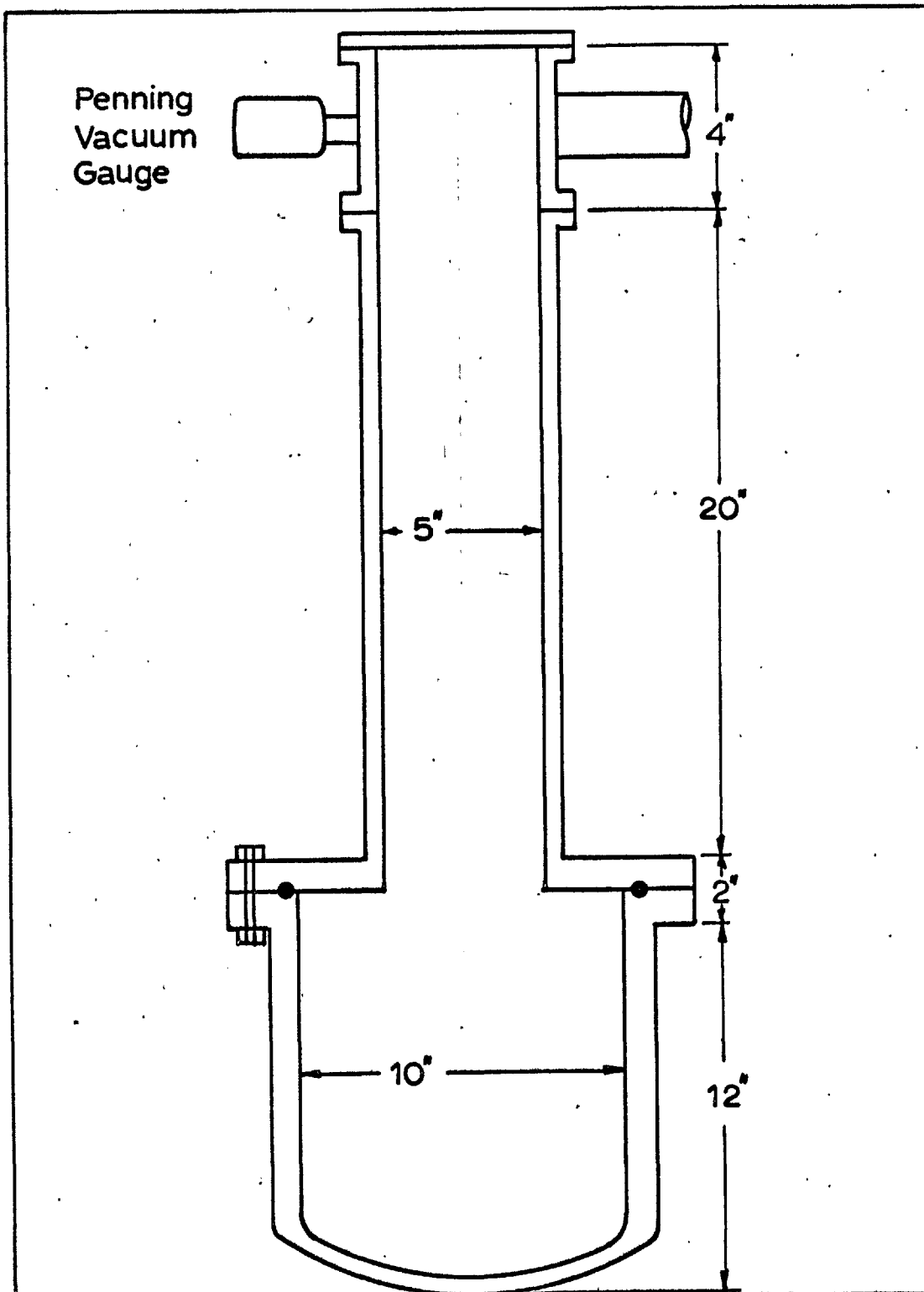


DIAGRAM 9. VACUUM SYSTEM.

head of the vacuum system also indicated in the diagram 9.

Vacuum seals at room temperature are made with 'O' rings fabricated out of neoprene rubber. The seal in the salt bath between the 14" flanges, see diagram 9 is made with 22 gauge copper wire welded at its free ends. The ring so formed is annealed and quenched to obtain a soft copper gasket.

Samples are added to the calorimeter through an air lock consisting of a highly polished 1" straight through Saunders valve. This valve is soft soldered into the top of the vacuum system as shown in diagram 25. The external sample addition tube consists of a 12 mm bore Pyrex tube bent so that its closed end can be placed in an ice jacket and can also be rotated with the use of a B. 19 cone and socket, dropping samples into the system.

To reload the addition tube it is removed from its position in the vacuum system by sliding it upwards through a Wilson seal which is attached at its other end to the straight through valve, and then isolating the sample tube by closing off the valve. After a sample has been placed in the addition tube and evacuated, the tube is returned to its operating position by opening the valve and lowering it into the vacuum system. A stainless steel extension of the glass tube runs down the main vacuum system. This tube is fabricated out of a $\frac{1}{2}$ " diameter tube bent to

slow the speed at which samples hit the tin bath in the calorimeter.

With the whole system under operation the final vacuum attained is better than 10^{-5} mm Hg.

The Calorimetric Unit

The calorimetric unit is located in the lower vacuum system. It consists of a crucible, radiation shields, tin stirrer and supports for the crucible.

The crucible is fabricated out of molybdenum by spinning; the wall thickness being 0.04" and its internal dimensions 2" diameter and .3" depth. This crucible which weighs 149 grams and holds 600 grams of molten tin, is supported on steel pins which are suspended from a radiation shield situated in the neck of the vacuum system. This radiation shield consists of two circular sheets of mild steel 5" in diameter, cut as shown in diagram 10(b), to allow a pumping path, the upper section is rotated through 60° to prevent direct radiation away from the crucible. The radiation shield and interior of the vacuum system are silver plated to reduce radiative transfer of heat from the calorimeter, thereby reducing the value of the system's thermal radiation constant. The radiation shield is located on three pegs fitting into three locating holes at the lower end of the vacuum system neck. The removal of the whole unit is facilitated by three silver steel rods

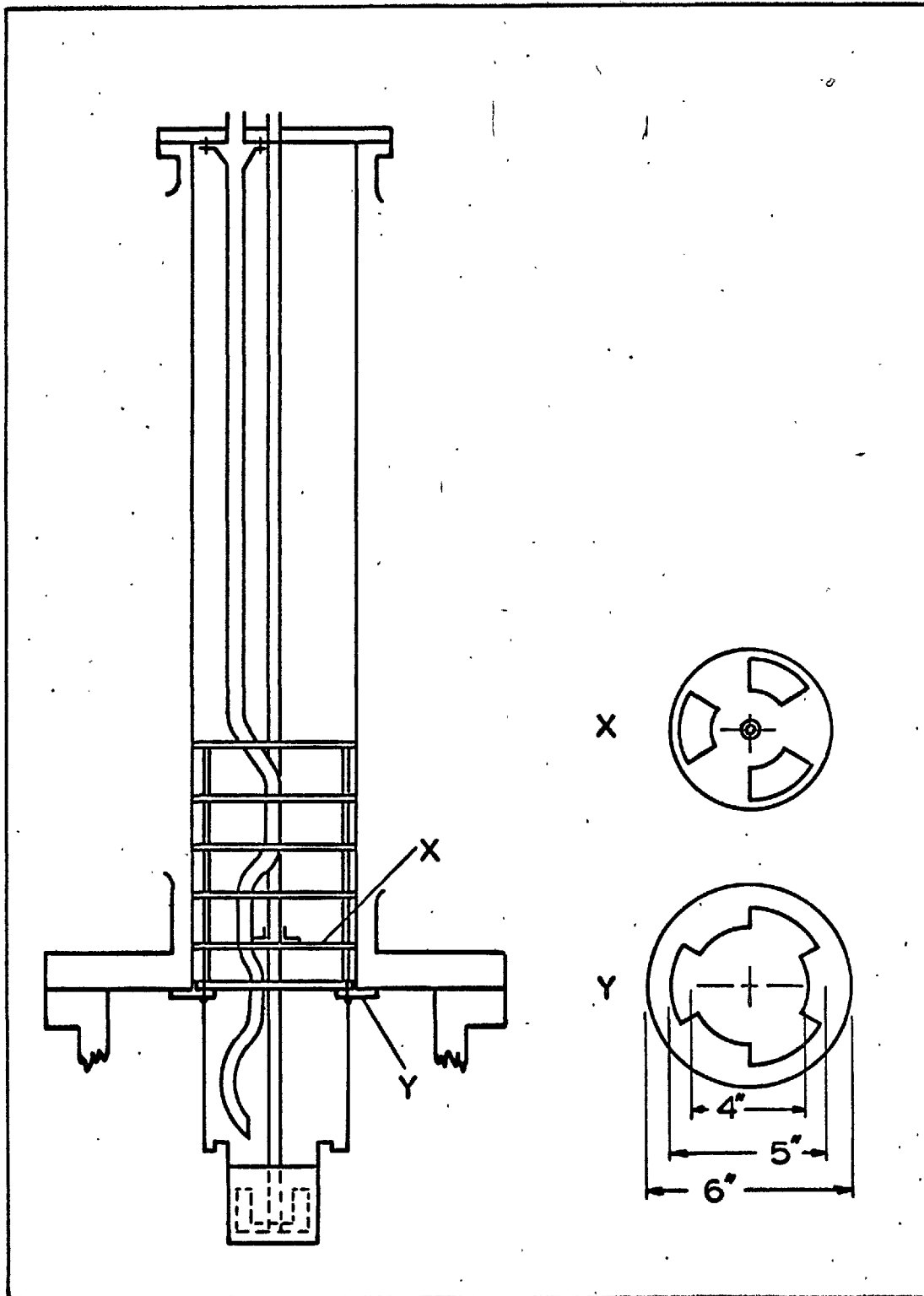


DIAGRAM 10a. INTERIOR ASSEMBLY.
10b. RADIATION SHIELDS.

connected to the top face of the radiation shield. These rods are fixed to the underside of the top plate by means of three blind tapped holes. The upper plate of the radiation shield also has a light ball race fitted to its centre, which locates the tin stirrer shaft.

The tin stirrer consists of a stainless steel tube with paddle blades welded to its ends by the electron beam welding technique. The tube has a wall thickness of 0.01", and is 36" long, the top end passes through a double Wilson seal which is vacuum tight, but permits the stirring motion of the tube. This motion is a reciprocating rotation and is maintained by a 1/30 HP rotary electric motor driving a reciprocating coupling to the stirrer shaft. This hollow stirrer tube is also used as the thermocouple well, reducing the number of seals in the vacuum system.

Molybdenum combines high thermal conductivity with insolubility in tin below 800°C and as such is used as the crucible material. A diagram 10(a) shows the interior assembly.

The Temperature Control System

To achieve the thermal stability required, the thermal mass of the thermostat has been increased to some 15 times that in the Bever calorimeter. Power to the controller and main heaters is supplied through a 3 KW voltage stabilizer, stable to $\pm 1\%$. The control heater is

mounted in the thermostat as shown in the diagram 6 and is constructed out of 40 feet of mineral insulated heater with a stainless steel sheath approximately 0.1" diameter. The control heater has a maximum power rating of 500 W, but is usually operated at about 150 Watts or 10% of the total power to the furnace (depending on the operating temperature).

The furnace temperature is set to any desired value, using a steady power from the main heaters, by consideration of diagram 8 showing the relationship between the total power supplied to the furnace and the temperature maintained by this power.

The thermal regulator is then switched on and deals with variations from thermal stability. A diagram (11), of the control circuit shows the units involved. Variations in the temperature of the salt bath are sensed with a platinum resistance thermometer, which has an average temperature coefficient of resistance of $0.36 \mu / ^\circ\text{C}$ in the range 250°C to 350°C . This thermometer is connected as one arm of a Wheatstone bridge network. The galvanometer in the bridge has an internal resistance of 532μ and deflects approximately $1600 \text{ mm} / \mu\text{A}$ at one metre. It can be calculated that a change of 0.001°C in the thermostat is represented by a change of 10^{-9} amp, using a 6 V battery to drive the bridge. The image of the light reflected by the galvanometer mirror then moves $2.5 \text{ mm} / 0.001^\circ\text{C}$ at 150 cm from the galvanometer, see appendix III. It is this change that is

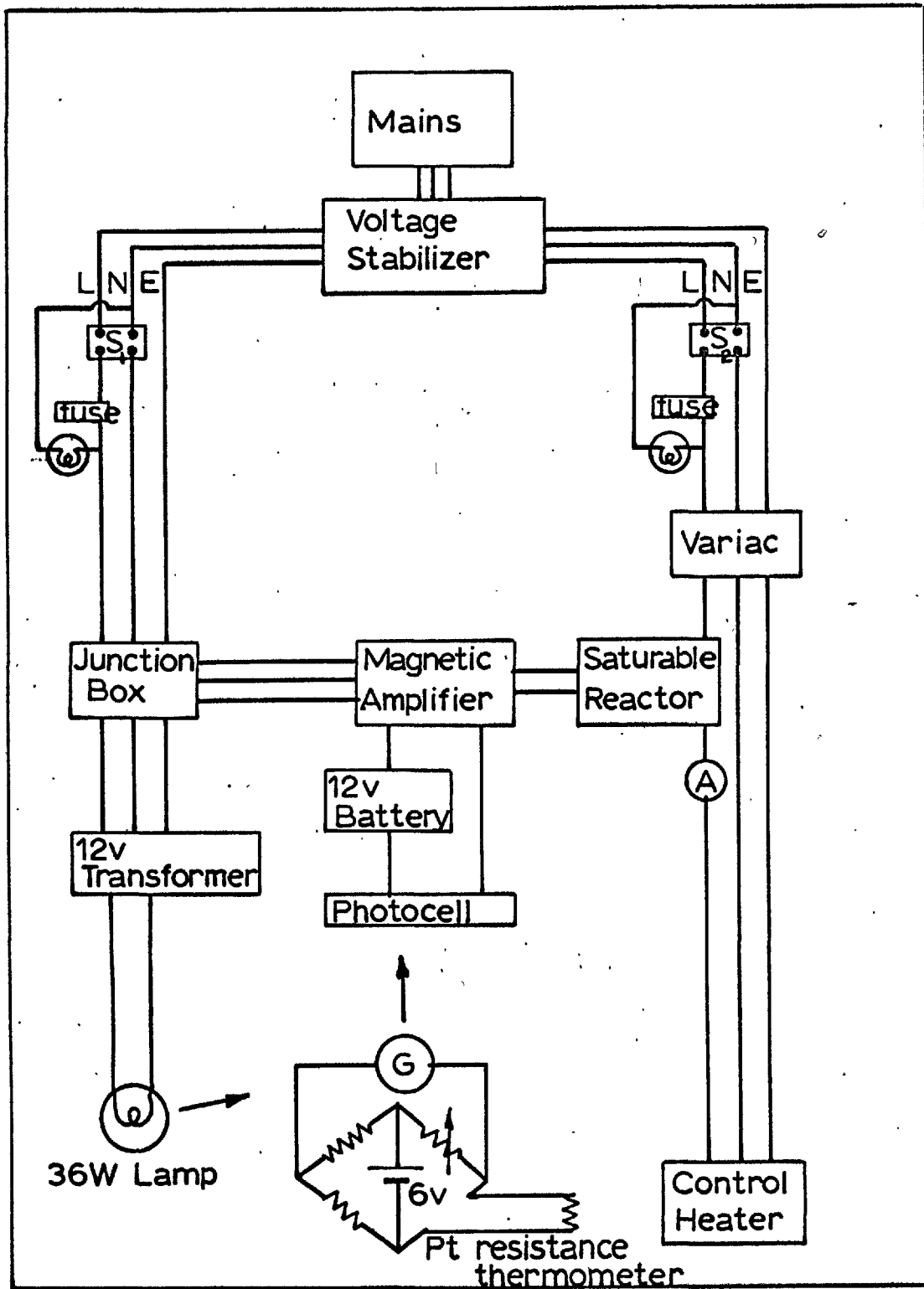


DIAGRAM 11. CONTROL HEATER SYSTEM.

made to govern the output from the control heater. The light image is focused on a Mullard ORP90 photo cell having an internal resistance of 4000 Ω when the light is full on the cell, and virtually infinite resistance in the absence of any light. This photocell is placed at the end of a box that does not allow light other than that from the galvanometer to fall on it. The photocell is connected in series with a 12 volt driving battery and a magnetic amplifier. The magnetic amplifier amplifies the current from the photocell and battery combination and delivers the output, which is of the order of one milliamp to a saturable reactor, which is a choke, whose impedance is varied by the flow of direct current from the magnetic amplifier, to a special winding. It is possible to alter the gain and bias of the amplifying circuit by means of two adjustments provided at the front of the magnetic amplifier. A setting has been selected where the characteristic is largely linear, and where light intensity increase on the photocell is represented as a decrease in output from the saturable reactor. The control heater is connected via the output of the saturable reactor to a power source.

The above description serves to illustrate the control equipment employed, however, before the control heater can stabilise the salt bath temperature, the bath must be stirred to remove natural convection currents. The

salt bath has a stirrer system consisting of a turbine situated at the base of the salt bath. The turbine and a pinion gear are mounted on corrosion resistant steel ball races and the pinion gear is connected to a motor outside the salt bath by a $\frac{1}{2}$ " steel shaft. The shaft passes through a self-adjusting bearing and is connected to the 1/8 H.P. motor by a flexible coupling. To help the 'radial' flow of the salt, and also to support the control heater, a 21" diameter, 20" deep stainless steel cylinder is used. The heater is coiled round it as shown in diagram 6, this cylinder serves as a flow barrier to the salt causing it to travel approximately radially over the top of the barrier and vertically up the side between the cylinder and salt bath container.

Studies of the effects of stirring speed on the control attained have been made, and have led to modifications in the stirring equipment. Originally the stirrer consisted of three paddles mounted vertically, and at 120° to each other on a gear wheel at the base of the salt bath. This was subjected to large variations in speed by use of a $\frac{1}{4}$ H.P. variable speed motor; paddle speeds of 96 r.p.m. down to 18 r.p.m. were tried comparing the control attained as a function of the stirrer speed. Results showed a marked improvement in control as the stirrer speed was increased. At the fast speeds, however, the wear on the ball races in the salt bath was rapid, a noticeable deterioration in

smooth running being noted after a few hours operation. From the results a speed combining good control without excessive wear on the races was chosen. The control as a function of stirrer speed is roughly hyperbolic as shown in diagram 12 control at 50 r.p.m. corresponding to $\pm 0.002^{\circ}\text{C}$ as measured by a recorder coupled to the output of the photo cell.

After these measurements were made the paddle stirrer was replaced by a twelve bladed turbine which, as measured by the same recorder coupled to the photocell, produces control equivalent to twice that of the paddles at the same speed. The turbine now moves at 45 r.p.m. driven by the 1/8 H.P. motor.

Measurements of the thermal stability of the salt bath by means of observations on the galvanometer indicate that control is better than $\pm 0.001^{\circ}\text{C}$, and can be maintained as such for several hours. The limit is set by variations in room temperature which produce stray e.m.f.s in the terminals of the resistance thermometer.

The Temperature Measuring Equipment

Measurement of temperature changes in the calorimeter are made with a chromel-alumel thermocouple. The emf from the thermocouple is detected by a sensitive potentiometer linked to a galvanometer-preamplifier combination.

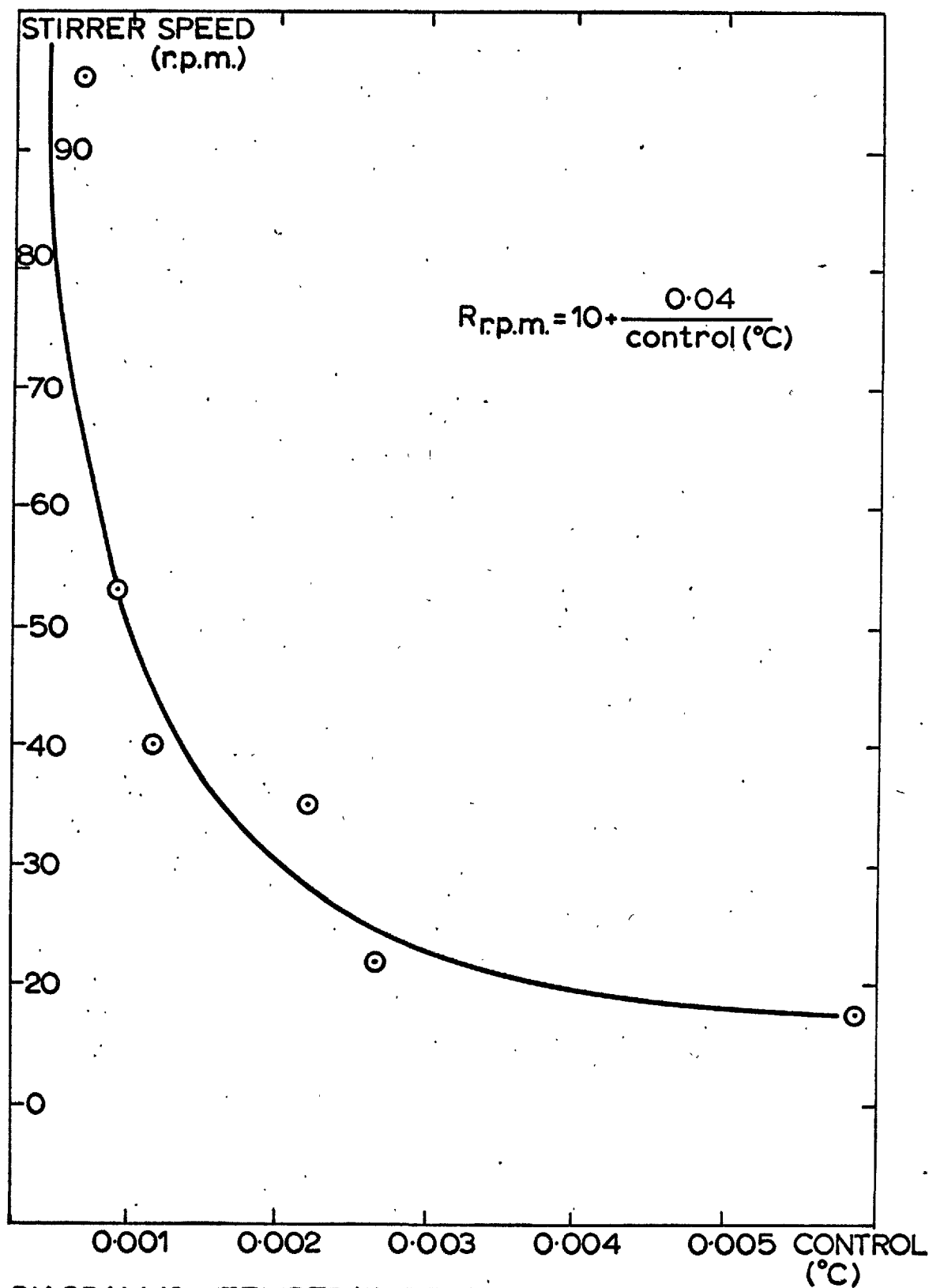


DIAGRAM 12. TEMPERATURE CONTROL OBTAINED AT VARIOUS SALT BATH STIRRING SPEEDS.

The thermocouple used is pressed to the bottom of the hollow stainless steel tin stirrer tube by means of a steel clip, formed as shown in diagram 13. This ensures good thermal contact with the tin bath, and also fixes the position of the thermocouple. The thermocouple leads are constructed from 36 gauge wires and are insulated with glass thread. The thermocouple is then soldered to 26 gauge copper wire, the junction being located in a large well stirred ice bath. The emf is measured on a three dial potentiometer (Tinsley Vernier) reading directly to $1\mu\text{V}$, more precise values being interpolated from the galvanometer deflection permitting temperature readings to be estimated to $\pm 0.001^\circ\text{C}$. The potentiometer is driven by a 2 V accumulator standardised with a standard Weston cell.

The preamplifier (ref 42), (Tinsley Type 5214), consists of an oil filled primary galvanometer and a pair of specially selected photo electric cells of barrier layer type connected in series opposition. The net current from the cells is due to differential illumination from the galvanometer light image. This current is fed to the external galvanometer, (Tinsley Type SS2-45E), and also provides negative feedback stabilising the amplifier. A control is provided to adjust feedback and sensitivity. A thermal compensator is in use which enables the electrical zero of the galvanometer to agree with the mechanical zero by counteracting any thermal e.m.f.s in the input circuit.

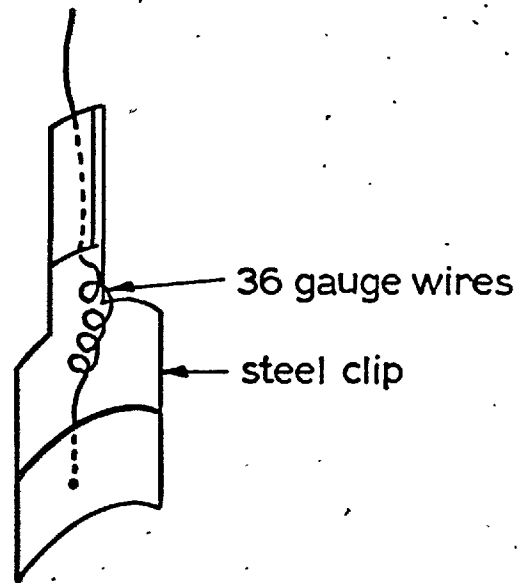


DIAGRAM 13. THERMOCOUPLE CLIP.

The compensator also combines a sensitivity control having four positions $\times 1$, $\times 10$, $\times 100$, and $\times 1000$. Power to the lamps of the galvanometer and preamplifier is supplied by a mains operated stabiliser supplying 40 W at 12 V.

The indicating galvanometer (Tinsley Type 4500A, 10f) is of a robust type not needing a special antivibration mounting. The galvanometer has an internal resistance of $450\ \Omega$, a periodic time of 2 seconds and a sensitivity of $500\ \text{mm}/\mu\text{A}$.

With the Cr/Al thermocouples in use an overall sensitivity of $50\ \text{mm}/\mu\text{V}$ can be obtained. Since this presents difficulties as the indicating spot can be lost in very rapid reactions the operating sensitivity is reduced to $20\ \text{mm}/\mu\text{V}$.

The galvanometer preamplifier combination is mounted on a wall bracket to reduce vibration and is accessible for adjustments to the zero and sensitivity prior to any addition.

The stability of the salt bath is also measured on this equipment and this confirms that control to better than $\pm 0.001^\circ\text{C}$ can be maintained for several hours.

An overall picture of the calorimeter parts can be seen in diagram 25 Appendix VI.

Experimental Materials and Procedure

Materials

Prior to any run, approximately 600 grams of tin, tin-bismuth or bismuth are loaded into the molybdenum crucible. The tin is cleaned first by scraping and then by careful washing in ether. Subsequently it is not touched by hand. The load now in the interior assembly (diagram 10) is put into the vacuum system under an argon atmosphere. The system is then evacuated to reduce oxidation of the tin. Calibration specimens of tin are cut from the same source as the main load, and are roughly spherical in shape. Gold samples are added in the form of short needles 3 to 4 mm long and 1 mm in diameter. Silver samples are of the same gauge wire as the gold, and are added in the same form. The copper wire that is used is approximately 0.5 mm in diameter. The 'inert' samples of tungsten are cylindrical in shape (2 mm in diameter and 5 mm in length) and are cleaned and weighed in a similar manner to the other materials. All solute additions are weighed to 0.1 mg. The tin and bismuth loads are weighed to the same limit.

The materials used are shown in Table 2, together with the source, purity and typical analysis.

Table 2

Material	Source	Purity %	Assay %
Tin	Capper Pass and Sons Ltd	99.999	Sb 0.0001
			Pb 0.0002
			< Cu 0.0001
			< Fe 0.0001
			Bi 0.0001
			< As 0.0001
			< Ag 0.0001
Copper	Johnson Matthey and Co. Ltd	99.9999	Fe 0.0001
			Si 0.0001
			Ag 0.0001
			< Mg 0.0001
Silver	Johnson Matthey and Co. Ltd	99.999	< Ag 0.0001
			< Pd 0.0001
			< Cu 0.0001
			< In 0.0001
Gold	Johnson Matthey and Co. Ltd.	99.999	Cu 0.0001
			Cd 0.0001
			In 0.0001
			Pb 0.0001
			Mn 0.0001
			< Na 0.0001
			Zn 0.0002
Bismuth	Johnson Matthey and Co. Ltd	99.999	Ag 0.0004
			Pb 0.0002
			Ca 0.0001
			Fe 0.0001
			Na 0.0001
			< Cu 0.0001
			< Mg 0.0001

Procedure

After the tin or bismuth load has been put into the crucible, the assembly (diagram 10(a) and 10(b)) is lowered into the vacuum system, locating the radiation shield on its pegs. The system is then evacuated. The pressure reaches 20 microns with the backing pump in 3 minutes and 4×10^{-4} is reached with the oil diffusion pump in another 2 minutes.

The melting point of the tin is recorded with the thermocouple in the tin stirrer shaft, thus providing a calibration for the thermocouple. At this time the vacuum pressure in the main system is better than 5×10^{-5} mm Hg, and there is little oxidation of the tin load as is verified by the conduction at the end of a run. In the time prior to an addition the vacuum improves to 10^{-5} mm Hg. The tin stirrer is started after the tin melts and continues to operate throughout a run.

As soon as the calorimeter assembly is located in the vacuum system, the temperature controller and salt stirrer are switched on and the main heater power is reduced slightly to accomodate for the extra power from the control heater. The Wheatstone bridge is set so that the galvanometer light image is on the photocell. The subsequent movements of the control system are watched carefully. With the light on the photocell the output to the control heater is reduced to a minimum value of about 30 Watts;

this together with the main power is normally insufficient to maintain the temperature of the thermostat. The cooling of the thermostat is detected rapidly (in 5 seconds) by the platinum resistance thermometer and the light image moves off the photocell slowly. As it does so the power to the control heater is increased. If the light moves right off the cell a maximum power of about 150 Watts at 120 Volts is supplied. This, if sufficient, will cause the furnace temperature to increase once again reducing the power available to the control heater. This cycle only occurs if the average power to the furnace is within 5% of the values shown in diagram 8 for a given operating temperature. Once the furnace is under control it is allowed to stabilize for some hours till readings of the tin bath temperature show no trend.

Meanwhile the sample tube is loaded with a sample of known weight and evacuated through a side arm, without being opened to the main system. The air lock is then opened (see description of vacuum system) and the sample-tube lowered into its operating position. An ice bath is put round the end of the sample tube and sample to standardise addition temperatures.

When the system has reached thermal equilibrium the sample is dropped into the calorimeter by rotating the sample tube. Readings are taken of the emf from the

thermocouple in the tin at fixed time intervals (15 seconds for a calibration addition). The thermocouple e.m.f. is deduced from two readings that are made, the first is the reading from the potentiometer which is calibrated to $1\mu\text{V}$; and the second reading is of the galvanometer deflection at any particular setting of the potentiometer, this gives the interpolated value of the thermocouple e.m.f. to $0.01\mu\text{V}$, since the galvanometer sensitivity is set at $2\text{ cms}/\mu\text{V}$ and readings are taken to 0.5 mm . A correction is made for the drift in the battery voltage during an addition and also for any drift in galvanometer zero, this is done by noting their values before an addition and immediately afterwards, and if there is any drift a correction factor is applied, (proportional to time) for the e.m.f. values obtained.

From a calibration addition it is possible to calculate the heat transfer coefficient for a system at the operating temperature and the energy equivalent of the calorimeter.

Data from a typical calibration addition is shown in Table 3, together with a plot of the data, diagram 14. The interpretation of this type of data has been discussed in the section describing basic calorimetry.

Results

For convenience the data obtained has been split into four sections, this division although somewhat artificial in I and II; and also in III and IV helps to clarify the following discussions.

I. Preliminary Data:

- a) A value of the heat transfer coefficient, k , at any given temperature T .
- b) A value of the energy equivalent, C_p of the calorimeter at any given mass of tin and/or bismuth load.

II. Derived Data:

- a) The variation of the energy equivalent of the calorimeter with mass of tin.
- b) The variation of k with T and C_p .

III Heats of Solution:

Partial heats of solution, $\Delta_S H$, of copper, silver, and gold in liquid tin at various temperatures.

IV Heats of Solution:

Partial heats of solution, $\Delta_S H$, of gold and silver in bismuth-tin alloys and in pure bismuth at 350°C.

I. Preliminary Data

As an example of how k and C_p are determined experimentally, Run 5 - 1 is shown below in detail, together with the application of equations (5), (7), and (8) to the

results.

Run No. 5 - 1

Weight of crucible	147.9215 g
Weight of tin load	600.9952 g
Weight of tin sample	1.9449 g
Controller resistance	190.00 Ω
Main Heater Power	1,100 Watts
Vacuum	$< 10^{-5}$ mm Hg
Control	$< \pm 0.001^{\circ}\text{C}$

Temperature measurements

Salt Bath	(a) Pt, Pt Rh thermocouple	1823 μV
	(b) Cr/Al* thermocouple	10059 μV
Tin Bath	Cr/Al* thermocouple	10027.28 μV

These results are shown on the graph (14), plotted in accordance with equation (5), using values shown in Table 3.

Results:

$$k = 0.0003850 \text{ sec}^{-1} \text{ by application of equation (5)}$$

$$\Delta\mu\text{V at 500 seconds} = 41.14\mu\text{V}$$

$$\int_0^{500} \Delta\mu\text{V} dt = 2,240.205\mu\text{V secs, see appendix IV}$$

$$\Delta T_{\text{corr}} = \Delta T_{\text{ob}} + k \int_0^{t_{\text{ob}}} \Delta T dt$$

$$\Delta\mu\text{V}_{\text{corr}} = 41.14 + 8.625$$

$$= 49.765\mu\text{V}$$

* Chromel-Alumel

Experimental Data:-

Time (secs)	μV	$\Delta\mu V(t_0-t)$	$\log \Delta\mu V(t_0-t)$
0	10027.28	0	
15	9977.67	49.61	1.6956
30	9977.33	49.95	1.6984
45	77.94	49.34	1.6932
60	78.33	49.95	1.6897
75	78.78	48.50	1.6857
90	79.00	48.28	1.6837
105	79.33	47.95	1.6808
120	79.56	47.72	1.6787
150	80.22	47.06	1.6727
180	80.76	46.52	1.6677
210	81.28	46.00	1.6628
240	81.89	45.39	1.6570
270	82.39	44.89	1.6522
300	82.78	44.50	1.6484
330	83.30	43.98	1.6433
360	83.89	43.39	1.6374
390	84.47	42.81	1.6315
420	84.87	42.41	1.6275
450	85.33	41.95	1.6227
480	85.83	41.45	1.6175
510	86.24	41.04	1.6132
540	86.83	40.45	1.6069
570	87.22	40.06	1.6027
600	87.72	39.56	1.5973

Run. 5 - 1 Table 3

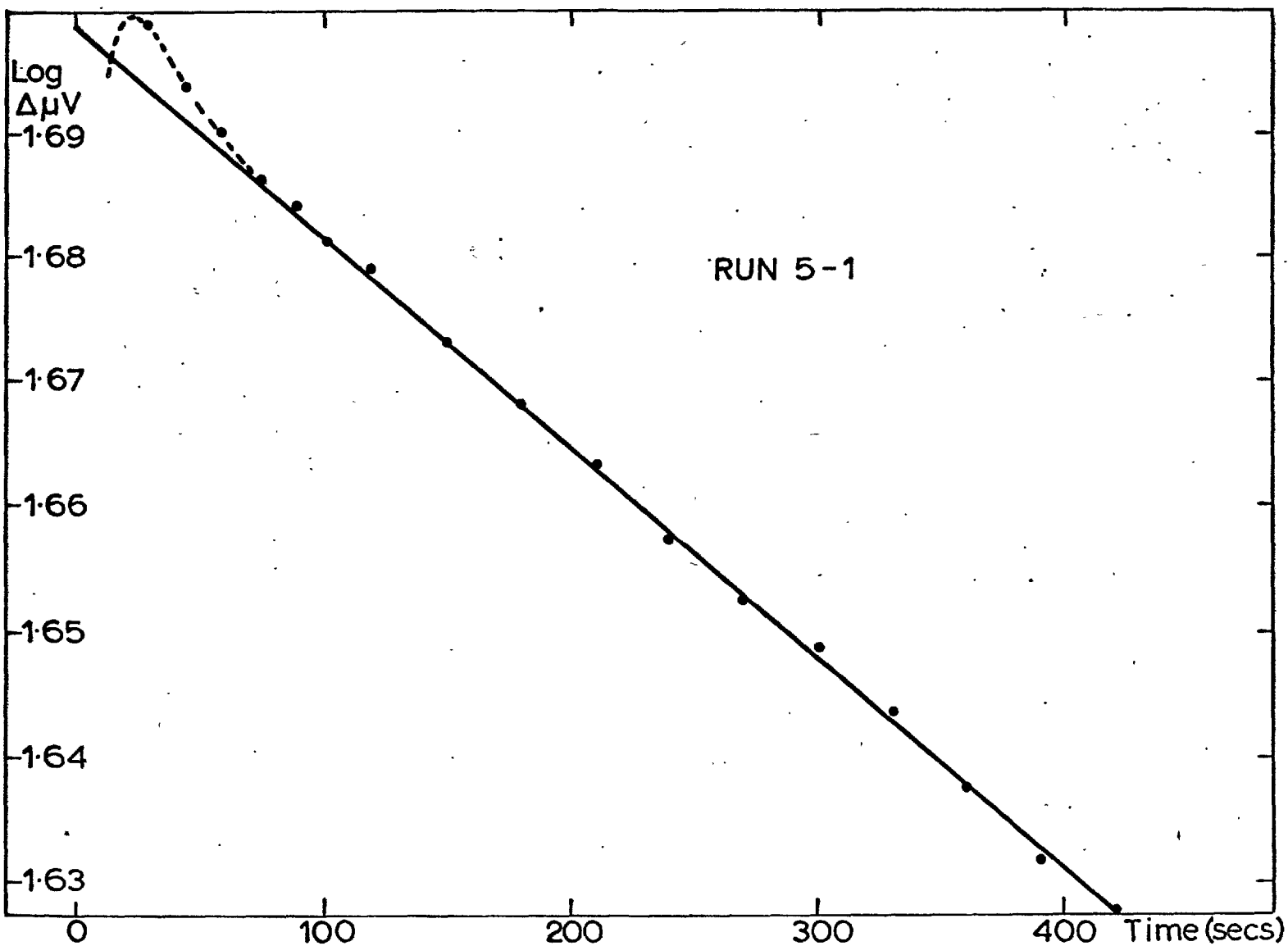


DIAGRAM 14.. ADDITION 5-1. CALIBRATION ADDITION.

$$\begin{aligned}
 \mu V_o - \Delta \mu V_{\text{corr}} &= 1.0027.28 - 49.765 \\
 &= 9977.515 \mu V \\
 &\equiv 237.99^\circ C
 \end{aligned}$$

using equation (8), the value of the energy equivalent is

$$\begin{aligned}
 C_p &= \frac{1.9449 \times 41.924 \times 3384.33}{118.7 \times 49.765} \\
 &= 46.715 \text{ cal } ^\circ C^{-1}
 \end{aligned}$$

$$\text{where } \int_0^{237.99} C_p \Delta T = 3384.33 \text{ calories (ref 26)}$$

and the thermocouple calibration against the melting point of tin indicates that $41.924 \mu V = 1^\circ C$.

II. Derived Data

a) By compiling data such as that obtained in Run 5 - 1, the variation of the energy equivalent with the mass of the tin load can be investigated. This gives an indication of the reproduceability of the data as well as supplying data relevant to the calculation of heats of solution, $\Delta_S H$, from equation (10).

Table 4

Run No.	Mass of tin load	Cp	Run No.	Mass of tin load	Cp
5 - 1	600.9952	46.714	6 - 1	544.2220	46.797
5 - 2	602.9215	46.878	6 - 2	596.051	48.85
5 - 3	604.9801	46.962	6 - 3	598.0451	46.63
5 - 4	607.0077	46.898	6 - 4	599.9806	46.655
5 - 5	608.9115	47.57	6 - 5	601.7124	47.3
5 - 6	610.7620	47.87	6 - 6	602.5266	46.726
5 - 7	612.5639	48.734	6 - 7	603.2817	47.43
5 - 8	615.7572	48.685	6 - 8	605.1799	47.28
5 - 9	617.5576	47.788	6 - 9	606.9155	47.84
5 - 10	619.3975	48.449	6 - 10	608.5756	46.947
5 - 11	621.3217	48.687	6 - 11	610.1659	47.53

These values are shown graphically in diagram 15.

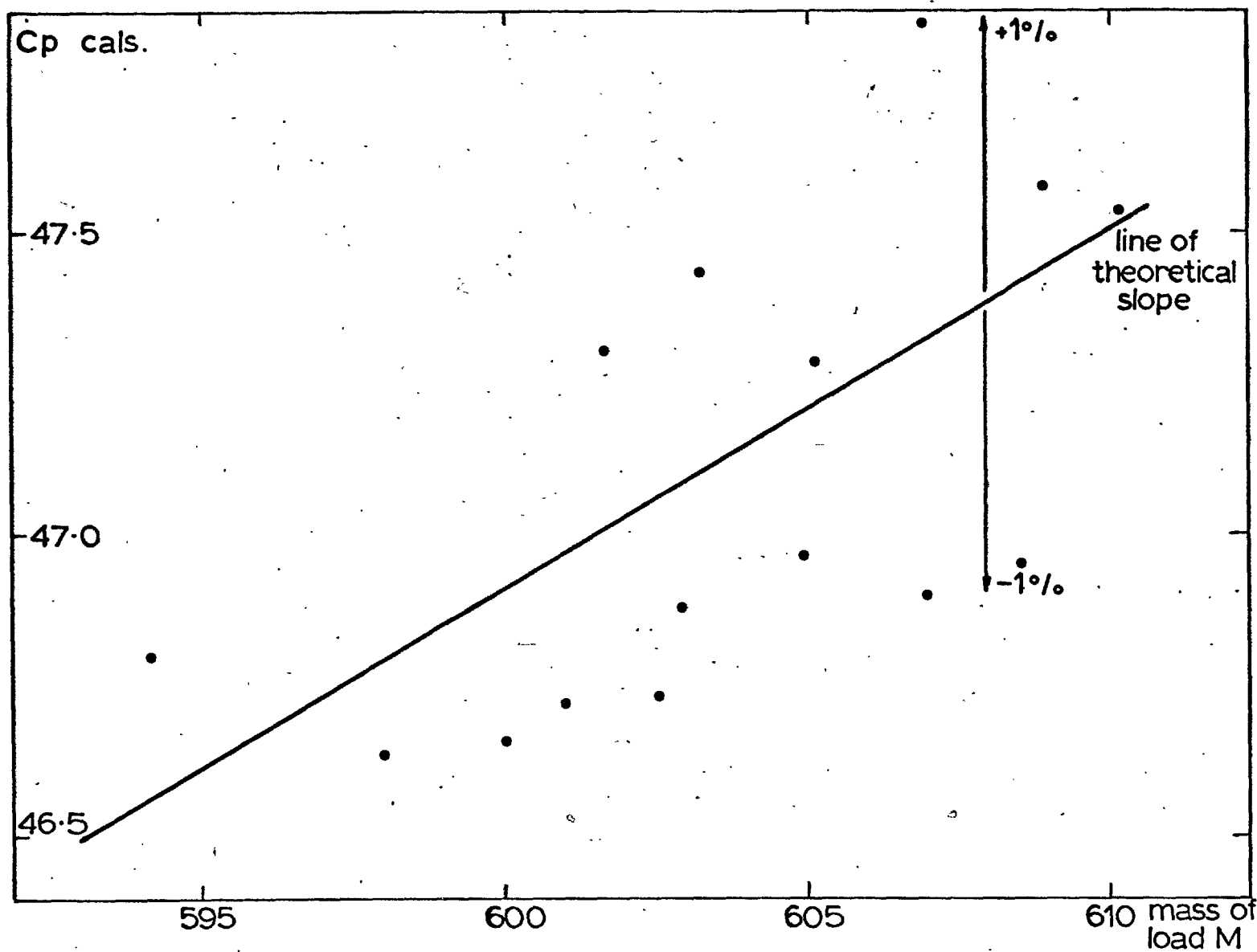


DIAGRAM 15. VARIATION OF ENERGY EQUIVALENT OF THE CALORIMETER WITH ITS MASS OF TIN LOAD.

b) The variation of k with T and C_p is of interest for evaluating the contribution of the radiative relative to the conductive and convective heat losses. The values of the average heat transfer coefficient k at various temperatures are shown in table 5, together with the approximate average energy equivalent C_p for the run. Values of $C_p.k$ are given in the last column, this being the form most useful for further discussion.

Table 5

$T(^{\circ}K)$	$k.(sec^{-1})$	C_p (cals)	$C_p.k.(cal\ sec^{-1})$
513	0.000385	46.9	0.0181
518	0.000380	49.5	0.0188
543	0.000440	50.5	0.0222
568	0.000590	45.5	0.0268
573	0.000570	47.0	0.0268
603	0.000620	47.5	0.0295
623	0.000720	49.0	0.0353

The values quoted for k and C_p are the average values obtained for a series of additions. The accuracies are $\pm 1\%$ for both quantities.

III Heats of Solution

Partial heats of solution, $\Delta_S^{\bar{H}}$ of copper, silver, and gold were determined using the value of C_p appropriate to the mass of tin (and metal) in the crucible prior

to the addition. Values of k for endothermic reactions, such as the solution of silver and copper in tin are obtained from the same additions, but values of k are more difficult to obtain accurately from exothermic reactions, such as the solution of gold in tin. This is because the magnitude of the observed effect is reduced due to 'cancellation' of the exothermic solution effect and cooling effect of the cold sample on contact with the solvent. (see diagram 5). In this latter case the value of k is taken from the preceding calibration addition.

Table 6

Sample	T(°C)	$\Delta_S H(\text{cals})$	$\int_0^T C_S dT (\text{cals})$
Au	247.74	-5880	1,524
Au	247.54	-5845	1,523
Au	247.59	-5855	1,523
Au	298.8	-5385	1,848
Au	298.97	-5530	1,849
Au	298.93	-5510	1,849
Au	347.766	-5340	2,161
Au	347.69	-5400	2,161
Au	350.2	-5430	2,177
Ag	246.15	3510	1,452
Ag	288.11	3690	1,780
Ag	299.933	3715	1,785
Ag	299.954	3635	1,786
Ag	346.497	3685	2,079
Ag	347.023	3720	2,082
Ag	347.02	3770	2,083
Cu	299.6	2350	1,798

IV Heats of solution

Partial heats of solution $\Delta_{\text{S}}^{\text{H}}$ of gold and silver in alloys of bismuth-tin and in pure bismuth were determined in a similar manner to those tabulated in III. This study was made after further refinements to the equipment (ref 43).

Calibration for the pure bismuth run was made with 'inert' additions of tungsten, using integrated heat capacity data from K.K. Kelley (ref 27). In several cases a comparison was made between calibrations with tin and with tungsten which confirmed that within the accuracy of the present work the data of K.K. Kelley was appropriate.

In some cases tin was the calibrating species and here the partial heat of solution of tin in the tin-bismuth alloy had to be considered. Values for these were taken from the following table (ref 44).

at % Bi	100	90	80	70	60	50	40	30	20	10	0
$\Delta_{\text{H}_{\text{Sn}}}^{\text{SnBi}}$	95	77	61	47	34	24	15	9	4	1	0

The results obtained in runs 16 to 20 are shown in the tables 7 to 12 and are further shown graphically in diagrams 16 and 17 where partial molar heats of solution of gold and silver in bismuth tin alloys are plotted against the mole fraction of solute; and in diagram 18 where the same parameter is plotted against the composition of the solvent.

A recent private communication from Bever has given some corroboration to the value for $\bar{\Delta}H_{\text{Au}(\text{Sn+Bi})}$. His values have been plotted on diagram 18 and are shown in appendix VII.

Run 1624.4 atomic percent Bismuth

Run No.	Sample	Sample Mass (g)	Moles of Sample	Moles of Sample (Au)		mean moles at addition	mean moles solvent	ΔH (cals)	$\int C_{pd} T$ (cals)	mole fraction	C_p (cals)
				Initially	Finally						
16-1	Sn	2.0822	0.017542	0	0						40.59
16-2	Au	1.6882	0.0085609	0.0000	0.0085609	0.0042805	4.451282	-4457	2179	0.000962	
16-3	Au	1.6650	0.0084432	0.0085609	0.017004	0.01278325	4.459784	-4444	2178	0.00287	
16-4	Au	1.7862	0.0090578	0.017004	0.0260618	0.0215329	4.468535	-4479	2178	0.00482	
16-5	Sn	2.1709	0.018289								40.87
16-6	Au	1.5714	0.0079686	0.0260618	0.0340304	0.030046	4.495257	-4472	2178	0.00668	
16-7	Ag	1.2195	0.011304					+4162			
16-8	Sn	2.1200	0.01786								41.13

Table 7

Run 1774.4 atomic percent Bismuth from 17-2

Run No.	Sample	Sample Mass	Moles of Sample	Moles of Sample Au		mean moles at addition	mean moles solvent	ΔH (cals)	$\int C_p dT$ (cals)	mole fraction	C_p (cals)
				Initially	Finally						
17-1	Sn	2.2991	0.019369	0	0						34.72
17-2	Au	1.6537	0.008386	0.0000	0.008386	0.004193	3.48934	-1282	2174	0.0012	
17-3	Au	1.8101	0.009179	0.008386	0.017565	0.012975	3.49812	-1279	2174	0.00371	
17-4	Sn	1.1099	0.093505								35.0
17-5	Au	1.8061	0.0091587	0.017565	0.026724	0.022144	3.596204	-1274	2174	0.00616	
17-6	Ag	1.2842	0.011903					+5320	2086		
17-7	W	3.4553	used to check the integrated heat capacity of tungsten								

Table 8

Run 18100% Bismuth

Run No.	Sample	Sample Mass	Moles of Sample	Moles of Sample (Au)		mean moles at addition	mean moles solvent	ΔH (cals)	$\int C_{pdt}$ (cals)	mole fraction	Cp cals
				Initially	Finally						
18-1	W	2.0189		0	0						34.29
18-2	Au	1.6323	0.0082774	0.0000	0.0082774	0.0041387	3.410555	+3697	2166	0.00121	
18-3	Au	1.6570	0.0084026	0.0082774	0.01668	0.0124787	3.418895	+3670	2166	0.00365	
18-4	W	2.2216									33.06
18-5	Au	1.7470	0.008859	0.01668	0.02554	0.02111	3.42753	+3655	2166	0.00616	
18-6	Au	1.5531	0.0078758	0.02554	0.0334158	0.029478	3.43589	+3684	2167	0.00858	
18-7	W	1.2303									34.38
18-8	Ag	0.9791	0.0090758					+6022	2089		

Table 9

Run 1949.14 atomic percent Bismuth

Run No.	Sample	Sample Mass	Moles of Sample	Moles of Sample (Au)		mean moles at addition	mean moles solvent	ΔH (cals)	$\int C_p dT$ (cals)	mole fraction	C_p (cals)
				Initially	Finally						
19-1	Au	1.2751	0.006466	0.0000	0.006466	0.003233	3.8932	-3324	2177	0.000830	
19-2	Au	1.32045	0.006696	0.006466	0.013162	0.009814	3.9000	-3303	2177	0.00252	
19-3	Au	1.3142	0.0066643	0.013162	0.019826	0.016494	3.9065	-3304	2177	0.00422	
19-4	W	1.2300	0.0066899								39.28
19-5	Au	1.2342	0.0062586	0.019826	0.026085	0.0229556	3.9130	-3292	2177	0.00587	
19-6	Sn	0.9622	0.0081061								38.9
19-7	Ag	0.9306	0.008555					+4999			

Table 10

Run 20100 atomic percent Bismuth

Run No.	Sample	Sample Mass (g)	Moles of Sample	Moles of Sample (Au)		mean moles at addition	mean moles solvent	ΔH (cals)	$\int C_{pd} T$ (cals)	mole fraction	Cp (cals)
				Initially	Finally						
20-1	Ag	1.1571	0.01076	0.0000	0.01076	0.00538	3.08603	+6191	2084	0.00174	
20-2	Ag	0.5284	0.004898	0.01076	0.015658	0.012829	3.09384	+6152	2093	0.00426	
20-3	Ag	0.52625	0.0048781	0.015658	0.020536	0.018111	3.09873	+6094	2093	0.00583	
20-4	W	1.0266	0.0055836						2126		32.54
20-5	Ag	0.4854	0.0044994	0.020536	0.025035	0.022785	3.10342	+6059	2094	0.00733	
20-6	W	1.1903	0.006474						2126		32.69

Table 11

The following table summarises the results obtained in runs 16 - 20.

Table 12

Run No.	Sample	at % Bi	$\bar{\Delta H}_{Au}^{\infty}$ (cals)	$\bar{\Delta H}_{Ag}$	$\bar{\Delta H}_{Ag}^{\infty}$
16	Au	24.4	-4470		
16	Ag	24.4		+4160	(4330)
17	Au	74.4	-1285		
17	Ag	74.4		+5320	(5490)
18	Au	100	+3710		
18	Ag	100		+6020	(6240)
19	Au	49.14	-3325		
19	Ag	49.14		+5000	(5150)
20	Ag	100			+6240

All $\pm$ 15 cals.

Results shown in brackets have been obtained after 'smoothing' as explained in the discussion section IV.

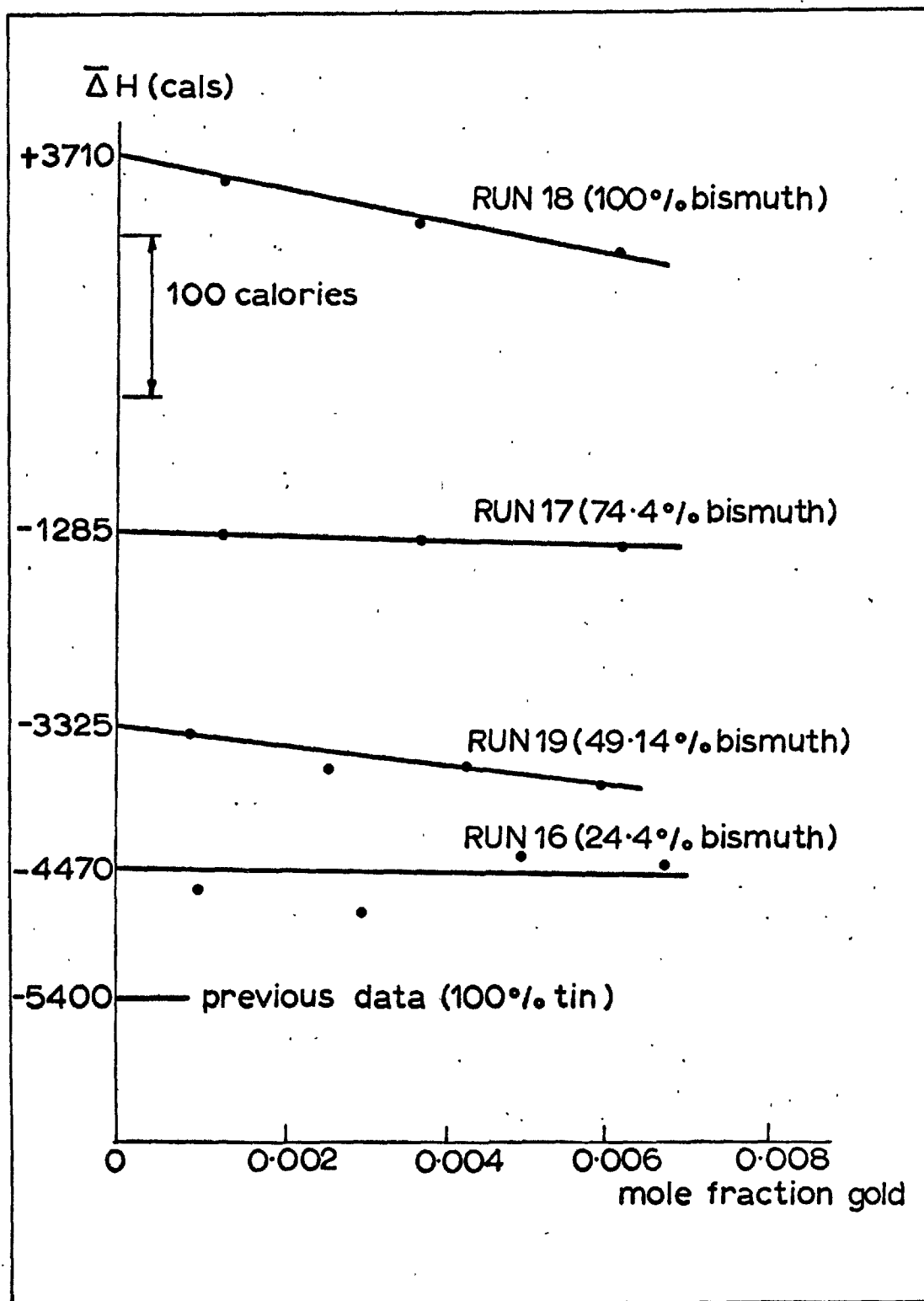


DIAGRAM 16. PARTIAL MOLAR HEATS OF SOLUTION OF GOLD IN TIN-BISMUTH ALLOYS AT 350°C.

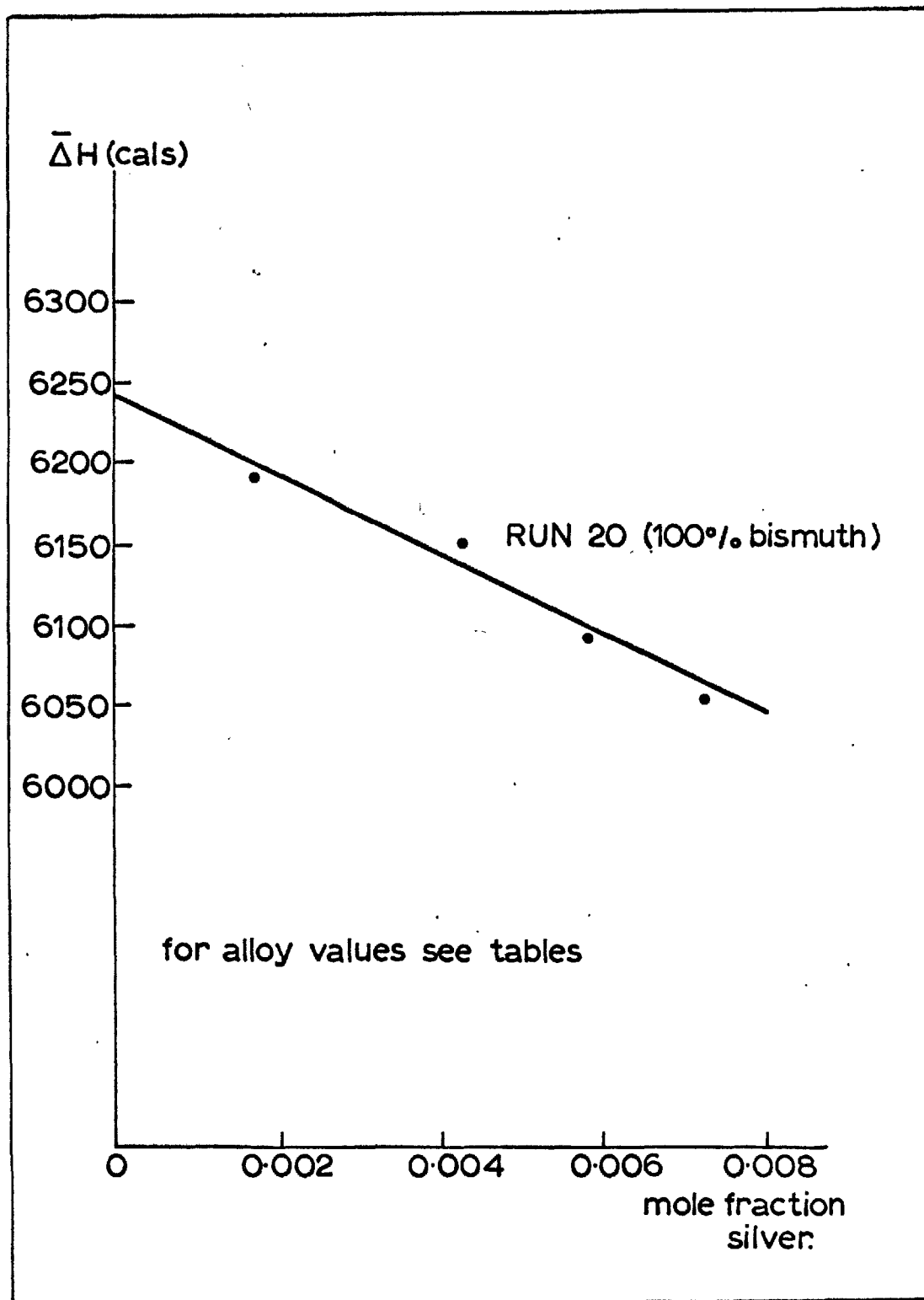


DIAGRAM 17. PARTIAL MOLAR HEAT OF SOLUTION OF SILVER IN PURE BISMUTH.

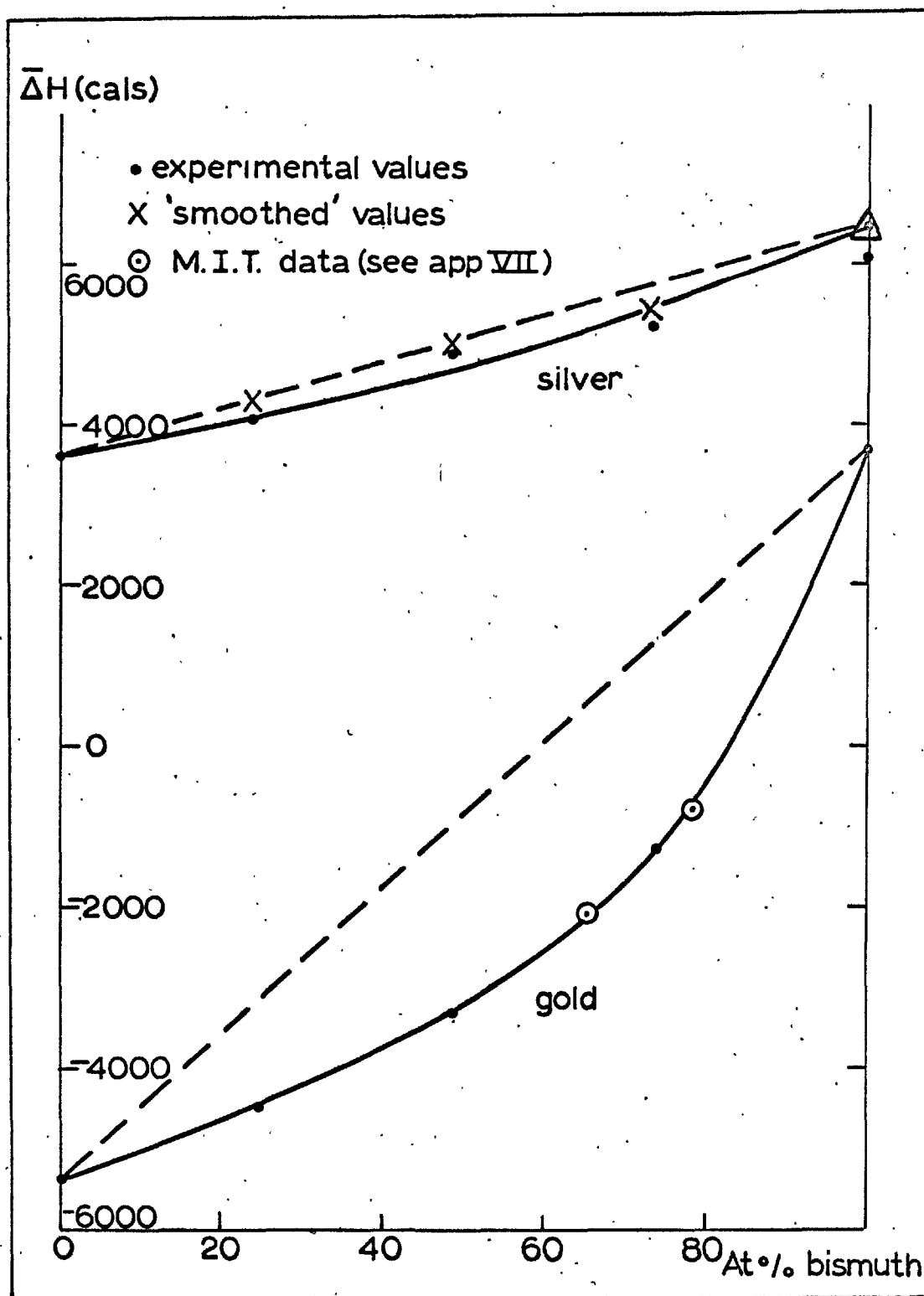


DIAGRAM 18. PARTIAL MOLAR HEATS OF SOLUTION OF GOLD AND SILVER IN TIN-BISMUTH ALLOYS.

Discussion

The Preliminary and Derived results present data which can be used to evaluate the overall performance of the equipment. The more important features can then be compared to similar data obtained from existing calorimeters. Heats of solution, being independent of the equipment, can only be compared with other workers in terms of their magnitude and accuracy.

The discussion is divided between the following sections, which correspond to the respective sections in the results.

- I. Performance of the equipment
- II. Comparative performance
- III. Comparison of heats of solution
- IV. Application of the quasi-chemical theory to heats of solution of gold and silver in bismuth tin alloys.

I. Performance of the equipment

Improvements in the accuracy of calorimetric data are achieved by careful design. As pointed out (in the section on previous work), criteria can be set up formulating the basic design considerations of a calorimeter. In the present instance these criteria were:-

a) A calorimeter cell contained in a thermal environment must only transfer heat between itself and the environment according to a known law.

b) There must be a way of measuring the energy equivalent of the calorimeter cell and changes of energy produced in it during a reaction.

These criteria have been satisfied as follows:-

a) The constant temperature environment is stable to $\pm 0.001^\circ\text{C}$ throughout a reaction. This is an essential feature of a 'heating' calorimeter as the basic heat transfer laws depend on this assumption.

b) The calorimeter is so constructed that heat transfer takes place mainly by radiation. It is possible to estimate the contribution due to conduction and convection as follows:

The total rate of heat transfer (using the notation in app. I) is,

$$\frac{-dH}{dt_2} = K(T_1^4 - T_2^4) + C(T_1 - T_2)$$

$$\text{and since } (T_1^4 - T_2^4) = (T_1 - T_2)(T_1^3 + T_1^2T_2 + T_1T_2^2 + T_2^3)$$

assuming $T_1 \approx T_2$

$$\frac{-dH}{dt} \approx 4KT_2^3(T_1 - T_2) + C(T_1 - T_2)$$

$$-\frac{dH}{dt} \approx (4KT_2^3 + C)(T_1 - T_2)$$

The experimental value of the heat transfer coefficient calculated at any temperature T_2 is given by

$$-\frac{dH}{dt} = kC_p (T_1 - T_2)$$

$$\text{hence } kC_p = 4KT_2^3 + C \text{ -----(16)}$$

A plot of kC_p against T_2^3 should give a straight line of intercept C and slope $4K$. The values obtained experimentally are shown in table 13 which is an extension of table 5.

Table 13

$T_2(^{\circ}K)$	$T_2^3 (^{\circ}K)^3$	$Cpk(\text{cal sec}^{-1})$
513	1.35×10^8	0.0181
518	1.39×10^8	0.0188
543	1.60×10^8	0.0222
568	1.83×10^8	0.0268
573	1.88×10^8	0.0268
603	2.19×10^8	0.0295
623	2.42×10^8	0.0353

These values are shown graphically in diagram 19.

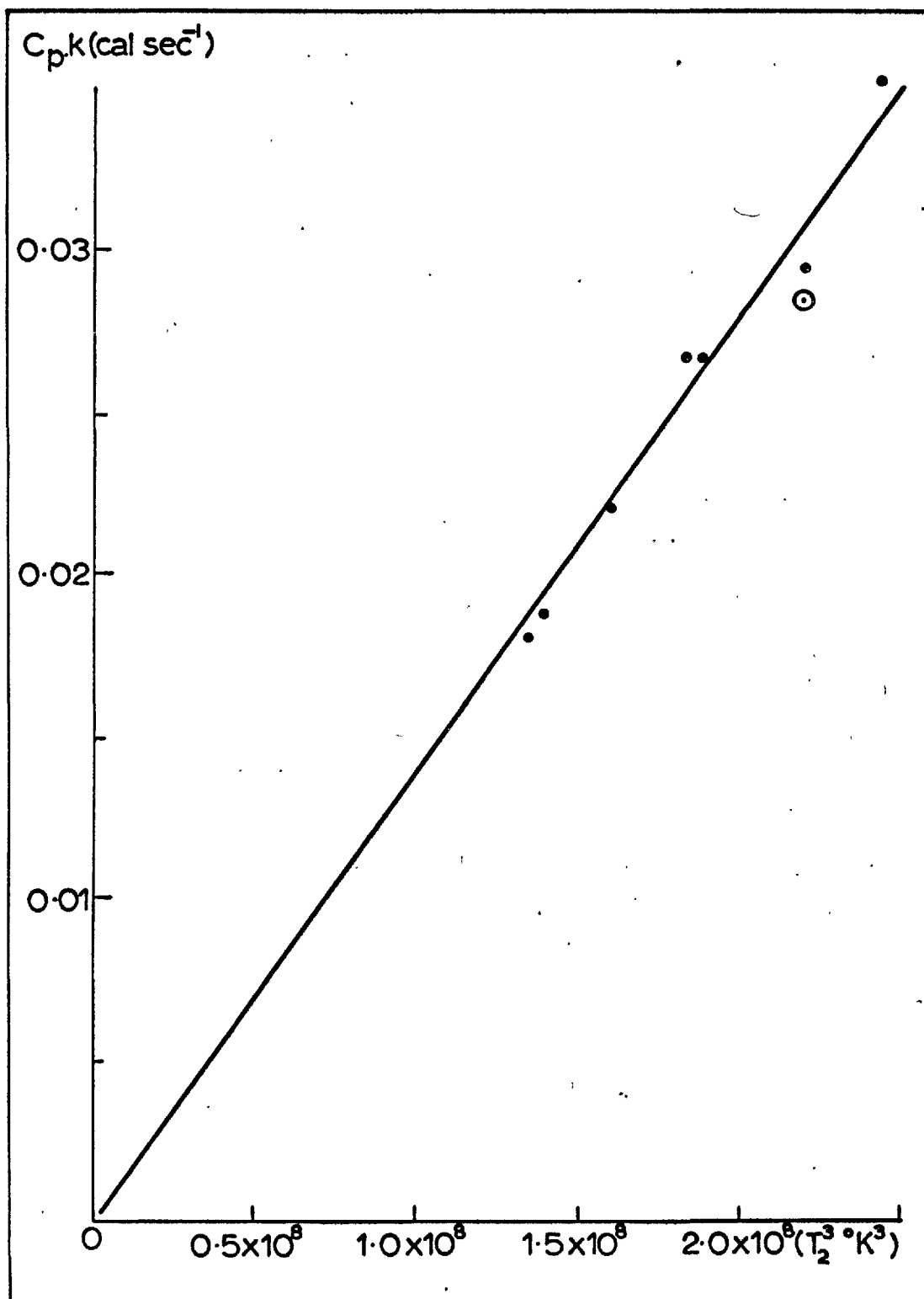


DIAGRAM.19. VARIATION OF THE COEFFICIENT OF HEAT TRANSFER AND ENERGY EQUIVALENT OF THE CALORIMETER WITH TEMPERATURE.

The slope of the line is

$$\frac{kCp}{T_2^3} = 1.4 \times 10^{-10} \text{ cal. sec}^{-1} \text{ } ^\circ\text{K}^{-3}$$

and the intercept is small indicating an insignificant contribution to heat transfer by conduction and convection.

One further deduction can be made from this value.

From equation 4

$$E = \frac{k \cdot Cp \cdot J}{4 \cdot T_2^3 \cdot 5}$$

assuming that tin and molybdenum have approximately the same emissivity

$$E = \frac{1.4 \times 10^{-10} \times 4.2 \times 10^7}{4 \times 5.7 \times 10^{-5} \times 160}$$

$$= 0.15$$

It is self evident that a value for k, in agreement with those found experimentally, could have been obtained by starting with this value for E; which is in good agreement with values for polished metals.

As these results are indicative of heat transfer directly in accordance with Stefan Boltzmann's equation, a very stringent test was applied. By making a heating curve from the melting point of tin where $T_2 > T_1$, deviations from equation (5) will be apparent. The integrated

version of Stefan Boltzmann's equation will remove any temperature dependence, i.e.

$$-2 \tanh^{-1} \frac{T_1}{T_2} - 2 \tan^{-1} \frac{T_1}{T_2} = -kt + \text{const}' \text{ -----(17 app.V)}$$

The values required by this equation and equation 5 are tabulated below in table 14, where $T_2 = 25,345 \mu\text{V} (\approx 600^\circ\text{K})$

Table 14

t (secs)	$\frac{\mu\text{V}}{10^\circ\text{K}}$	$\Delta\mu\text{V}$	$\log \Delta\mu\text{V}$	T_1/T_2	$\tan^{-1} \frac{T_1}{T_2}$	$\tanh \frac{T_1}{T_2}$	$-2 \tanh^{-1} \frac{T_1}{T_2}$ $-2 \tan^{-1} \frac{T_1}{T_2}$
0	21330	4015	8.2976	0.84159	0.6996	1.2261	-3.8514
300	21851	3494	8.1588	0.86214	0.7115	1.3071	-4.0264
600	22309	3036	8.0183	0.88021	0.7217	1.3767	-4.1968
900	22714	2631	7.8753	0.89570	0.7304	1.4500	-4.3608
1200	23072	2273	7.7289	0.91032	0.7385	1.5293	-4.5356
1500	23387	1958	7.5795	0.92275	0.7453	1.6027	-4.6960

These values are shown graphically in diagram 20 on the same scales.

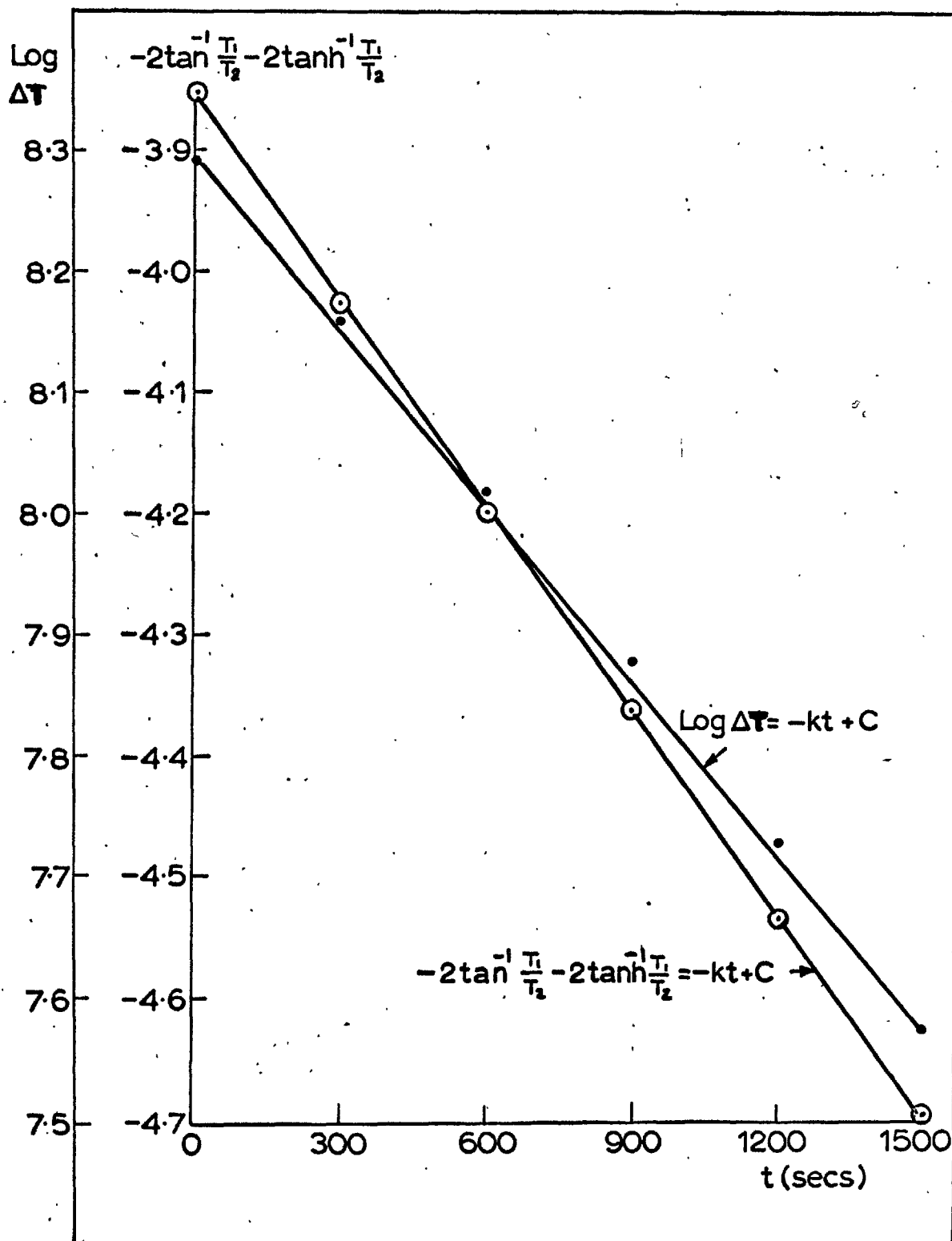


DIAGRAM 20 STEFAN'S COOLING LAW COMPARED TO NEWTON'S COOLING LAW.

The line given by equation (17) has a value of k equal to 0.000570, coupled with a value of $C_p = 50$ cal/s, at $T_2 = 600^\circ\text{K}$. This value of k is in good agreement with those found by application of equation (5) for $T_1 \approx T_2$.

This value is plotted on graph 19, as a circle. It is slightly below the general spread of results; this difference could be due to the variation of emissivity of the calorimeter with temperature, as here the results are calculated at $T_2 > T_1$ whereas actual results are for $T_1 \approx T_2$. The value of emissivity increases with temperature, and as such this value is acceptable within the general error.

The two criteria are satisfied both in sensitivity of the measuring system and in terms of the 'rational' nature of the heat transfer which takes place in the system.

Estimate of Errors

The uncertainty in the temperature measurements results in an uncertainty in the energy equivalent of the calorimeter of $\pm 0.02\%$.

The value of the heat transfer coefficient is precisely known, but there are variations from one addition to another. This could be caused by uncertainty in the true equilibrium temperature, but is as yet, not fully understood. The uncertainty in k is reduced as the run proceeds, but even so, there is an uncertainty in k of $\pm 2\%$.

The contribution by k to the total error in ΔT_{corr} is small as k is small. The value of $\Delta T_{\text{observed}}$ is usually four or more times as great as $k \int_{t_0}^{t_{\text{ob}}} \Delta T dt$ in a calibration addition. The error in ΔT_{corr} is about $\pm \frac{1}{2}\%$.

There is also a systematic error in values of the heat capacities of the calibrating substances, taken from tables, these errors amounting to $\pm \frac{1}{2}\%$.

The scatter observed in C_p for runs specifically designed to test this parameter is about $\pm 1\%$. This error is apparent in the derived heats of solution.

Discussion of Errors

As experience has been gained in operation, and understanding of the calorimeter, the source of error has been investigated. It was initially assumed that errors were caused by a varying temperature gradient within the vacuum shell. Recent work by A.K. Jena (ref 43) has shown that there is no gradient exceeding $\pm 0.001^\circ\text{C}$ within 4" of the calorimeter crucible. There was an appreciable gradient near the top radiation shield, which appeared to be at a lower temperature than that of the environment.

By incorporating three extra shields at the top of the radiation 'barrier' it has been found that minor divergences have been eliminated from 'k' lines and the scatter in values of C_p have been reduced to less than $\pm \frac{1}{4}\%$,

or 10 calories in 5000, in terms of the derived heats of solution. As a consequence early results up to run 14 were performed at the lower precision. The more recent data including that for estimating z from the quasi-chemical theory was obtained at the higher level of precision.

II Comparative Performance

The most obvious improvements achieved in this instrument are the linearity of the 'k' lines and the great sensitivity combined with rapid response of the temperature measurement. In all other calorimeters of the liquid metal solution type known to the author some form of correction is required to eliminate non linearity. The probable reason for this 'rational' heat transfer coefficient is discussed in the section on basic calorimetry.

The calorimeter operated by Hultgren has non linearity in k of a type that could be explained by the small internal dimensions of the metal block environment, as compared to those of the crucible. This introduces a reflective factor into the heat transfer equation.

A similar effect is observed in the calorimeter of Pratt and Morris which is of a similar design to that used by Hultgren.

Errors in Kleppa's calorimeter have been described in full in the section on previous work, but appear to stem

mainly from non isothermal conditions and temperature measurements outside the crucible rather than inside it.

Metal block calorimeters (so far constructed) are noticeably irrational in their heat transfer characteristic with the surroundings. The non-linearity in k must be allowed for in calculations of heat losses experienced in a system. This necessarily introduces errors where the heat transfer coefficient is related to temperature in a complex way.

The calorimeter developed by Bever falls into the same classification as the calorimeter described in this work, namely, a liquid metal solution calorimeter with a fluid environment.

The diagram of this equipment (Diagram 25) can be compared to that of Bever (Diagram 1) and the similarities will be apparent. The most obvious difference between the two is size. The size of the crucible-vacuum chamber in the Bever calorimeter is about 3" across by 4" deep.

The size of the crucible in this equipment is 2" across by 3" deep, but the vacuum system container is some 10" across and 12" deep. It is ^{due to} this fact, coupled with the relatively few heat conduction paths in this calorimeter, that equation (5) holds without modification in the post solution period.

A comparison of the two calorimeters is tabulated below:

Table 15

Property	Bever Calorimeter	This Calorimeter
Salt melt constitution	KNO_3 , NaNO_3 , LiNO_3 eutectic stable up to 450°C	KNO_3 , NaNO_3 eutectic stable up to 500°C
Power required to maintain 300°C	app 400 W	app. 1650 W
Thermal stability	$\pm 0.002^\circ\text{C}$	$\pm 0.001^\circ\text{C}$
Ultimate vacuum	app. 5×10^{-5} mm Hg	10^{-5} mm Hg
Calibration material	Sn (W used until 1954)	Sn and W
Precision of temperature measurement	$\pm 0.002^\circ\text{C}$	0.001°C
Response time of thermocouple galvanometer to temperature changes	app. 2 secs.	1 sec
k value at 250°C	app. 0.003 sec^{-1}	app. 0.0004 sec^{-1}
k lines	non linear in initial section	linear over the measurable range
Cp value	app. 40 cal	app. 50 cal
Final accuracies	between $\pm 0.2\%$ and $\pm 2\%$ depending on reaction time and 'sign' of reaction	$\pm 0.25\%$

III. Comparison of heats of solution of gold in tin

Below are tabulated heats of solution of gold in tin found by various workers over a range of temperature.

Table 16.

Temperature	ΔH cal mole ⁻¹	Worker	ref. no.
450	-5038	Kleppa	45
427	-5173	Hultgren	21
425	-5193	Oriani	46
418	-5197	Oriani	47
350	-5350	Kleppa	45
300	-5610	Bever	48
270	-5721	Kleppa	45
244	-5928	Hultgren	49
242	-5890	Kleppa	45
240	-5980	Bever	48
247	-5860	This investigation	
299	-5510	This investigation	
350	-5400	This investigation	

These values are plotted in
diagram 21

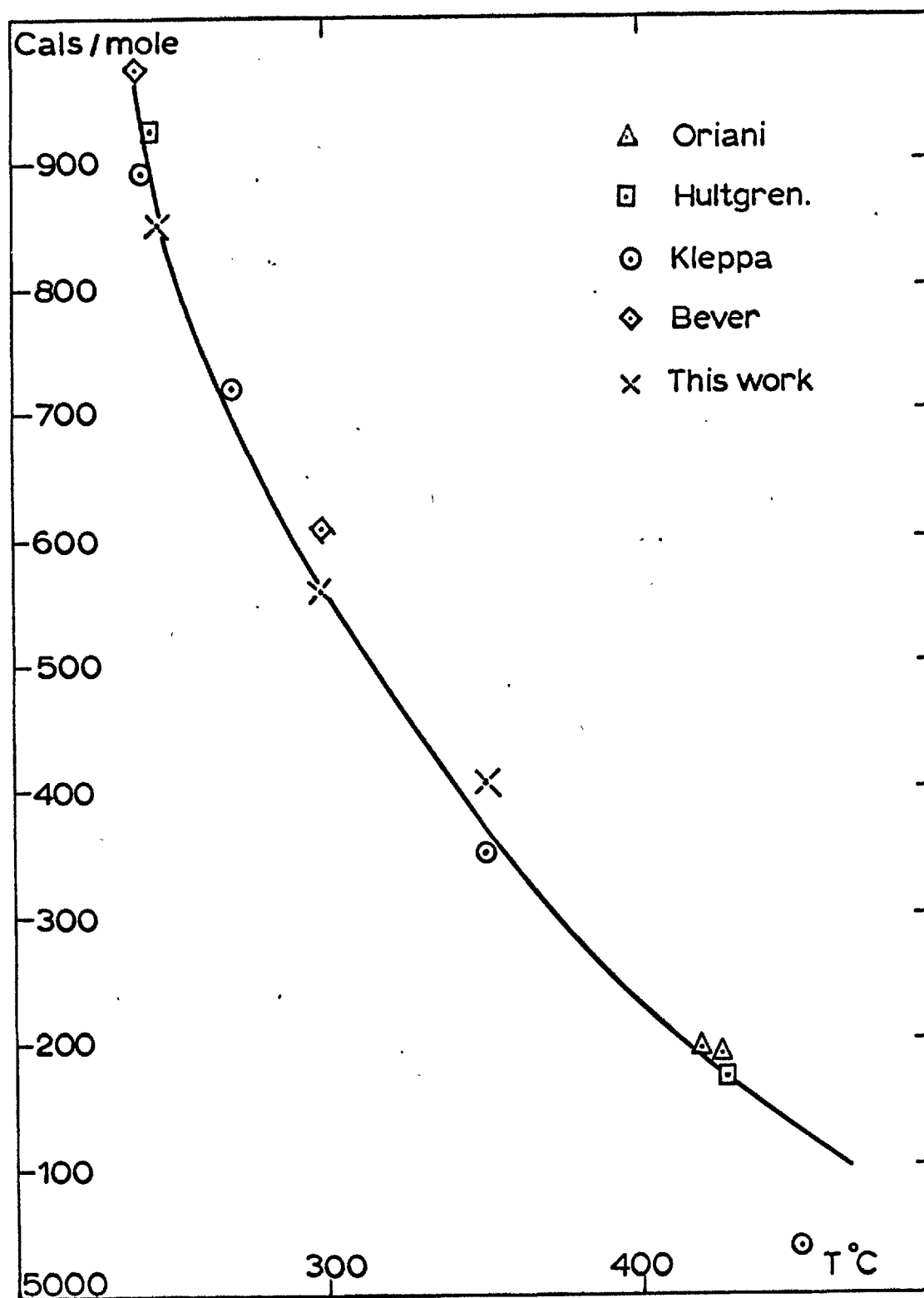


DIAGRAM 21. PARTIAL HEATS OF SOLUTION OF GOLD IN TIN AS A FUNCTION OF TEMPERATURE.

IV. Application of the quasi-chemical theory to partial heats of solution of gold and silver in bismuth-tin alloys.

As the number of components in a solution increase, it becomes increasingly more difficult to theoretically describe its properties. It has been said that the application of a regular solution model to a ternary alloy system will only achieve some success if the three elements are in the same periodic group (ref 50). For a ternary alloy A,B,C, the regular solution model will be

$$\Delta G_{ABC}^E = ax_Ax_B + bx_Bx_C + cx_Cx_A$$

where $x_A + x_B + x_C = 1$.

and a, b, c are constants depending on the system.

A method which has been applied to the ternary solution in which one element is present as a dilute species has been discussed in the section on previous work. This method of describing ternary solutions has been applied by Alcock and Richardson to systems in which the dilute species is a non metal. This favours the formation of compounds which would account for the low value of z necessary to make the experimental data and theory similar.

(For the present investigation, however, three metals are used in the ternary solution and provide the correct conditions required by the quasi-chemical theory in the form given in the introduction; namely that the two elements present in excess are chosen so that:-

$$\overline{\Delta H}_{X(X+Y)} = \overline{\Delta H}_{Y(X+Y)} = 0$$

and that the dilute species will not alter their coordination numbers appreciably.

For clarity the relevant equations used for calculation of $\overline{\Delta H}_{S(X+Y)}$ are repeated below:-

$$W = \overline{\Delta H}_{S(X)} - \overline{\Delta H}_{S(Y)} \text{-----(13)}$$

$$N_X^{\circ} = \frac{N_X}{N_X + KN_Y} ; N_Y^{\circ} = \frac{KN_Y}{N_X + KN_Y} \text{-----(14)}$$

where $K = \exp(W/zRT)$

and

$$\overline{\Delta H}_{S(X+Y)} = N_X^{\circ} \overline{\Delta H}_{S(X)} + N_Y^{\circ} \overline{\Delta H}_{S(Y)} \text{-----(15)}$$

The values obtained experimentally for $\overline{\Delta H}_{S(X+Y)}$ for various compositions of X and Y (bismuth and tin) are listed in tables 7 to 12 and the diagram 18 shows values of $\overline{\Delta H}_{S(X+Y)}$ as $S \rightarrow 0$ plotted against mole fraction of X. It remains to consider how well the quasi-chemical theory fits the experimental data.

From the tables 7 to 12 it can be seen that in each of the runs three or four gold additions were made, the final addition at the end of a run being silver. For this reason not too much reliance can be placed on the silver additions. To check the silver additions one run (20) was made adding pure silver only to bismuth. This

run is represented on diagram 18 by a dot with a triangle round it. It is interesting to note that the value obtained for the partial heat of solution of silver in bismuth is some 220 calories higher than that observed in bismuth containing 0.00858 mole fraction of gold. For this reason it is quite likely that 'smoothed' values for the partial heat of solution at infinite dilution (shown in brackets in table 12) are higher than those observed. Further, there is a large contribution to the partial heat of solution at infinite dilution due to the contribution of $\frac{d\bar{\Delta H}}{dx_{Ag}}$, which amounts to about 25,000 calories in pure bismuth (see diagram 17). The corresponding value of $\frac{d\bar{\Delta H}}{dx_{Ag}}$ in pure tin is much less, about 5000 cal (ref 46).

The values in table 12, shown in brackets, are 'smoothed' first for the effect of $\frac{d\bar{\Delta H}}{dx}$, considering only the silver in solution, and secondly for the apparently larger effect of the gold. These 'smoothed' values are marked on diagram 18.

From table I, showing coordination numbers of tin and bismuth as obtained by X-ray diffraction studies, a value of z_{Sn} between 8 and 11 appears acceptable and for bismuth, z_{Bi} would be between 6 and 8. For the purposes of the simple quasi-chemical theory a uniform value of z should be taken over the whole composition range. If there

is evidence for a change in z this will show up in the curve obtained experimentally when compared to a calculated curve. To show how changes in z affect the position of the curve for $\bar{\Delta H}_{\text{Au(Bi+Sn)}}$ values of $z = 1, 6, 10$ have been considered. The calculations for $\bar{\Delta H}_{\text{Au(Bi+Sn)}}$ are shown below in table 17 and the results are plotted on diagram 22 together with the experimentally observed values.

Values for $\bar{\Delta H}_{\text{Ag(Bi+Sn)}}$ have also been calculated; but since W is small deviations in z make only small changes in ΔH .

$$T = 623^\circ\text{K} ; \quad W = -9110 \text{ cal.}$$

if : $z = 1$	6	10
then: $K = 6.6 \times 10^{-4}$	2.9×10^{-1}	4.8×10^{-1}

Table 17

z	N_X	0	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	1(pure tin)
1		0.000	1.000	1.000	1.000	1.000
6	N_X°	0.000	0.530	0.772	0.910	1.000
10		0.000	0.410	0.674	0.861	1.000
1		1.000	0.000	0.000	0.000	0.000
6	N_Y°	1.000	0.470	0.228	0.090	0.000
10		1.000	0.590	0.326	0.139	0.000
1		3710	-5400	-5400	-5400	-5400
6	$\bar{\Delta H}_{\text{Au(Sn+Bi)}}$	3710	-1115	-3315	-4590	-5400
10		3710	-30	-2430	-4135	-5400

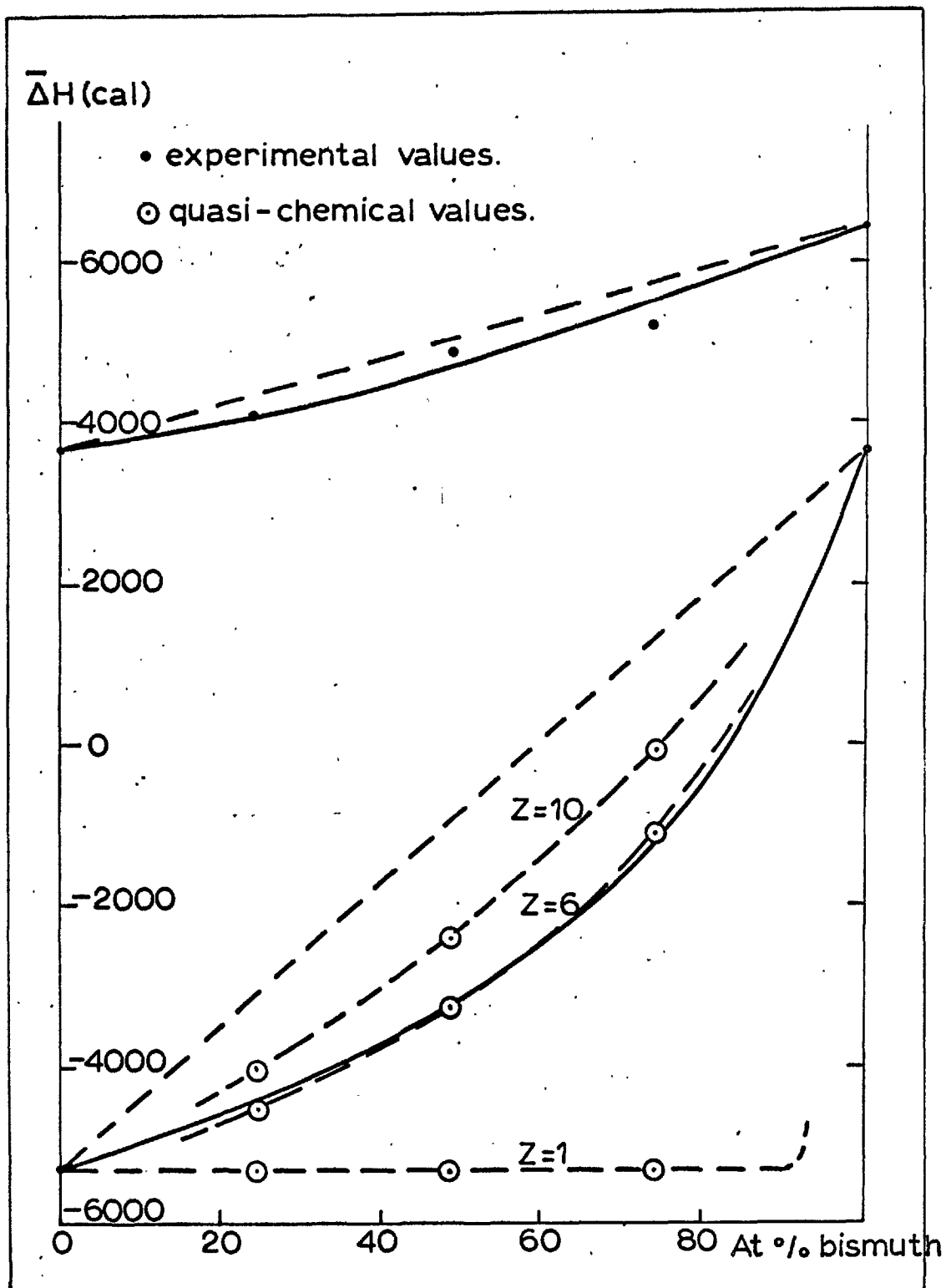


DIAGRAM 22. PARTIAL MOLAR HEATS OF SOLUTION OF GOLD AND SILVER IN TIN-BISMUTH ALLOYS COMPARED TO THE QUASI-CHEMICAL THEORY.

It is evident from the graphs that $z = 6$ gives the closest fit. There is a slight drift in the value of z , in the direction expected, namely it would be a better fit if z were slightly larger at the tin end and smaller at the bismuth end. To show in detail how z affects the final value of $\overline{\Delta H}_{\text{Au}(\text{Sn+Bi})}$ a graph of z against $\overline{\Delta H}_{\text{Au}(\text{Sn+Bi})}$ for different compositions of the tin-bismuth alloy has been drawn (diagram 23). This diagram clearly shows that this data will resolve two coordination numbers.

The value $z = 6$ is low as compared to that expected from X-ray diffraction data, but as the X-ray data shows a considerable scatter the discrepancy is not unreasonable.

The following table shows more clearly the similarity between the results predicted by the quasi-chemical theory and the observed values for $z = 6$

Table 18

Atomic % Sn, N_X	0	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	1
$\overline{\Delta H}_{\text{Au}(\text{Sn+Bi})}(\text{q.c})$	(3710)	-1115	-3315	-4590	(-5400)
$\overline{\Delta H}_{\text{Au}(\text{Sn+Bi})}(\text{obs})$	3710	-1285	-3325	-4470	-5400

Further, it can be clearly seen from the diagrams 22 and 23 that the 'drift' across the observed curve for $z = 6$ could be accounted for by a change in coordination number across

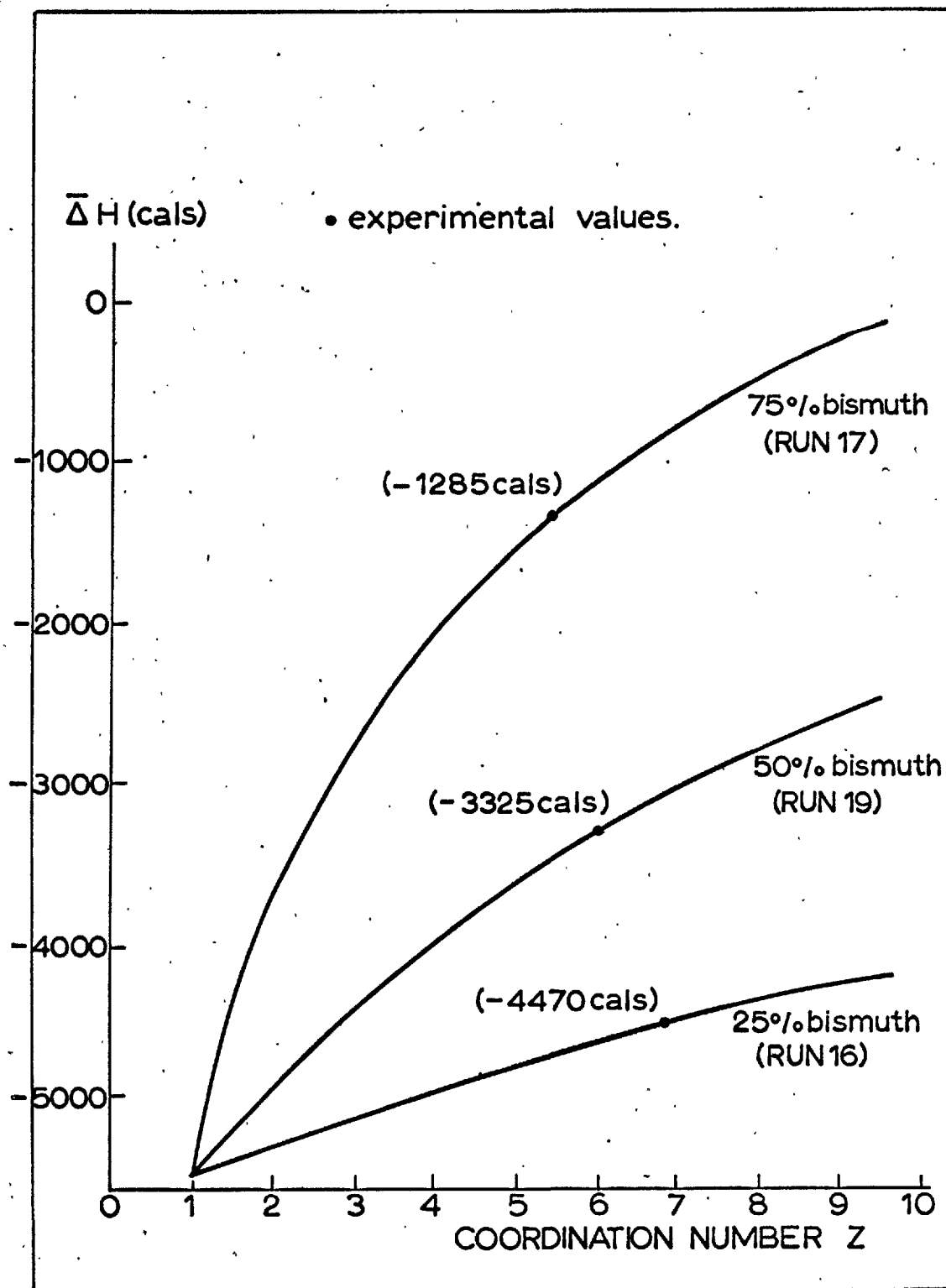


DIAGRAM 23. VALUES OF PARTIAL HEATS OF SOLUTION OF GOLD IN TIN-BISMUTH ALLOYS FOR DIFFERENT VALUES OF Z , AT THREE ALLOY COMPOSITIONS AS PREDICTED BY THE QUASI-CHEMICAL THEORY.

the system favouring a higher coordination number for tin than bismuth; this being in agreement with X-ray diffraction measurements.

A possible explanation of the higher value of z obtained at the tin end of the system might lie in the different sizes of the tin, bismuth and gold atoms. Their atomic radii are 1.86×10^{-8} , 2.03×10^{-8} , and 1.59×10^{-8} cms respectively. Since gold is the dilute species and has the smallest atomic volume it is very likely that more tin could coordinate with the gold than bismuth.

Although it is also not immediately apparent from diagram 23, the variation of z with composition through the system is linear. This indicates that the tin-bismuth system is ideal, further, extrapolating this variation of z to the pure tin end indicates that the coordination number of tin approaches 8.

Summary

1. The design of the calorimeter has realised a machine which provides precise temperature control and measurement; and provides environmental conditions to the calorimetric cell which give rise to a rational form of heat transfer.

The specifications of the system are as follows:

1. The temperature control system regulates the furnace temperature to $\pm 0.001^{\circ}\text{C}$ for periods of several hours.
2. The precision of the temperature measurement is 0.001°C .
3. The value of the heat transfer coefficient, k , is known precisely for a particular addition but there are apparent variations within a run. For a whole run the variation in k is $\pm 2\%$.
4. The uncertainty in k results in the largest uncertainty in C_p , $\pm 1\%$. Since the addition of three more radiation shields (ref 43) the overall uncertainty in C_p has been reduced to $\pm \frac{1}{4}\%$.
5. The reproduceability of heats of solution are directly related to the error in C_p , hence reproduceability in ΔH is $\pm \frac{1}{4}\%$ for the most recent data.

The most important improvement achieved with this instrument is the linearity of the 'k' lines. In all other calorimeters, known to the author, a correction is required to eliminate non linearity in k. The great sensitivity of the temperature measurement combined with rapid response enable small effects to be observed.

II. The heats of solution of gold, silver, and copper have been measured and shown to agree with the best available data, but with a smaller scatter establishing the accuracy as well as the precision of the equipment.

The equipment has been used to determine precisely $\bar{\Delta H}_{\text{Au}(\text{Sn+Bi})}$ and has used these values to test the quasi-chemical theory of ternary solutions as derived by Alcock and Richardson. From this theory results show that the coordination number z of tin surrounding gold is about 7 and that of bismuth surrounding gold about 5. At the 50/50% mixture of bismuth-tin the value 6 has been calculated.

Preliminary measurements of $\bar{\Delta H}_{\text{Ag}(\text{Sn+Bi})}$ indicate that a similar picture may be obtained as that of gold, but precise values of z cannot be given at this time, as the data so far obtained is insufficiently precise to resolve z . This uncertainty in z arises in part out of the small value of W (-2550 calories), compared with that for gold (-9110 calories), hence deviations in z for silver will make only small changes in $\bar{\Delta H}_{\text{Ag}(\text{Sn+Bi})}$.

Suggestions for Further Work

I. There are some minor modifications to the equipment which would increase its scope. In the original design, room was left in the 'neck' of the vacuum system (diagram 9) to insert an addition device which could add specimens at various temperatures up to that of the calorimeter. This would remove the inherent error in integrated heat capacities. A sample dispenser unit would prove helpful as it would eliminate disturbances to the vacuum system several times during a run.

Economy of calculation has been suggested in appendix IV, which is a direct result of linear k lines.

Unfortunately, automatic recorders of the precision and speed required to measure temperature changes are expensive, but with an appropriate machine the production of data could almost be doubled.

It would certainly prove interesting to measure the temperature changes accompanying a reaction in parts of the system other than in the crucible. Values on the outside of the crucible wall would be most useful in gaining understanding of the mixing rate of a sample.

II. The calorimeter has been designed to operate up to 500°C and as such only one half of its range has been used. At the higher temperatures systems such as tin-gold, copper-nickel can be investigated nearly across their whole alloy composition. This work is now under investigation (ref 43).

Finally, it would be invaluable to have further thermodynamic data for ternary alloy systems for application to the quasi-chemical theory.

The theory, as applied in this thesis, predicts the variation of z across a binary liquid alloy system (Sn - Bi), and values obtained for the pure components are in fair agreement with those obtained by the X-ray diffraction technique.

Precise data for $\overline{\Delta H}_{\text{Ag}}(\text{Sn Bi})$ and $\overline{\Delta H}_{\text{Cu}}(\text{Sn Bi})$ at 350°C would give corroboration to the data so far obtained, further the temperature dependence of z could be studied by this method.

Other ternary systems can also be used e.g. (Ag - Au)Sn to predict coordination numbers. With sufficient data it would not be necessary to restrict the ternary system chosen to an ideal binary plus soluble solute, and the assumption:

$$\overline{\Delta H}_{\text{X}(\text{X+Y})} = \overline{\Delta H}_{\text{Y}(\text{X+Y})} = 0$$

could be avoided.

Appendix IDefinition of Symbols

E	Emissivity of calorimeter
A	Absorptivity of calorimeter
T_2	Temperature of environment
σ	Stefans constant
q	Rate of heat loss from the calorimeter
T_1	Temperature of the calorimeter
ΔT	$T_1 - T_2$
C_p	Energy equivalent of the calorimeter
S	Surface area of the calorimeter
J	Mechanical equivalent of heat
k	Radiation heat transfer coefficient
C	Conductive and convective heat transfer coefficient.
$\Delta T_{(obs.)}$	Observed temperature difference $T_1 - T_2$ at any time t.
$\Delta T_{(corr.)}$	Adiabatic equivalent temperature difference
C_s	Heat capacity of sample/grm.
n	No. of grm. moles of sample
ΔH	Heat of solution
K	σE

Appendix II

$$\Delta T = T - T_1 = 480^\circ\text{F}$$

Thermal conductivity of the brick

$$k_b = 0.12 \text{ B.T.U./hr/ft}^2/\text{ft}/^\circ\text{F}$$

The rates of heat lost in the directions indicated in diagram 24 are:

$$Q_1 = \frac{2 \pi l k_b \Delta T}{\log r_2/r_1} \text{ ----- (18)}$$

$$= \frac{2 \pi 3. 0.12. 480}{0.2} \text{ B.T.U./hr}$$

$$Q_2 = \frac{k_b A \Delta T}{x} = \frac{0.12 \pi 2^2 480}{(2/3)} \text{ B.T.U./hr ----- (19)}$$

$$Q_3 = \frac{0.12 \pi 1^2 480}{(1/3)} \text{ B.T.U./hr}$$

$$Q_1 + Q_2 + Q_3 = Q = 0.12. 480. 36. \text{ B.T.U./hr}$$

$$1 \text{ Watt} = 3.41 \text{ B.T.U./hr.}$$

$$\text{hence } Q = 2\text{KW} \pm 20\%.$$

In fact, at this temperature 1.6KW is sufficient. Losses overestimated.

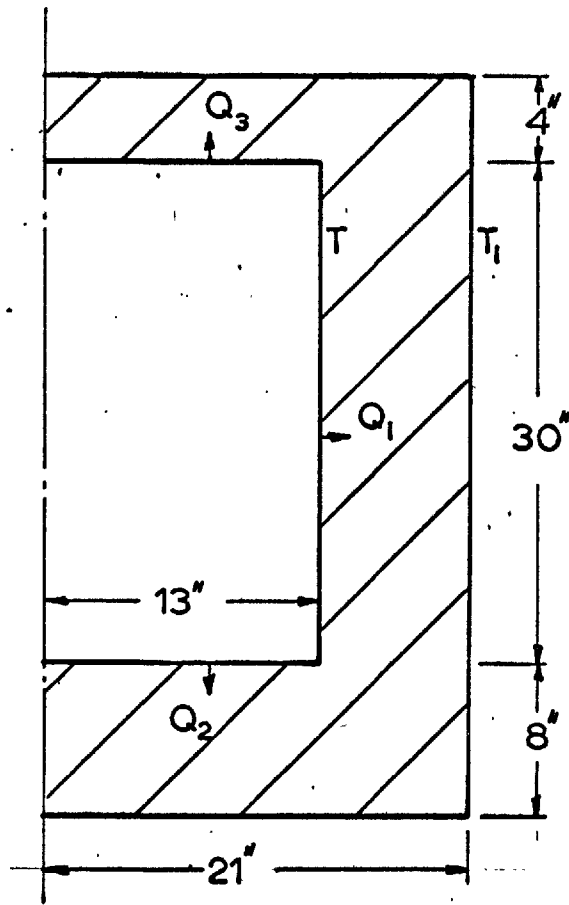


DIAGRAM 24. FURNACE LOSSES.

Appendix III

Sensitivity of the Wheatstone bridge network

The current through the galvanometer, I_g , of a Wheatstone bridge can be shown to be

$$I_g = \frac{V(PS - QR)}{(Q+P)(R+S)G + PQ(R+S) + RS(P+Q)} \text{ -----(20)}$$

where

PSQ are the bridge arm resistances

R is the resistance of the thermometer

and V is the driving cell voltage

At balance when there is no bridge current through the galvanometer $I_g = 0$

and $PS = QR$ -----(21)

the familiar relationship.

The components as used under experimental conditions have the following values:

$V = 6$ volts

$P = R = 200\Omega$

$Q = S = 2000\Omega$

$G = 500\Omega$; sensitivity = $1500 \text{ mm}/\mu\text{A}$. at 1 metre.

If the furnace temperature drifts 0.001°C then R changes by 0.00036 (as $\frac{dR}{dt}_{pt} = 0.36 / ^\circ\text{C}$) to 200.00036 ; this

results in a change in I_g of

$$\begin{aligned}\Delta I_g &= \frac{6(200 \times 2000 - 200.00036 \times 2000)}{(2200 \times 2200 \times 500) + (2 \times 200 \times 2000 \times 2200)} \quad \text{amps} \\ &= \frac{6 \times 0.00036 \times 2000}{418 \times 10^7} \quad \text{amp} \quad \text{from equation (20)}\end{aligned}$$

$$\text{i.e., } \Delta I_g = 1.032 \times 10^{-9} \text{ amps.}$$

Since the galvanometer is placed at 150 cms from the sensing element, the effective displacement of the galvanometer image is

$$\frac{3}{2} \times 1.032 \times \frac{10^{-9}}{10^{-6}} \times 1500 \text{ mm}/0.001^\circ\text{C}$$

$$= 2.25 \text{ mm}/0.001^\circ\text{C}$$

Hence for control to be effective to $\pm 0.001^\circ\text{C}$ the photo-cell has to be sensitive to displacements of a band of light shifting 4.5 mm. This is sufficient as is shown by experimental observations on the control system.

Appendix IV

To evaluate the area under an exponential curve, a numerical integration is adopted. Where a calibration addition is made and the area that is required is extended appreciably after solution is complete, the following method is convenient.

$$\text{Since } \frac{d\Delta T}{dt} = -k\Delta T$$

$$[\log \Delta T]_{\Delta T_1}^{\Delta T} = [-kt]_{t_1}^t$$

where t_1 is the time that the first experimental point falls on the k line.

$$\therefore \frac{\Delta T}{\Delta T_1} = e^{-k(t-t_1)}$$

The area under the curve is given by $\int_{t_1}^t \Delta T dt$

$$\therefore \int_{t_1}^t \Delta T dt = \Delta T_1 \int_{t_1}^t e^{-k(t-t_1)} dt$$

$$= \frac{\Delta T_1}{-k} [e^{-k(t-t_1)}]_{t_1}^t$$

$$= \frac{\Delta T_1}{-k} [e^{-(t-t_1)k} - e^0]$$

$$\int_{t_1}^t \Delta T dt = \frac{\Delta T_1}{k} [1 - e^{-(t-t_1)k}]$$

$$\text{but } e^{-k(t-t_1)} = \frac{\Delta T}{\Delta T_1}$$

$$\therefore \int_{t_1}^t \Delta T dt = \frac{1}{k} [\Delta T_1 - \Delta T] \text{ -----(22)}$$

Corollary

$$\text{Since } \Delta T_{\text{corr}} = \Delta T_{\text{ob}} + k \int_0^{t_{\text{ob}}} \Delta T dt \text{ -----(7)}$$

from (13)

$$\Delta T_{\text{corr}} = \Delta T_{\text{ob}} + k \int_0^{t_1} \Delta T dt + k \int_{t_1}^{t_{\text{ob}}} \Delta T dt$$

$$\Delta T_{\text{corr}} = \Delta T_{\text{ob}} + \Delta T_{t_1} - \Delta T_{\text{ob}} + k \int_0^{t_1} \Delta T dt$$

$$\Delta T_{\text{corr}} = \Delta T_{t_1} + k \int_0^{t_1} \Delta T dt \text{ -----(23)}$$

Equation 23 is the most economical

to evaluate numerically, however, t_1 is somewhat difficult to estimate; hence to reduce errors equation (7) is used and the integrated area between $t_1 + dt$ and t_{ob} is evaluated

using equation (22).

As an example consider Run 5 - 1 :-

$$\begin{aligned} \Delta\mu V \text{ at } 500 \text{ seconds} &= 41.14\mu V \\ \Delta\mu V \text{ at } 75 \text{ seconds} &= 48.50\mu V \end{aligned} \quad k \int_{75}^{500} \Delta T dt = 7.36\mu V \text{ from (22)}$$

$$k \int_0^{75} \Delta T dt = 1.28\mu V \text{ numerically}$$

$$\Delta T_{\text{corr}} = 41.14 + 7.36 + 1.28$$

$$\Delta T_{\text{corr}} = 49.78\mu V$$

$$\text{and numerically } \Delta T_{\text{corr}} = 49.765\mu V$$

a difference of 0.03%

Appendix V

$$\dot{q}_r = - \frac{dH}{dt} = \sigma E(T_1^4 - T_2^4)$$

$$- \frac{dT_1}{dt} = K(T_1^4 - T_2^4)$$

where $k = 4T_2^3 K$

Separating the variables and integrating:

$$\int \frac{dT_1}{T_1^4 - T_2^4} = -Kt + \text{constant}$$

$$\int \frac{dT_1}{2T_2} \left(\frac{1}{T_1^2 - T_2^2} - \frac{1}{T_1^2 + T_2^2} \right) = -Kt + \text{constant}$$

$$a) \quad \frac{1}{4T_2} \log \frac{T_1 - T_2}{T_1 + T_2} - \frac{1}{2T_2} \tan^{-1} \frac{T_1}{T_2} = -Kt + \text{constant}$$

$$\text{i.e. } \log (T_1 - T_2) - \log (T_1 + T_2) + 2 \tan^{-1} \frac{T_1}{T_2}$$

$$= -kt + \text{constant} \text{-----} (24)$$

compare equation (5): $\log(T_1 - T_2) = -kt + \text{constant}$

b) For the purposes of calculation it is better to integrate as follows:

$$- \frac{1}{2T_2} \tanh^{-1} \frac{T_1}{T_2} - \frac{1}{2T_2} \tan^{-1} \frac{T_1}{T_2} = -Kt + \text{constant}$$

i.e.

$$-2 \tanh^{-1} \frac{T_1}{T_2} - 2 \tan^{-1} \frac{T_1}{T_2} = -kt + \text{constant} \quad \text{----(17)}$$

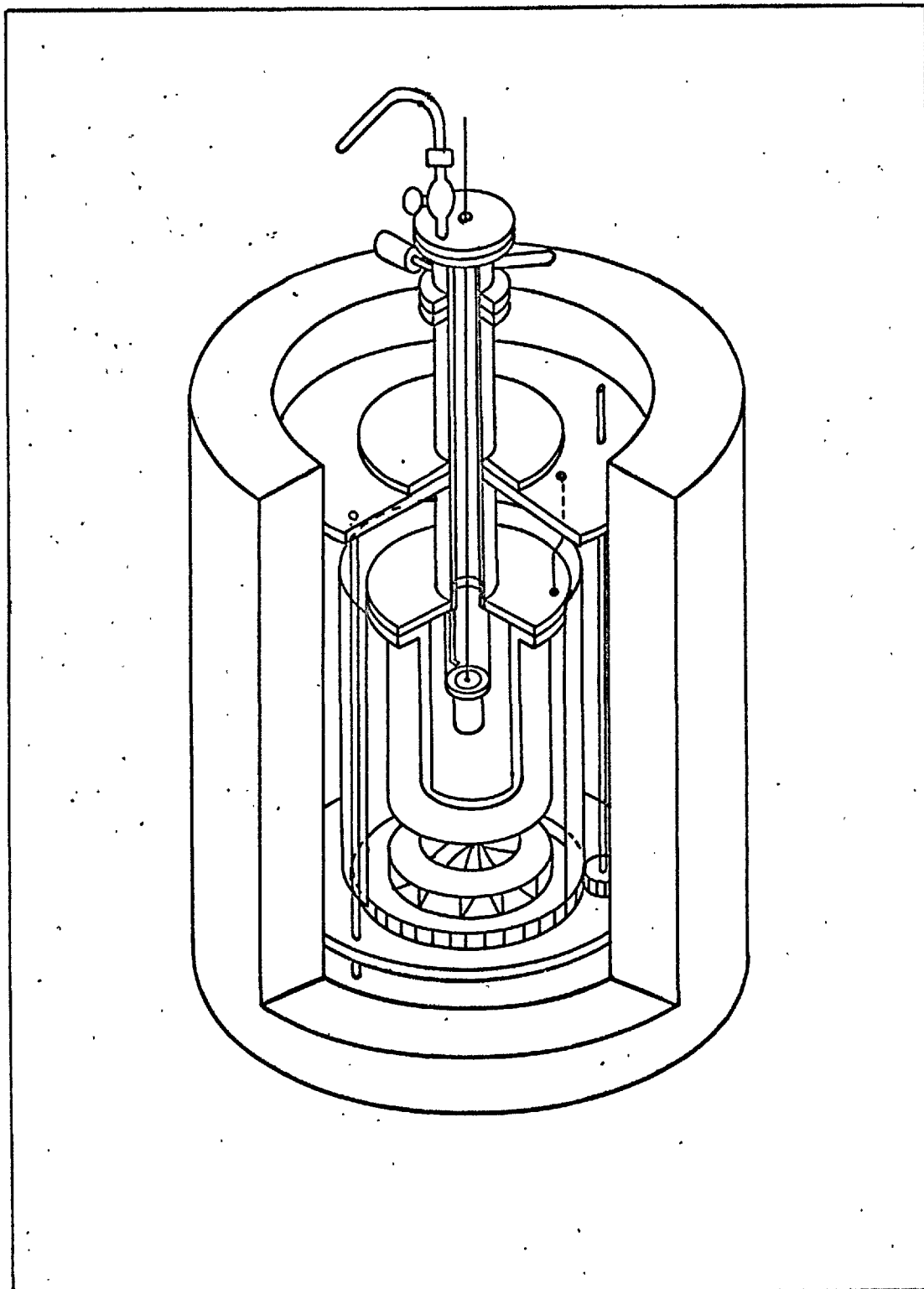


DIAGRAM 25. THE CALORIMETER ASSEMBLY.

Appendix VII

Heats of solution of gold in tin-bismuth alloys at infinite dilution have been recently obtained by Bever. His values are:

Composition of bath	Temperature of bath	Heat of soltn at infinite dilution (cals/g.atom)	No. of runs
66.25%Bi 33.75%Sn	350°C	-1951 $\pm$ 50	13
65% Bi 35% Sn	350°C	-2055 $\pm$ 30	4
80% Bi 20% Sn	350°C	-696	1
80% Bi 20% Sn	390°C	-497	1

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