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APPLICATION OF THE HIGH TEMPERATURE CALORIMETER TO THE DETERMINATION OF THE HEATS OF FORMATION OF Na-Sn AND Li-Sn ALLOYS

by

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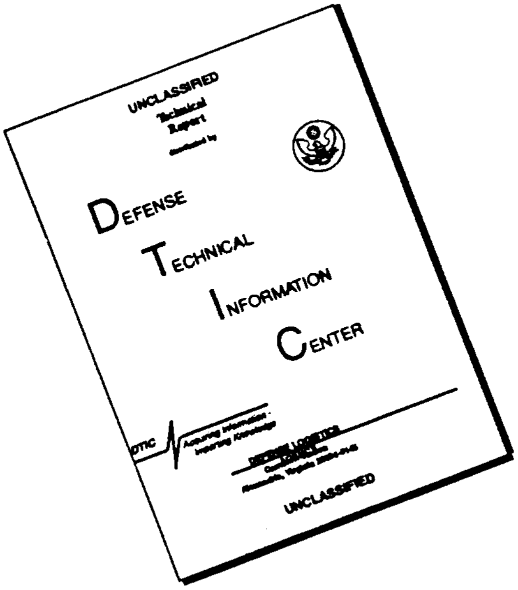
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APPLICATION OF THE HIGH TEMPERATURE CALORIMETER TO THE DETERMINATION OF THE HEATS OF FORMATION OF Na-Sn AND Li-Sn ALLOYS

By George R. Barber, Leo Brewer, LeRoy A. Bromley, and Raleigh L. McKisson

ABSTRACT

A method has been devised for using the high frequency induction coil as a high temperature calorimeter. The method enables one to determine the heat effects produced at high temperatures. The method has been applied to the determination of the heats of formation of the alloys Na-Sn and Li-Sn. The average heat of formation (ΔH) determined for Na-Sn is -9.63 ± 0.40 kilocalories per mole at 873° K. This value becomes -10.6 ± 0.6 kilocalories per mole when extrapolated to 298°K. The average heat of formation (ΔH) determined for Li-Sn is -17.57 ± 0.83 kilocalories per mole at 850°K. This value becomes -18.62 ± 1.50 kilocalories per mole when extrapolated to 298°K. These results are compared with the results of other investigators.

PART I

INTRODUCTION TO THE WORK ON Na-Sn

The high frequency induction coil was first used as a calorimeter by Chipman and Grant.[1] Their equipment consisted of a large silica crucible containing the charge, which was heated in an induction coil. The cover of the crucible was provided with a small hole so that additions and sampling could be readily performed. An inert atmosphere was maintained by bleeding argon into the cavity and letting it sweep out the hole. Iron was placed in the crucible and heated to the desired temperature, then weighed samples of silicon and iron were dropped into the melt. The iron was used to estimate the heat capacity. The heat effect was calculated from the heat capacity and the temperature difference.

The system that Chipman and Grant selected was an excellent choice, as the temperatures involved were quite high, and considerable electromagnetic stirring was present. This stirring made for rapid approach to thermal equilibrium. The large melt with its heat capacity prevented a great temperature rise, since a relatively small sample was added.* Thus the temperature remained in a small range, and the heat losses could be considered quite constant during a run. The corrections for heat transfer were quite small, and even though they could not be calculated with great accuracy, the effect on the result was small.

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*The melts consisted of from 65 to 90 pounds of molten iron, into which one pound or less of silicon was dropped per addition.

The apparatus used in the present research is similar to that of Chipman and Grant in that high frequency induction heating is used. However the melts are much smaller,* consequently the temperature rises are greater, and heat losses cannot be considered constant.

The primary purpose of this research was to devise a method of analysis of the temperature-time curves obtained from the apparatus. The secondary purpose of this research was to measure the heat of formation of Na-Sn. The measurement was to be performed by adding weighed sodium pellets to a molten tin melt, obtaining a temperature-time curve, and analyzing this curve by the method devised.

This heat of formation has been measured by several investigators. Biltz and Holverscheit[2] in 1924 reported the heat of formation of Na-Sn to be eleven kilocalories per mole. This result was obtained by a differential solution method, using ferric chloride in about 6N hydrochloric acid as the solvent. In 1928, Biltz and Meyer[3] offered recalculated values of the heat of formation, using what they considered to be a better heat value for one of the intermediate reactions, and quoted a value of sixteen kilocalories per mole. Biltz[4] again gives this value in 1937.

Kubaschewski,[5] and Kubaschewski and Seith,[6] report twelve kilocalories per mole for this reaction. Their measurement was direct, the alkali metal being melted and poured into the molten tin in an argon atmosphere, and the mixture being quickly placed in a large copper-block calorimeter. They calculated their result from the temperature rise of the calorimeter and its heat capacity.

Many investigators have measured heats of formation of various intermetallic compounds, and others have derived useful facts from theoretical considerations. A few references to work of this type are listed in the bibliography, items 10 to 24.

DESCRIPTION OF APPARATUS AND OPERATING PROCEDURE

The apparatus consists of a 20 kilowatt spark-gap converter† and a calorimeter which is surrounded by one of four inductance coils (the heating coil). The other three coils are used to adjust the power dissipated in the heating coil.

The calorimeter (see Figure 1) consists of a cylindrical pyrex tube which is surrounded by a water jacket; a water cooled copper base which supports the zircon stand upon which the crucible rests; and a "head" which supports the various devices which pass through packing glands into the interior. These devices are the thermocouples, the dispenser, the dispenser-cooler, the operating rod, and the flexible drive for the stirrer. Two thermocouples are used; one, sheathed in a molybdenum tube, dips into the melt; the other passes through a copper well to a position near the bottom of the dispenser.

The dispenser (see Figure 2) was designed to be an air-tight compartmented container which could be loaded in a dry-box and transferred to the calorimeter, thus preventing, to a great extent, any contact of the sodium with oxygen or water vapor. The division of the dispenser into four compartments is effected by three pivoted plates which extend across the opening and are held in position by cams on the thermocouple well. These cams are arranged so that rotating the thermocouple well in increments of 90° causes a section to dump its contents onto the trap door forming the bottom of the dispenser. This trap door, which is shielded from the radiation of the hot melt by three molybdenum plates attached to the bottom, is actuated by a rod passing through the dispenser cavity. The rod then passes through a packing gland in the top, and ends in an eye. Between the top of the dispenser and the rod-eye, there is a spring under tension which keeps the trap door closed tightly. When it is desired to open the door, the operating rod, whose end is hooked, can be inserted in the eye and a downward pressure applied.

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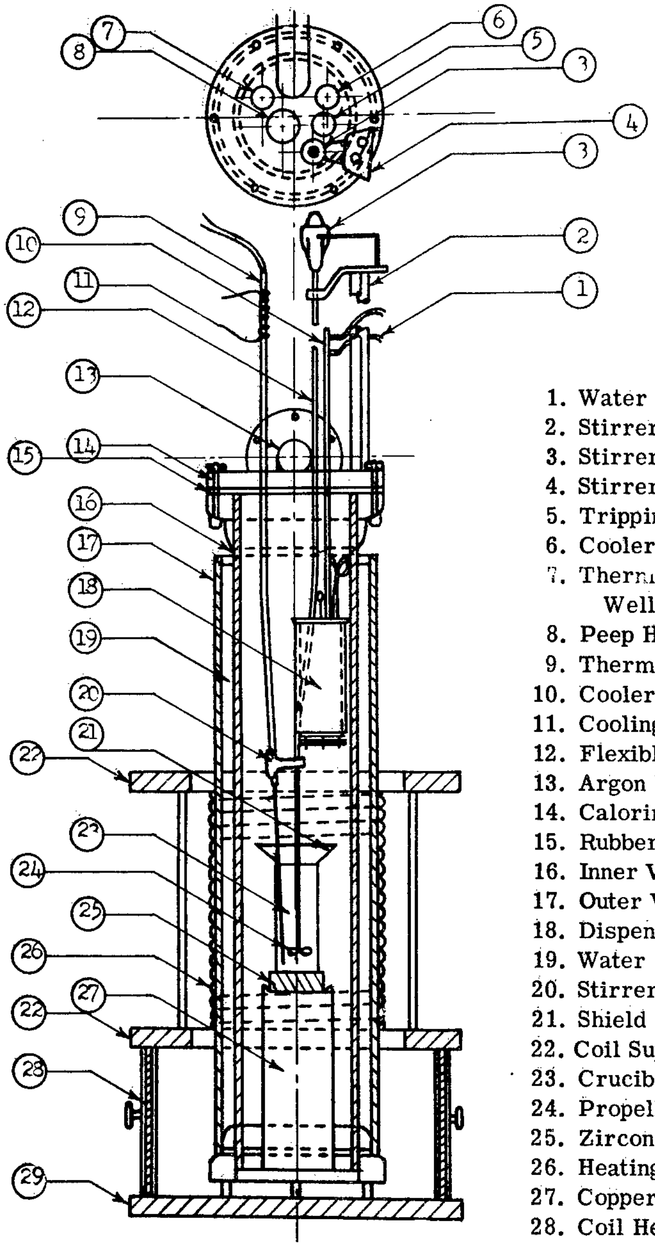
*The melts in this research were about 100 grams of Sn, to which from 4 to 10 grams of Na were added per addition.

†Ajax 20 kw. Converter, Ajax Electrothermic Corporation, Trenton, New Jersey.



1. Water Inlet
2. Stirrer Support
3. Stirrer Motor
4. Stirrer Bracket
5. Tripping Devise
6. Cooler Inlet
7. Thermocouple Well Inlet
8. Peep Hole
9. Thermocouple
10. Cooler Support
11. Cooling Coil
12. Flexible Shaft
13. Argon Inlet
14. Calorimeter Head
15. Rubber Gasket
16. Inner Vessel
17. Outer Vessel
18. Dispenser
19. Water Jacket
20. Stirrer Guide
21. Shield
22. Coil Support
23. Crucible
24. Propeller
25. Zircon Stand
26. Heating Coil
27. Copper Block
28. Coil Height Adjuster
29. Base

Figure 1. Calorimeter

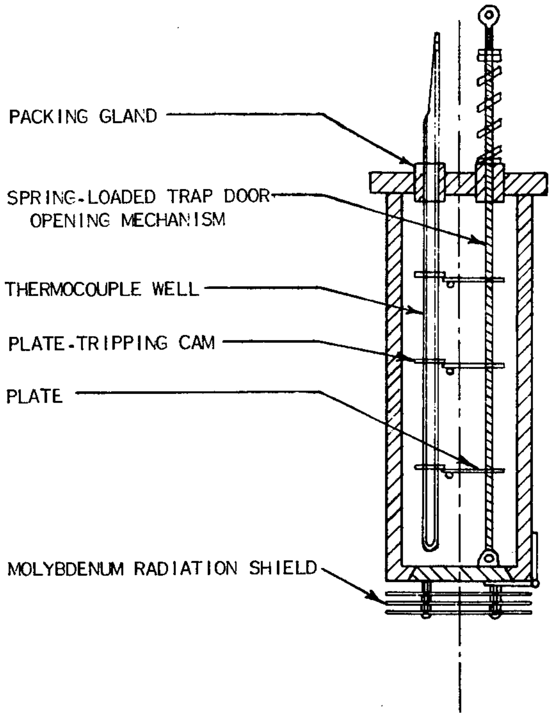


Figure 2. Air-tight dispenser

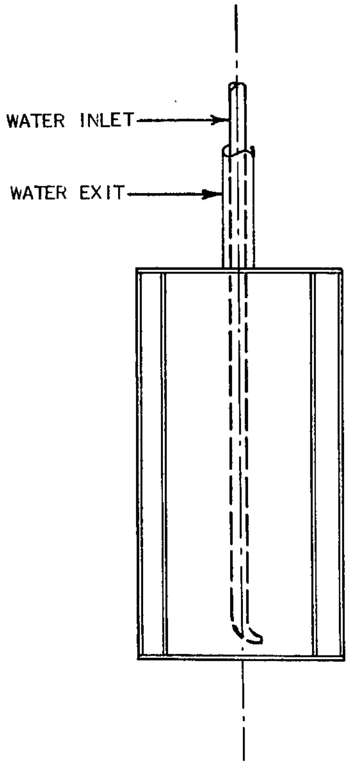


Figure 3. Dispenser Cooler

The operating rod is also used to rotate the thermocouple well by means of an eye in the top of the well.

The dispenser is enclosed and supported by the dispenser-cooler (see Figure 3). This consists of two concentric copper tubes with the annular space closed at each end and supported by a copper tube leading through the head. Concentric to and inside of this tube is a second tube which passes into the annular space to the bottom and serves as the water inlet. Thus cold water is introduced at the bottom, swirls up to the exit tube at the top, and thence up inside the supporting tube to a drain. The dispenser-cooler can be raised or lowered by sliding through the packing gland so that when an actual addition is to be made the dispenser will be near the crucible, and after the addition is completed it can be raised away from the hot crucible and thereby kept cooler.

The stirring device (see Figure 1, items 3, 12, 20, 24) consists of a 28-volt, DC, 250-rpm motor coupled by means of a sleeved flexible shaft to the stirrer. The lower end of the sleeve is clamped securely to the thermocouple support and provides a sort of bearing for the shaft. The flexible shaft is welded to a molybdenum rod which is guided by a molybdenum sleeve bearing supported by the thermocouple well. The end of the rod is slotted and fitted with the stirrer blades.

The crucible is surrounded with two 0.001-inch thick molybdenum shields to minimize radiation losses. This thickness of molybdenum heats but very little in the high frequency field* and the outside shield never reaches dull red heat even though the inside of the crucible be at bright red heat.

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*The frequency is about 20,000 cycles per second.

Any desired atmosphere may be used in the calorimeter by using tanked gas. In addition, the piping system permits flow of gas into either the top or bottom of the calorimeter. Any desired pressure may be used, as the gas exit line has a solenoid valve which is operated by a mercury-level contact device. By adjusting this contact device, the pressure at which the solenoid valve releases is selected. This system cannot be used at present when the stirrer is used, as there is too great a gas leak between the flexible shaft and its sleeve. In this case the valve at the tank is set so that the gas flow out of the shaft is sufficient to prevent the diffusion of any air into the apparatus.

The electrical system is indicated in Figure 4. The large variable inductance consists of a solenoid 2 feet in diameter, made of copper tubing, with shorting switches arranged as indicated. Power

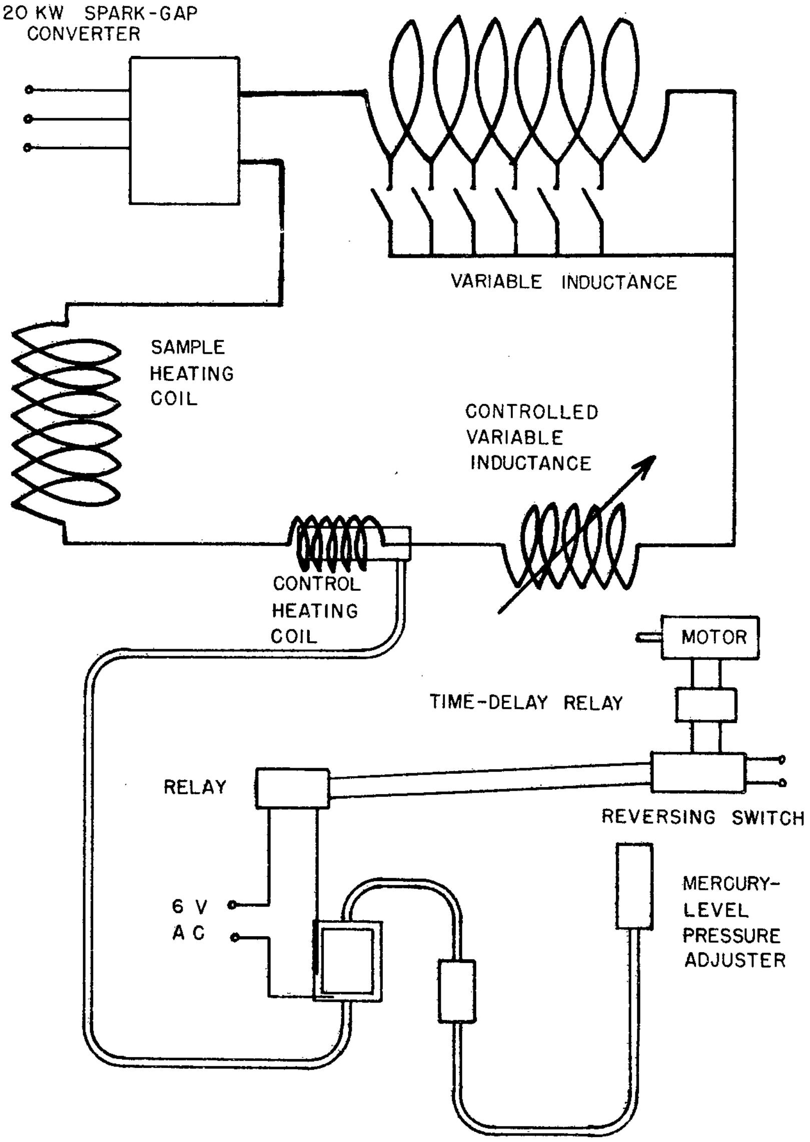

Figure 4. Schematic diagram of high-frequency circuit, and constant temperature mechanism.

dissipation in the heating coil can be increased by shorting out turns of this coil, thus decreasing the total inductance of the circuit.

The heating coil consists of a 28-turn solenoid, 6 1/2 inches in diameter. It is arranged on a support so that the coil may be raised or lowered to center the crucible in the coil.

The other two coils make up a temperature control device. The smaller coil, 20 turns on a 3 1/2 inch diameter, surrounds a water jacketed iron vessel in which there are a few milliliters of water. The only opening in the vessel is in the bottom, at which point a tube filled with mercury leads to a pyrex tube fitted with two electrodes. The pressure above the mercury in this tube can be controlled by a mercury bulb and reservoir as shown on the diagram. The two electrodes are part of an electrical control system which actuates a reversible motor. The motor, controlled in part by a time-delay relay, is coupled to the controlled variable inductance coil (20 turns on an 8-inch diameter) such that the length of the coil is changed to respond to a change in pressure in the iron vessel.

With this arrangement of coils and contacts, a small increase of power increases the heat generated in the iron vessel and consequently increases its temperature. This increase in temperature causes an increase in the vapor pressure of the water in the iron vessel and raises the mercury in the contact chamber. When the contact circuit is completed, the motor, which normally decreases the inductance of the controlled variable inductance coil, reverses and increases its inductance. This increases slightly the power dissipated in this inductance and consequently reduces the power dissipated in the other coils in the system. This decrease in power lowers the temperature and vapor pressure of the water and ultimately causes the mercury circuit to break. At this time the motor reverses, and the controlled variable inductance decreases. This decrease results in an increase in power, increases the vapor pressure of the water in the iron vessel, and closes the mercury contact. Then the cycle repeats. The entire cycle causes a temperature variation in the melt of about 1°C.

The time-delay relay on the motor was necessary because the system's reaction time was too slow. If the motor ran continuously it would cause the coil to over-correct and no control would be effected. Satisfactory operation is obtained with a relay setting to give a 15-second "on" period and a 5-second "off" period.

Thus, this system controls the power dissipation in the entire high frequency circuit, and various levels of power can be maintained merely by adjusting the height of the mercury bulb.

To operate the apparatus, one loads the dispenser with weighed quantities of sodium, assembles the calorimeter, and starts the converter. When the tin has melted, the stirrer and the thermocouple are set in place. Temperatures are recorded on the micromax,* and when the system is near the desired temperature, the power setting and incremental inductance are adjusted so that the system approaches equilibrium. The control device is then set in operation. When the temperature of the melt remains constant for a few minutes, the temperature of the dispenser is taken and the sodium addition made. Before and as soon as possible after the addition, millivolt readings are taken on the potentiometer† to check the values recorded by the micromax.

When the temperature has reached its new equilibrium, the power may be adjusted to yield the desired temperature for the next addition. This procedure is repeated for all additions. When the run is completed, the calorimeter is opened and the dispenser examined to see if all the pellets were added. The melt is removed, ground in the dry box, and anaylzed. From the analysis, the amount of sodium vaporized is determined.

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*Micromax, Leeds and Northrup Company, Philadelphia.

†Precision potentiometer, Leeds and Northrup Company, Philadelphia.

DERIVATION OF NEW METHOD OF ANALYSIS OF TEMPERATURE-TIME CURVES

The principal data received from a run consist of a temperature-time curve traced by the micromax, and in addition, a few points taken on the potentiometer as checks. It is therefore necessary to devise a method of interpretation of these curves. Typical curves are shown in Figure 5.

The rate of heat loss at temperature, t, can be expressed by the following equation*:

$$-q_{1t} = \sigma A_1 \epsilon (t^4 - T_r^4) + A_2 h (t - T_r), \tag{1}$$

in which the coefficient for heat transfer by conduction is combined with that for convection. When the system reaches a steady-state temperature, t, the thermal energy lost to the surroundings is equal to the thermal energy gained from the high frequency heating coil.

The rate of heat loss or gain at any temperature, T, is,

$$-q_{1T} = \sigma A_1 \epsilon (T^4 - T_r^4) + A_2 h (T - T_r). \tag{2}$$

The difference in rates of heat loss at T and t is the net rate of heat transfer at T, and is represented by,

$$-(q_{1T} - q_{1t}) = \sigma A_1 \epsilon (T^4 - t^4) + A_2 (T - t). \tag{3}$$

$(T^4 - t^4)$ may be expanded in powers of $(T - t)$, thus:

$$(T^4 - t^4) = 4t^3(T - t) + 6t^2(T - t)^2 + 4t(T - t)^3 + (T - t)^4. \tag{4}$$

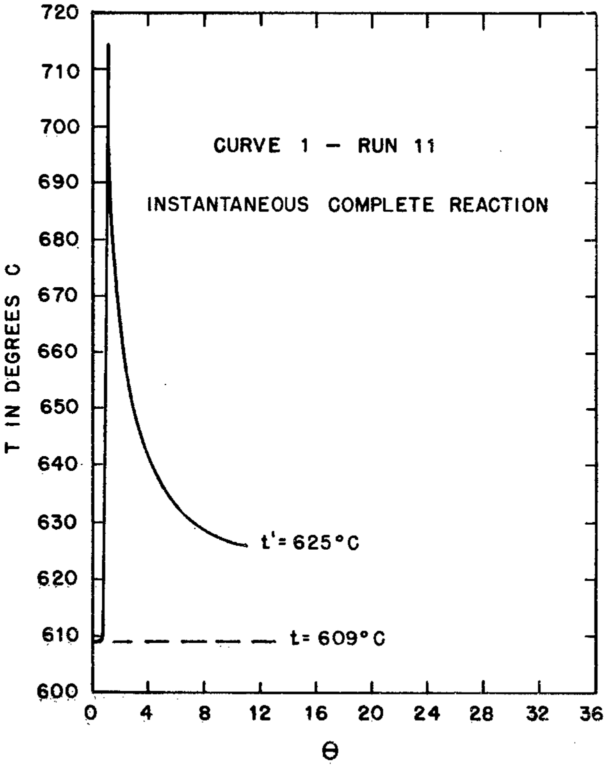

Figure 5. Typical temperature-time curves.

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*Definitions of symbols following end of Part II.

For the case in which t equals 873°K., and (T − t) is 125°K., the contributions to the total of the various terms in the expansion are: 80.9%, 17.4%, 1.66%, and 0.04%. For the case in which t equals 873° K., and (T − t) is 50°K., the contributions to the total of the various terms in the expansion are: 91.8%, 7.9%, 0.3%, and less than 0.1%. From the above, it is evident that if one limits (T − t) to less than 125°K, neglecting the last two terms in the expansion will introduce less than 2% error. Therefore, an allowable substitution for $(T^4 - t^4)$ in equation (3) is $4t^3(T-t) + 6t^2(T-t)^2$. Rewriting equation (3),

$$-(q_{1T} - q_{1t}) = \sigma A_1 \epsilon \left[4t^3(T-t) + 6t^2(T-t)^2\right] + A_2 h(T-t). \tag{5}$$

The corresponding equation written for any temperature, T, and the final equilibrium temperature, t′, is:

$$-(q_{1T} - q_{1t'}) = \sigma A_1 \epsilon [\, 4t'^3(T-t') + 6t'^2(T-t')^2] + A_2 h\,(T-t'). \tag{6}$$

Letting $\sigma A_1 \epsilon = B$, $A_2 h = D$, $-(q_{1T} - q_{1t'}) = f$, and $\Delta T' = (T - t')$, equation (6) becomes, upon rearranging,

$$f = (4Bt'^3 + D)\Delta T' + 6Bt'^2(\Delta T')^2. \tag{7}$$

Now let $(4Bt'^3 + D) = P$, and let $6Bt'^2 = R$, then,

$$f = P\Delta T' + R(\Delta T')^2. \tag{8}$$

If we can evaluate P and R, then f can be calculated for a number of $(\Delta T')$'s and an f curve plotted from which one can read values for the rate of heat transfer for the system at any temperature difference.

The change in convection characteristics and the change in radiation characteristics are considered small for any run, therefore values of P, or P′, and R, or R′, calculated for a portion of the run, are representative of the entire run. Thus f values relative to any steady-state temperature may be read from the f curve mentioned above when temperature differences are used as the basis of comparison.*

By plotting f (cal/min) against θ (min), one obtains areas directly representing quantities of heat. This fact will be used later in the discussion.

To evaluate P and R, one can use the cooling portion of the temperature-time curve beyond point "a", Figure 6, if one assumes this curve to approach a theoretical cooling curve type. Then,

$$f = P\Delta T' + R(\Delta T')^2; \tag{8}$$

$$dQ = -f\, d\theta; \tag{9}$$

$$dQ = \sum wc_p\, dT = C_p\, dT; \tag{10}$$

$$f = -\frac{dQ}{d\theta} = -\frac{C_p dT}{d\theta}; \tag{11}$$

$$\text{and } \frac{dT}{d\theta} = -\frac{f}{C_p} = -\frac{1}{C_p}\,[P\Delta T' + R(\Delta T')^2]\,. \tag{12}$$

Rearranging for integration,

$$-\int \frac{dT'}{R(\Delta T')^2 + P\Delta T'} = \int \frac{d\theta}{C_p}. \tag{13}$$

---

*For the case of $t_1 = 873°K$ and $t_2 = 890°K$, a comparison of f's for equal values of B, D, and T′, is: for t_1, 214; for t_2, 220. The difference is less than 3%. B was taken as $2(10^{-9})$, D as 3.0, and the temperature difference as 25°K.

Since $\Delta T' = (T - t')$, $d(\Delta T') = dT$. Substituting and integrating,

$$-\left[-\frac{1}{P}\ln\frac{P + R\Delta T'}{\Delta T'}\right] = \frac{\theta}{C_p} + C \qquad (14)$$

Then, solving for θ, and rearranging,

$$\theta = -\frac{C_p}{P}\ln\frac{\Delta T'}{1 + \frac{R}{P}\Delta T'} - \ln P + C, \qquad (15)$$

or,

$$-\frac{P\theta}{C_p} = \ln\frac{\Delta T'}{1 + \frac{R}{P}\Delta T'} + C. \qquad (16)$$

If the region of the cooling curve does approach a theoretical cooling curve, one obtains a straight line whose slope is $-P/C_p$ by plotting

$$\ln\frac{\Delta T'}{1 + \frac{R}{P}\Delta T'} \text{ against } \theta.$$

Since R and P are both unknown, this plot cannot be made directly. However, as a first approximation, one can plot $\ln \Delta T'$ vs. θ and obtain a value from the slope, from which P can be calculated when C_p is known. This value should be quite close to the correct value of P, if R is small relative to P*, as can be seen in equation (16).

Using this value of P, one can solve for B from the definition $P = 4B(t')^3 + D$, knowing D (Appendix I). With B, R can be calculated from the relation $R = 6B(t')^2$. These approximate values of P and R now permit calculation and plotting of

$$\ln\frac{\Delta T'}{1 + \frac{R}{P}\Delta T'} \text{ vs. } \theta.$$

From the slope of the smoothed curve, new values P′ and R′ can be calculated. This procedure may be repeated until sufficient accuracy is obtained. The values of P and R, necessary for plotting the f curve, are now found.

It is desirable to be able to extrapolate the cooling curve obtained from the experimental data to such time that the ΔT can be evaluated as if the reaction had proceeded instantaneously. This is most easily accomplished by making use of the final

$$\ln\frac{\Delta T'}{1 + \frac{R}{P}\Delta T'} \text{ vs. } \theta.$$

curve obtained above. Select values of

$$\ln\frac{\Delta T''}{1 + \frac{R}{P'}\Delta T''}$$

from the straight line determined by values of the similar expression in $\Delta T'$. Solve for values of $\Delta T'$ and plot the corresponding extrapolated T's on the T vs. θ graph, as indicated on Figure 6. If one can obtain the θ_i corresponding to an instantaneous reaction, then one can also obtain the accompanying ΔT from the extrapolated curve above.

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*The calculations show P to be about 10, and R to be about 10^{-3}.

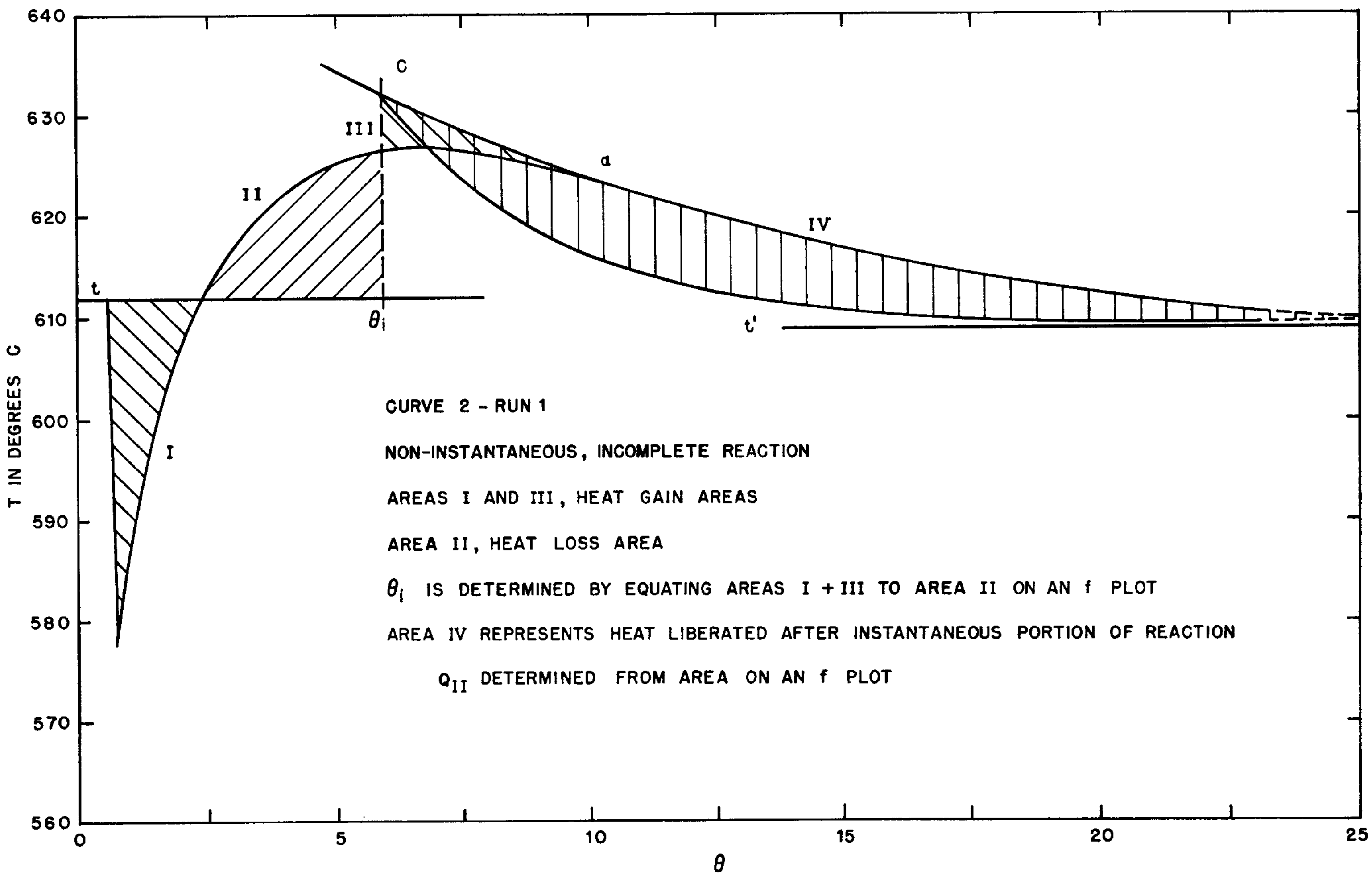

Figure 6. Temperature-time curve, Run 1, Curve 2, Na.

Superposing an ideal, instantaneous T vs. θ curve on a typical T vs. θ curve defines areas which represent relative heat gains and losses by the system. (Areas I, II, and III on Figure 6.) Those areas in which the ideal curve lies above the actual are "heat gain" areas, since the system is losing heat at a lower rate than it gains heat ($T<t$, area I); or the system, although losing heat at a higher rate than it gains heat, is losing heat at a lower rate than the ideal system would, resulting in a net equivalent gain of energy (area III). Those areas in which the ideal curve lies below the actual curve are "heat loss" regions, because in this case (area II) the system loses heat at a higher rate than it gains heat, resulting in a net loss of energy. The proper θ, θ_i, for the instantaneous reaction is the one for which the heat losses exactly equal the heat gains. This θ is obtained by trial-and-error balancing of Area I plus Area III against Area II on an f plot.

In the construction of the f plot, an f curve should be used which was calculated for the system in a completely nonreactive state, for any other f, such as one determined from values of P' and R' for a sodium addition, is a function of the rate of reaction.* The only f that is not a function of the rate of reaction is the one determined from the molybdenum addition.

The f plot is constructed by reading T's for values of θ on the T vs. θ curve, calculating the corresponding $T - t$, reading the values for f on the f curve, and plotting the value of f, at the proper θ, on the f plot vs. θ plot, Figure 7.

Since the units of f are calories per minute, an area produced by plotting f vs. θ in minutes represents a quantity of heat. In the ideal reaction, there would be no loss or gain of heat by heat transfer because of its instantaneous character. It is therefore necessary to choose the θ_i as the θ for which the net heat transferred in the actual case is zero. The physical significance of the ideal plot is, for convenience in graphical calculation, to combine an instantaneous reaction in which equilibrium is partially reached with a subsequent reaction period during which equilibrium is quantitatively approached.

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*The rate of heat transfer, f, at any time, θ, is the sum of two rates, thus: $f_{obs.} = f_{react.} + f_{heat\ trans.}$ Since we wish to balance heat losses and gains due to heat transfer, we must not use an f which may have an $f_{react.}$ included, therefore, we must use the f determined from the characteristics of a molybdenum addition.

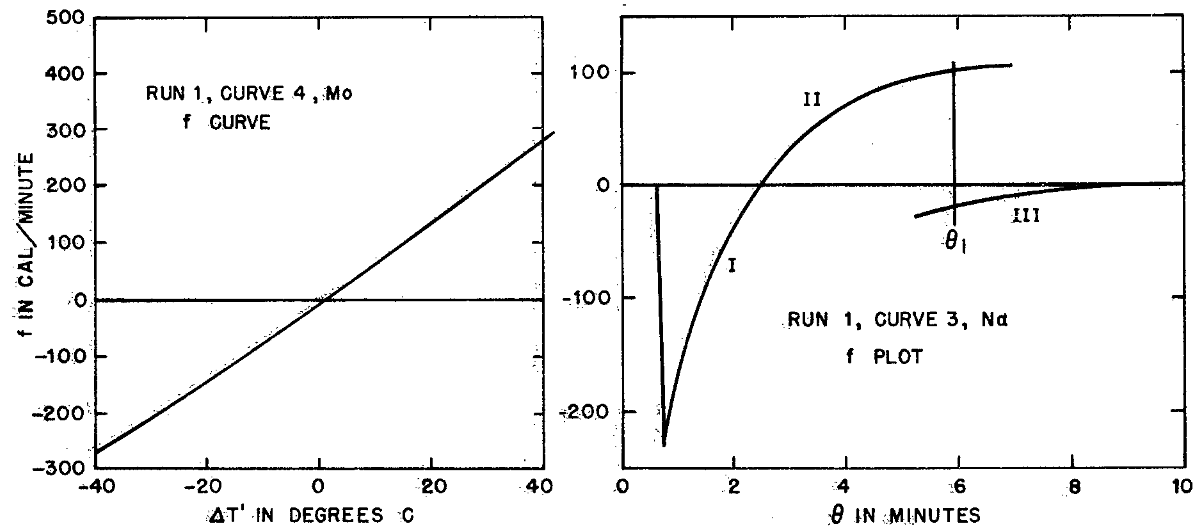

Figure 7. f curve, and f plot.

While Area I is bounded, so that it represents a definite amount of heat absorbed, Area II is not bounded on the right. The aim is to locate the bound of Area II such that the effective net heat transferred from the system (represented by Areas I, II, and III) is zero.

Now let us consider the temperature-time curve of Figure 6. If the curve beyond point a is a typical cooling curve-type, which can be determined by plotting on a ln $\Delta T'$ vs. θ plot, then it is also a part of the ideal temperature curve, and as such, can be extrapolated to the left.* Since we are transferring the actual T vs. θ curve to an ideal curve, there is a point on the extrapolated curve which represents the highest temperature that the system would attain in the ideal reaction. This temperature is defined by the condition that net heat transfer at the corresponding time is zero.

The extrapolated T vs. θ curve and the actual temperature-time curve partially define a third area, Area III, which, when plotted† on an f plot, represents a quantity of heat gained by the system. Area III, like Area II, is unbounded. When these two areas are plotted at their respective times, as shown on Figure 7, a unique bounding vertical line can be found such that the sum of Area I plus Area III equals Area II. This is exactly the condition placed on the θ_i, and since the line is unique, it determines θ_i. Then the point of intersection of the vertical θ_i line with the extrapolated temperature curve defines the temperature which an ideal reaction would have attained. The temperature difference between this derived temperature and the initial steady-state temperature defines a quantity of heat, Q_I, from the relation,

$$Q_I = C_p \Delta T. \tag{17}$$

The C_p that should be used in equation (17) is the C_p of the system after the sodium has been added. For runs in which multiple additions are made, values of C_p must be calculated for all sodium additions but the last. This is done by assuming that the C_p for the system at any time is equal to Σ C_p less a factor, F, times the C_p of all the sodium added <u>after</u> the addition in question. The evaluation of F is presented in Appendix II.

In the event that the reaction is not complete at this point, and heat is being liberated throughout the "cooling" part of the T vs. θ curve, an estimation of this added heat must be made.

The criterion for determining whether the reaction was complete at "a" is whether the final slope of the

$$\ln \frac{\Delta T'}{1 + \frac{R}{P}\Delta T'} \text{ vs } \theta$$

plot for a sodium addition is less than the corresponding slope for the molybdenum addition at the end of the run. If the slope is materially less, the reaction was not complete at a. Any unreacted sodium present at point a will liberate its heat of reaction before the system reaches its final equilibrium temperature.

At this point in the development, the T vs. θ curve obtained experimentally has been transformed to an equivalent theoretical instantaneous reaction T vs. θ curve, and we have accounted for some fraction of the added sodium which can be assumed to have reacted instantaneously to arrive at point C, Figure 6. The characteristics of a cooling curve of a completely reacted system can be approximated from the molybdenum addition, in which addition no reactive material is introduced. By passing such a curve through point C so that its equilibrium temperature, at θ equals infinity, is t′ an area is defined (Area IV) which represents the quantity of heat liberated by the remaining fraction of the sodium

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*The method can be modified to apply where the ideal curve is not approximated.

†The ordinates of this area are plotted as the difference between the f for the temperature on the extrapolated curve and the f for the temperature on the actual curve.

before the system reaches t′. This quantity of heat may be determined by plotting the area on an f′ plot, on which areas are proportional to heat. Any ordinate of the corresponding area on the f′ curve is found by subtracting the f determined for temperatures on the lower (molybdenum-type) curve from the f determined for temperatures on the upper (actual) curve, both temperatures being taken at the same θ.

Since it is impossible to measure an area out to infinite time, the area can be broken up into two parts for actual measurement. The direct measurement of area on the f′ plot should be extended to some practical limit at which time it may be safely assumed that the reaction is complete, and that the T vs. θ curve is an exact cooling curve beyond this limit. The heat represented by this measurable area is designated by the symbol Q_{II}. The heat represented by the area out to infinite time can be calculated analytically, thus:

$$dQ = -f\,d\theta, \qquad (9)$$

and,

$$f = P\Delta T' + R(\Delta T')^2. \qquad (8)$$

For small $(\Delta T')$,

$$f = P\Delta T', \qquad (18)$$

and,

$$dQ = -P\Delta T'\,d\theta \qquad (19)$$

From equation (12), when $\Delta T'$ is small,

$$-\frac{dT}{d\theta} = \frac{1}{C_p}P\Delta T', \qquad (20)$$

and,

$$\frac{d(\Delta T')}{d\theta} = -\frac{P}{C_p}\Delta T'. \qquad (21)$$

Transforming, and integrating,

$$[\ln \Delta T']_{(\Delta T')_0}^{(\Delta T')_\theta} = \left[-\frac{P}{C_p}\theta\right]_{\theta_0}^{\theta} \qquad (22)$$

When θ_0 is taken to be zero, and $\Delta T'$ at θ_0 equals $(\Delta T')_0$,

$$\ln\frac{(\Delta T')_\theta}{(\Delta T')_0} = -\frac{P}{C_p}\theta \qquad (23)$$

and

$$(\Delta T')_\theta = (\Delta T')_0 e^{-(P/C_p)\theta}. \qquad (24)$$

Let Q_{III} be the heat in question, then,

$$dQ_{III} = (dQ_{\text{actual curve}} - dQ_{\text{theo. curve}}), \qquad (25)$$

then, using equation (19),

$$dQ_{III} = (-P(\Delta T')_{\text{actual curve}} + P(\Delta T')_{\text{theo. curve}})\,d\theta. \qquad (26)$$

Substituting equation (24) in equation (26) and integrating,

$$\int_0^{Q_{III}} dQ_{III} = -\int_0^{\infty} P\,(\Delta T')_{0\ \text{actual}}\,e^{-(P/C_p)\theta}\,d\theta$$

$$+ \int_0^\infty P(\Delta T')_{0\ \text{theo.}}\, e^{-(P/C_p)\theta}\, d\theta, \tag{27}$$

or,

$$Q_{III} = C_p \left[(\Delta T')_{0\ \text{actual}} - (\Delta T')_{0\ \text{theo.}}\right], \tag{28}$$

which, by definition, is set equal to,

$$Q_{III} = C_p\, \overline{\Delta T}\,. \tag{29}$$

This simple expression, then, gives a means of measurement of the area from some point of small $(\Delta T')$'s to infinite time.

To account for the heat lost from the system due to vaporization of sodium, one must first determine the amount of vaporization occurring during the particular addition. The total vaporization can be calculated from an analysis of the final melt since the extremely low vapor pressure of tin prevents its vaporization. The problem then becomes one of determining the fraction of the total sodium vaporized that was vaporized in the particular addition.

It is assumed that since sodium has a much lower density than tin, a phase of molten sodium tends to cover the tin phase until the sodium reacts. Therefore the ratio of duration of a particular addition to the total for all additions of a run is used to proportion the amount of sodium vaporized during the addition. The quantity of heat lost by vaporization is designated by the symbol Q_0, and can be calculated from the known heat required to heat solid sodium at the temperature of the dispenser to sodium vapor at the temperature of the melt.

The total amount of heat liberated in any addition is the sum of the various Q's as calculated above. The ΔH for the reaction, $Na_{cold}(s) + Sn_{hot}(l) \rightarrow NaSn_{hot}(l)$, is this summation of Q's (ΣQ) divided by the moles of sodium added. Then the ΔH of the reaction $Na_{hot}(l) + Sn_{hot}(l) \rightarrow NaSn_{hot}(l)$ can be calculated by adding to the ΔH above the heat required to raise the sodium from the dispenser temperature to the temperature of the melt, t.

SAMPLE CALCULATION

The sample calculation presented is of the third sodium addition of the first run. The molybdenum addition is calculated first, to find the C_p of the system.

Table 1. Data for ln $\Delta T'$ vs. θ plot, run 1, curve 4, Mo.

θ	$\Delta T'$	$\Delta T'$ *	$\dfrac{\Delta T'}{1 + (R/P)\Delta T'}$
9	2.3	-	2.3
8	3.2	-	3.2
6	6.1	6.1	6.1
4	11.0	11.0	10.9
2	19.6	19.9	19.2
1.5	23.3	-	22.8
1	27.8	26.8	27.1
0.5	-	31.0	-
0	-	36.0	-

*These values are read from the line drawn through the $(\Delta T')$'s to extrapolate T's to the θ's indicated.

In the calculation of ΣC_p, the interpolated and extrapolated values of T'* above, which were read from the line on the $\ln \Delta T'$ vs. θ plot, Figure 9, are plotted on the T vs. θ plot, Figure 8, and a smooth curve is drawn through these points. By balancing the areas on the T vs. θ plot as if they were on an f plot, the approximate time θ_i and the corresponding ΔT can be found. This value of ΔT permits calculation of a ΣC_p. It was found that θ_i was 0.27 minutes and ΔT was (614 − 575) or 39.0°C. From heat capacity data given by K. K. Kelley,[7] the ΔH for molybdenum is calculated:

$$\Delta H = 5.69(848 - 318) + 0.94(10^{-3})(848^2 - 318^2) + (5.03)(10^4)/848 - (5.03)(10^4)/318;$$

$$= 3020 + 581 + 59.4 - 158 = 3502.4 \text{ or } 3.50 \text{ kcal/mole}$$

The weight of molybdenum was 25.85 grams or 0.269 moles. Then $\Sigma C_p = (0.269)(3.50)/(39.0) = 0.02414$ or 24.14 cal/ °C. Using this value for ΣC_p, P can be calculated; $P = (0.291)(24.14)$ or 7.03. Using the value for D, 2.62, as calculated in Appendix I, and the value for P, B is found from the equation, $B = (P-D)/4(t')^3 = (7.03 - 2.62)/4(881)^3$, or $B = 1.61(10^{-9})$. Then, since $R = 6B(t')^2$, $R = 6(1.61)(10^{-9})(881)^2$ or $R = 0.0075$.

These values of P and R allow the calculation of the

$$\frac{\Delta T'}{1 + \frac{R}{P}\Delta T'}$$

column of Table 1. These points are plotted as shown on Figure 9. The slope of the line does not change, and the values of P and R were used to calculate an f curve and make an f plot, but since the θ_i was not changed from its original value, these graphs are not shown. This effect is due to the fact that the areas are small, and the $(\Delta T')$'s are small.

Calculation of Sodium Vaporized in Run 1

The molal ratio of tin to sodium from amounts added for the run is equal to (22.997)(95.8)/(118.7)(17.97) or 1.033. The molal ratio of tin to sodium from analysis is 1.060. The amount of sodium in the final melt, assuming that no tin is vaporized during the run, is (1.033)(17.97)/(1.060) or 17.51 grams. Therefore the sodium vaporized is (17.97 − 17.51) or 0.46 g. This total amount of vaporization is prorated in proportion to the time of an addition, thus:

Time, Curve 1 (20.0 − 0.8) = 19.2 min
Curve 2 (23.1 − 0.6) = 22.5 min
Curve 3. (25.0 − 0.1) = 24.9 min
Total 66.6 min

Amounts vaporized in each addition are:

Curve 1, (19.2)(0.46)/(66.6) = 0.133 g
Curve 2, (22.5)(0.46)/(66.6) = 0.155 g
Curve 3, (24.9)(0.46)/(66.6) = 0.172 g

Actual amounts of sodium added per addition:

Curve 1, (8.27 − 0.133) = 8.137 g
Curve 2, (5.20 − 0.155) = 5.045 g
Curve 3, (4.50 − 0.172) = 4.328 g

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*These values are read from the line drawn through the $(\Delta T')$'s to extrapolate T's to the θ's indicated.

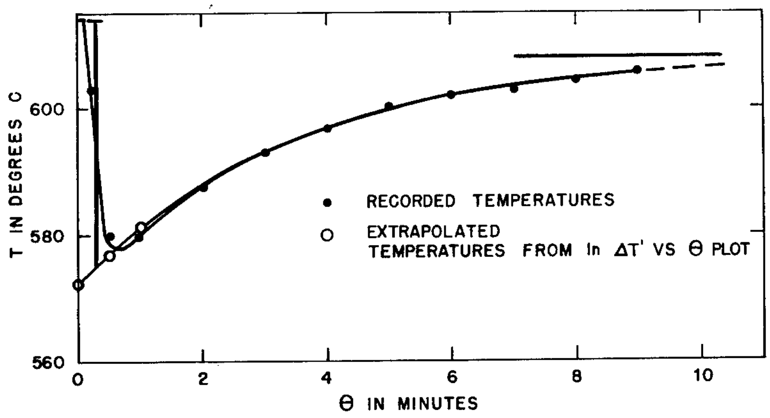

Figure 8. Temperature-time curve, Run 1, Curve 4, Mo.

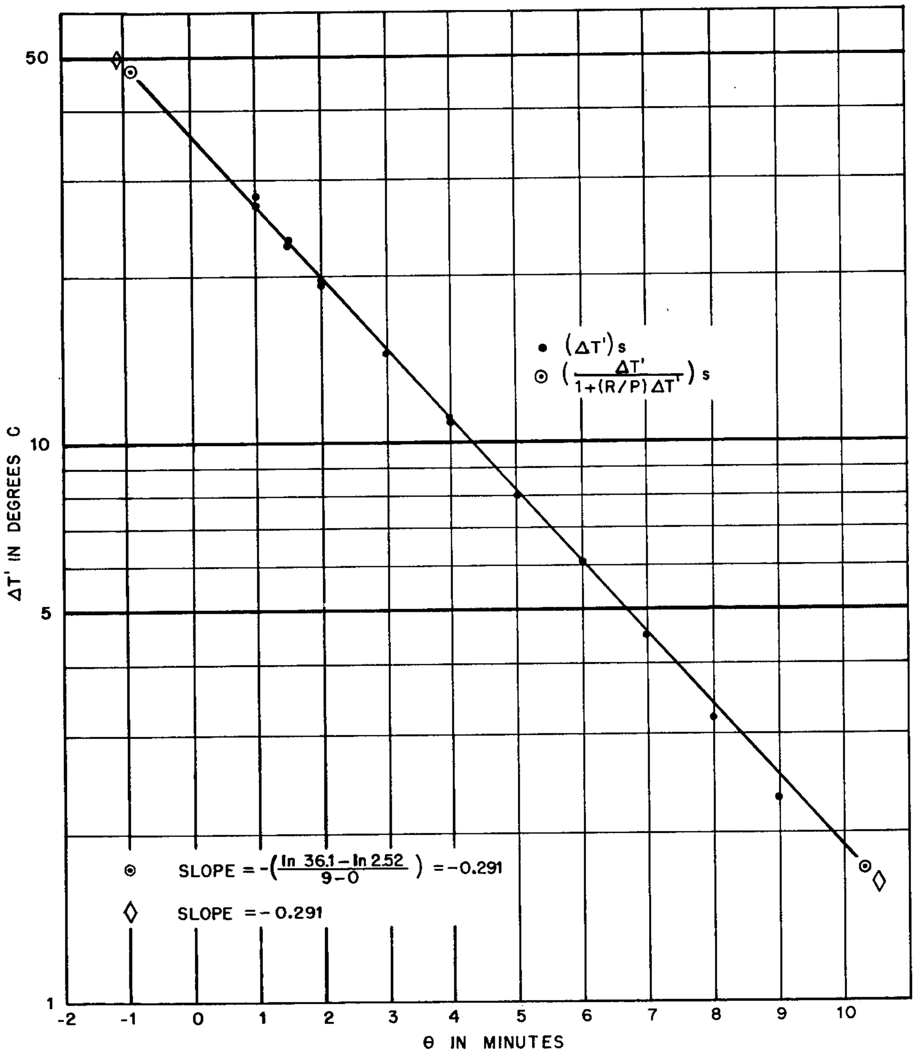

Figure 9. Ln ΔT vs θ plot, Run 1, Curve 4, Mo.

Calculation of the Heat of Reaction from Curve 3, Run 1

The weight of sodium added in this addition is 4.328 grams. The C_p for the system for this addition is 24.14 cal/°C. The equilibrium temperature for this run was found to be 613°C, t′, and D was 2.62.

The values of data given in Table 2 for this addition give a slope on the ln $\Delta T'$ vs. θ plot of −0.108. Using this slope, and the value for the C_p of the system, P is (0.108)(24.14) or 2.61. Then B is $(P - D)/4(t')^3$, or when the values are substituted, $(2.61 - 2.62)/4(886)^3$ or $-3.60(10^{-12})$. R is $6B(t')^2 = 6(-3.60)(10^{-12})(886)^2$ or $-1.70(10^{-5})$.*

Table 2. Data for ln $\Delta T'$ vs. θ plot, run 1, curve 3, Na.

θ	$\Delta T'$	$\frac{\Delta T'}{1 + \frac{R}{P}\Delta T'}$	$\frac{\Delta T''}{1 + \frac{R'}{P'}\Delta T''}$	$\Delta T''$
27	0.9	0.9	-	-
23	2.1	2.1	-	-
20	3.4	3.4	-	-
17	5.3	5.3	-	-
15.5	6.4	6.4	-	-
14	7.6	7.6	7.5	7.5
12.5	8.8	8.8	8.8	8.8
11	10.1	10.0	10.3	10.3
10	-	-	11.6	11.6
9	-	-	12.8	12.8

Since R is very small, the values of

$$\frac{\Delta T'}{1 + \frac{R}{P}\Delta T'}$$

are practically the same as the corresponding values of $\Delta T'$. The slope remains the same, and $P = P'$, $B = B'$, and $R = R'$. Values of

$$\frac{\Delta T''}{1 + \frac{R'}{P'}\Delta T''}$$

read from the plot and the corresponding $(\Delta T'')$'s, are tabulated in Table 2 above. The T's calculated from the $(\Delta T'')$'s are plotted on the T vs. θ plot, Figure 10. An f curve must now be plotted from the relation, $f = P'\Delta T' + R'(\Delta T')^2$, where P' and R' are the values from the molybdenum addition. Data appear in Table 3. The f plot is constructed using values of $(T - t)$ read from the T vs. θ curve to find the correct value of f from the f curve, and then plotting the values of f against the proper θ. This plot appears in Figure 13. Areas are balanced on this f plot as indicated, and the θ_i is found. At this θ_i, the ΔT is read from the T vs. θ curve, for the ideal reaction, and is 11.6°C. at $\theta_i = 9.85$ minutes (Figure 10).

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*It is possible for R and B to be negative for a sodium addition when there is a great deal of sodium reacting in the latter part of the addition. The negative value occurs because the slope of the T vs. θ curve is quite flat in cases of this type.

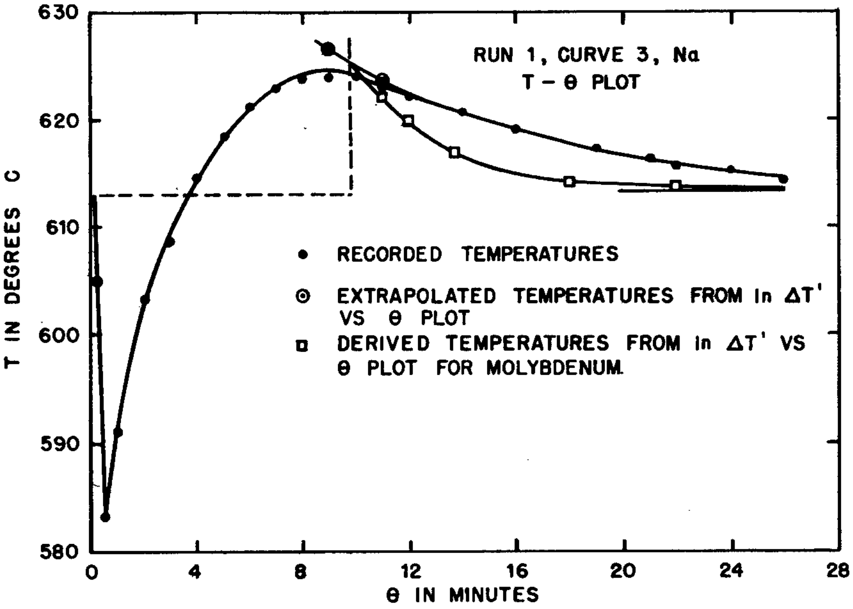

Figure 10. Temperature-time curve, Run 1, Curve 3, Na.

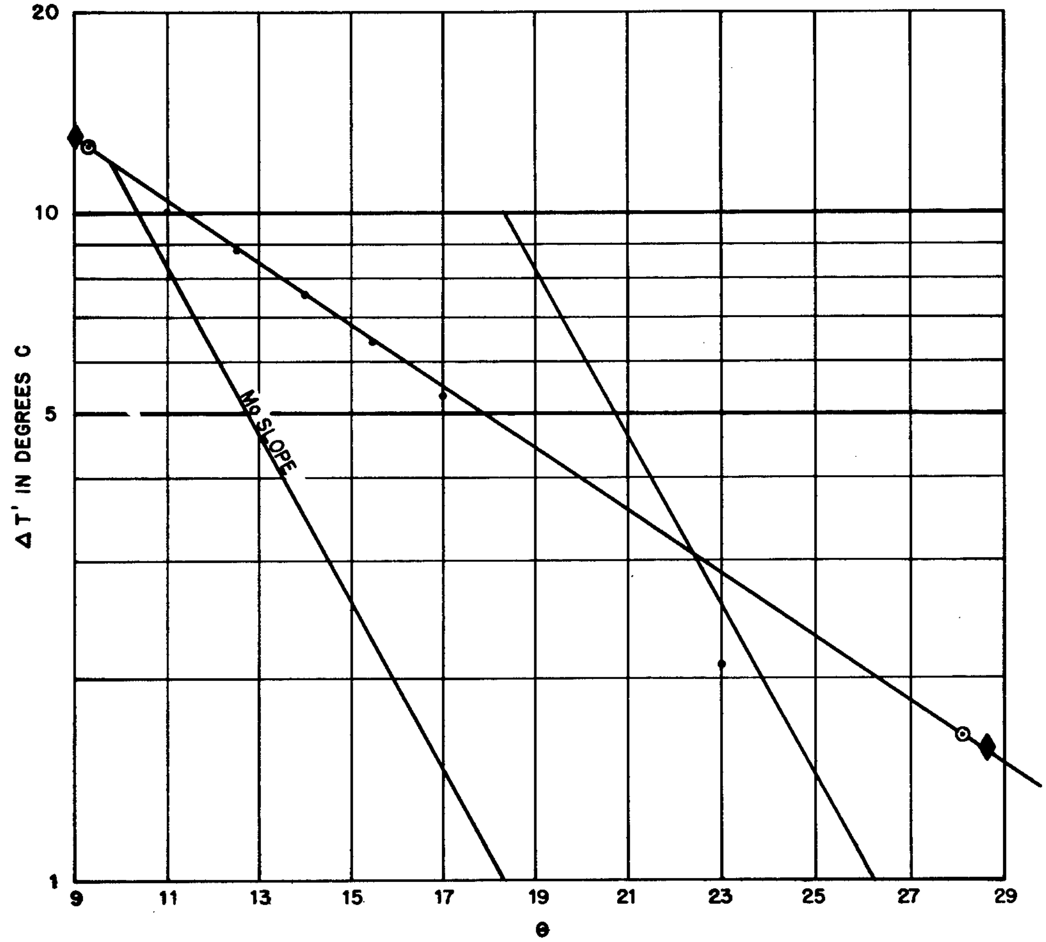

Figure 11. Ln ΔT' vs. θ plot, Run 1, Curve 3, Na.

Table 3. Data for f curve, run 1, curve 4, Mo.

$\Delta T'$	f	$\Delta T'$	f
50	370.0	0	0
30	217.5	−15	−104.1
15	107.1	−30	−204.5

The value of Q_I can now be calculated. Q_I is equal to $C_p(\Delta T) = (24.14)(11.6)$ or 280 calories.

Using data from K. K. Kelley,[7] Q_0 can be calculated.

$$Q_0 = (0.172/22.997)\left[5.01(371 - 318) + (5.36/2)(10^{-3})(371^2 - 318^2) + 630 + 7.50(886 - 371) + 23890^{8}\right]$$

$$= (0.0075)(266 + 98 + 630 + 3863 + 23890) \text{ or } 0.216 \text{ kcal.}$$

The calculation of Q_{II} involves plotting an f′ plot. This involves plotting f's from the table above, as determined from the $(\Delta T')$'s of area IV, Figure 10, against the corresponding θ's. The resulting f′ plot is shown in Figure 14. The area was measured and found to be 1004 units, at 5/16 cal/unit, which equals 314 calories.

The calculation of Q_{III} consists of calculating the quantity $\overline{(\Delta T)}$ from the T vs. θ plot, and substituting in the equation $Q_{III} = C_{p\overline{(\Delta T)}}$; Q_{III} is therefore equal to (24.14)(1.2) or 29 calories.

$Q_0 + Q_I + Q_{II} + Q_{III} = (0.216 + 0.280 + 0.314 + 0.029)$ or 0.839 kilocalories for 4.367 grams of sodium.

$(Q_0 + Q_I + Q_{II} + Q_{III}) = (0.839)(22.997)/(4.328)$ or 4.458 kilocalories per mole.

$Q = (266 + 98 + 3863 + 630)$ or 4.857 kilocalories per mole.

$-\Sigma Q$ is equal to the Δ H for the reaction,

$$Na_{886} + Sn_{886} \longrightarrow NaSn_{886},$$

and this ΔH is $-(4.458 + 4.857)$ or -9.315 kilocalories per mole.

For the reaction,

$$Na_{873} + Sn_{873} \longrightarrow NaSn_{873},$$

the Δ H from the third sodium addition is:

$$-9.315 - (1 - 0.8)(7.5)(886 - 873)(10^{-3}), \text{ or } -9.33 \text{ kilocalories per mole.}$$

TABULATION OF RESULTS ON Na-Sn

In calculating the final result, the three additions of run 1 were averaged, the three additions of run 10 and run 11 combined were averaged, and the average of these two averages taken as the result. This is indicated on Table 5.

Errors were calculated* for each type of run, and it was assumed that the same error was present in all runs of the same type.

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*Errors were calculated on run 1, addition 2; and on run 11, addition 1.

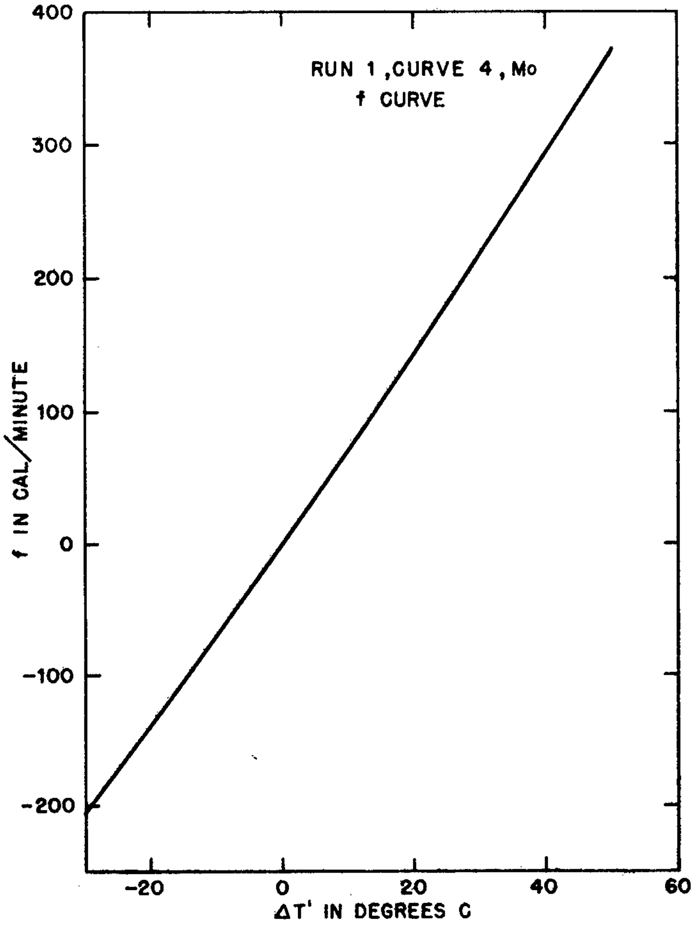

Figure 12. f curve, Run 1, Curve 4, Mo.

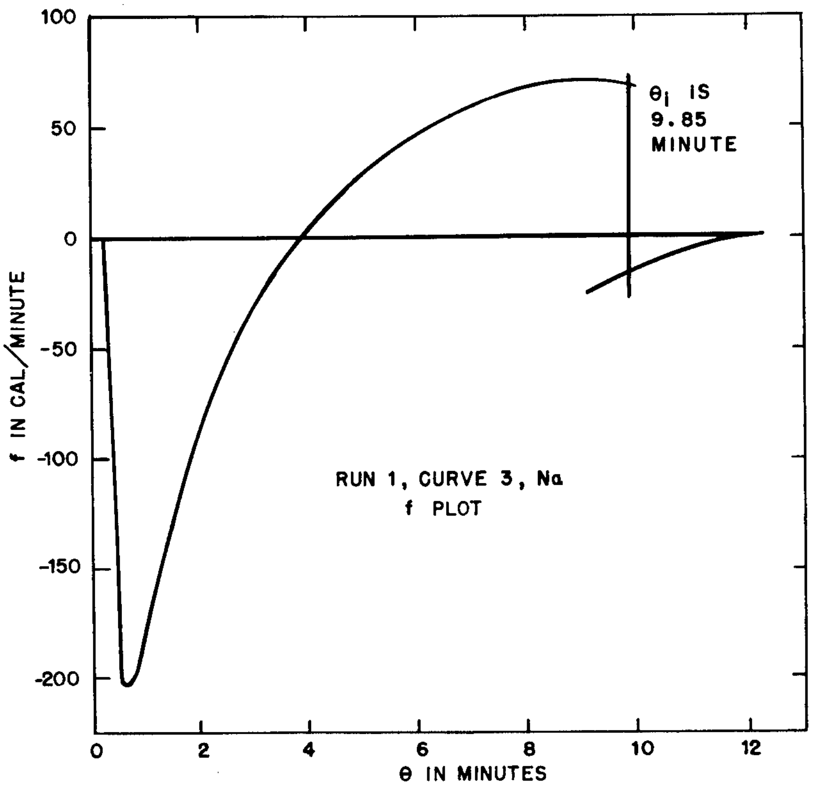

Figure 13. f plot, Run 1, Curve 3, Na.

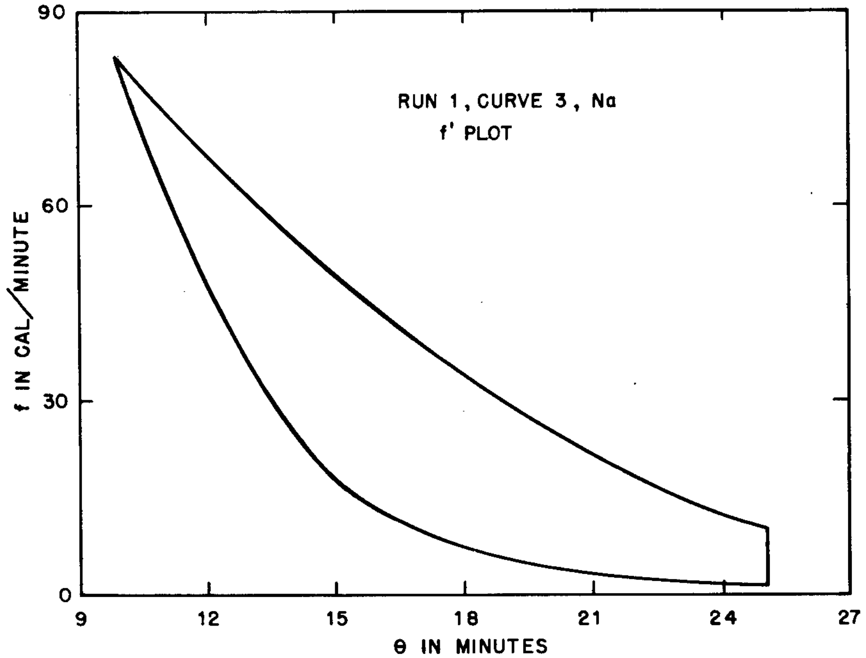

Figure 14. f′ plot, Run 1, Curve 3, Na.

Table 4. Summary of runs and results.

Run	No. Na additions	Heat of reaction kcal/mole	Comments
1	3	1st − 9.77 2nd − 10.76 3rd − 9.33	No stirrer. No stirrer. No stirrer.
2	3	−	Dispenser failed.
3	3	−	Vaporization losses excessively high.
4	-	−	Dispenser failed.
5	3	−	Third addition incomplete.
6	-	−	Deflecting shield failed.
7	-	−	Crucible leaked.
8	2	−	Vaporization losses excessively high.
9	2	−	Deflecting shield failed.
10	1	− 8.87	With stirrer.
11	2	1st − 9.73 2nd − 9.30	With stirrer. With stirrer.

Table 5. Results of determinations, Na-Sn.

Run	Addition	Result Kcal/mole at 873°K
1	1	−9.77 ± 0.77
	2	−10.76 ± 0.77
	3	−9.33 ± 0.77
	Average	−9.95 ± 0.45
10	1	−8.87 ± 1.14
11	1	−9.73 ± 1.14
	2	−9.30 ± 1.14
	Average	−9.30 ± 0.66
	Overall average	−9.63 ± 0.40

An estimation of the heat of formation at 298°K can be made on the basis of the assumption that the change in heat content of the Na-Sn is equal to the change in heat content of the tin plus 0.8 times the change in heat content of the sodium. Values for heat capacities are taken from K. K. Kelley.[7] The ΔH so calculated is −10.6 kcal/mole.

DISCUSSION OF THE WORK ON Na-Sn

Although a conclusive proof of the method of analysis cannot be claimed, the fact that an average result from the unstirred run is not far different from the average result from stirred runs, and the fact that the final average of the two sets of additions includes two of three individual results of each type in its probable error range, indicate that the method has merit. This number of coincidences is quite improbable.

A second indication is that the estimated heat of formation for the temperatures at which other investigators have quoted data is in the same range. Table 6 lists the results of the other investigators. The value of -16 kilocalories given by Biltz[4] is the result of a recalculation of old data using corrected heats for some of the intermediate reactions. One reaction in particular,

$$FeCl_3 + 1/2\ H_2 \rightarrow FeCl_2 + HCl + \Delta H,$$

was changed by a very large factor. In 1924, Biltz and Holverscheit[2] used the value 10.3 kilocalories for the above reaction in 6.3N HCl, and calculated −10.7 for the heat of formation of Na-Sn. In 1928, Biltz and Meyer[3] recalculated the old data using a value of 16.0 kilocalories for the above reaction. They reported −16.0 kilocalories for the corrected value. No late data are available for this reaction, so that a recalculation is not possible.

Table 6. Summary of heat of formation data for Na-Sn.

Heat form. kcal/mole	Prob. error kcal	Method	Temp. °K	Observer
−11	0.5*	Diff. sol'n.	298	Biltz and Holverscheit[2]
−12.0	0.7†	Cal.	298	Kubaschewski[5] Kubaschewski and Seith[6]
−16		Diff. sol'n.	298	Biltz,[4] and Biltz and Meyer[3]
−9.63	0.40	Cal.	873	This research
−10.6‡	0.6	Cal.	298	This research

In the solution methods, small errors in either of the heats of solution whose difference is the desired value cause a relatively large error in the result. In Kubaschewski's[5] experiments a source of error is that the paraffin coating the pure sodium would tend to evaporate at the high temperature of molten Na-Sn. This would leave the highly reactive surface of the melt unprotected. Any oxidation of this surface would directly affect the result, tending to increase the heat of formation.

Kubaschewski[5] describes a source of error in his procedure, namely, that the heat content of the crucible above the temperature of the calorimeter is only approximately known. In addition, the hot crucible will lose an almost indeterminate amount of heat while it is outside the calorimeter.

The results of the present research would tend to be low, as all of the approximations made in the development result in the neglect of small factors whose inclusion would tend to increase the measured heat effect. Any increase would be small, probably not over 3% of the calculated value or about 300 calories.

No definite conclusions regarding the accuracy of the result obtained by comparison with other values is possible except that the results obtained in this research tend to be lower than the other results quoted.

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*Estimated from data given by Biltz and Holverscheit.
†Calculated from value of ∿ 6% given by Kubaschewski and Seith.
‡Estimated value at this temperature, see Table 5 and following paragraph.

Runs were first made with no stirrer as it was thought that the stirring caused by the electromagnetic field would be sufficient to keep the melt mixed. After several runs were completed, it was evident from the reaction rate that stirring would be necessary. It was also hoped that stirring would minimize vaporization losses as these were so large in run 3 and run 8* that the runs could not be used. (A contributory fact to the high vaporization losses was that the temperatures in run 3 and run 8 were higher than in run 1.)

That stirring did increase the reaction rate is evident when results of run 10 and run 11, Table 7, are compared with runs 1, 3, and 8; in addition, vaporization was reduced markedly.

Table 7. Amounts of sodium vaporized in various runs.

Run	Approx. av. temp. °C	% Na vaporized	Av. time for addition, Min.
1	615	2.42	24
3	660	22.4	22
8	630	11.6	18
10	660	0.4	11
11	640	0	13

One aspect of the stirred runs that was not anticipated was that local heating was apparently present. The location of the stirrer just below the thermocouple well is presumed to have caused a flow of reacting melt to pass over the thermocouple and raise its temperature above the actual average temperature of the melt. No attempts to avoid this type of irregularity have been made, as the dimensions of the present calorimeter are such that any other configuration of apparatus would necessitate major changes in design.

The dispenser was quite erratic in its operation. This was attributed to the fact that the sodium pellets were so light that the plates did not always operate properly. In addition the sodium metal is quite soft, and almost any small force is sufficient to warp the pellets out of shape so they would wedge themselves in the constrictions in the dispenser. This wedging caused several runs to be worthless.

A minor difficulty encountered was that the converter was, at times, difficult to control, and seemed to operate in a stable manner at only a few power settings. This made it quite difficult to operate at any temperature other than the equilibrium temperature for the stable settings. The spark-gap was cleaned twice and appeared to be in good condition each time, so that the peculiarities were attributed to a worn control mechanism.

CONCLUSION (Na-Sn)

A new method of analysis of the temperature-time curve has been devised. Various types of curves have been obtained for the same reaction, and the application of the method has given results which are consistent within the limits of probable error.

The heat of formation of Na-Sn was measured and found to be −9.63 ± 0.40 kilocalories per mole for the reaction at 873°K. On the basis of an assumption, the heat of reaction was extrapolated to 298°K at which temperature it is estimated to be −10.6 ± 0.6 kilocalories per mole.

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*Comparison of runs 1, 3, and 8, shows the following:

Run	Av. T. °C	% Na vaporized
1	615	2.42
3	650	22.4
8	625	11.6

PART II

INTRODUCTION TO THE WORK ON Li-Sn

As brought out in the introduction to the work on the determination of the heat of formation of Na-Sn alloys, the high-frequency induction coil was first used as a calorimeter by Chipman and Grant[1] in about 1943. LeRoy A. Bromley* patterned such a calorimeter along the same lines in 1946, including suitable control features which are described in the section on "Description of Apparatus and Operating Procedure," Part I.

Where similar experimental methods have been employed, the reference data now available largely fail to present the equations and theoretical bases whereby the final results tabulated were obtained. In the work on Na-Sn, a mathematical method of analysis is derived enabling one to interpret the data collected using the high-frequency calorimeter. The analytical procedure evolved and the basic assumptions stated will be found in the "Derivation of New Method of Analysis of Temperature-Time Curves," Part I, and other sections of this report. This derivation was used in calculating the final results tabulated in the summary.

The method does possess definite shortcomings. This can be seen from the sample calculations included for the Na-Sn determinations. The calculations themselves are long and laborious, especially so until one becomes familiar with the method of attack. On the other hand, shortening the method would, of necessity, cut down one's accuracy of analysis.

Kubaschewski and Seith[6] list a value for the heat of formation of Li-Sn, and in the absence of any further data, values determined using the high-frequency calorimeter will be compared with theirs.

The real test of the method lies in the consistency of results obtainable. Barring experimental error, if consistent values can be obtained from different runs in which the reaction exhibited varying rates of reaction, then a real contribution has been made in providing a means of analysis for such measurements. This research endeavors to put the equations to a further test.

Table 9. Results of determinations, Li-Sn.

Run	Addition	Kcal/mole at 850°K
6	1	−17.83 ± 2.03
	2	−17.36 ± 2.03
	3	−18.21 ± 2.03
		−17.80 ± 1.17 Average
9	1	−17.09 ± 2.03
	2	−17.14 ± 2.03
	3	−17.75 ± 2.03
		−17.33 ± 1.17 Average
		−17.57 ± 0.83 Overall average

As shown in Table 9, the three additions for run 6 and the three for run 9 were averaged. The final result tabulated is the average of these two averages.

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*Unpublished work of LeRoy A. Bromley, Ph.D., instructor in chemical engineering, University of California.

TABULATION OF RESULTS ON Li-Sn

Table 8. Summary of runs and results.

Run	No. of Li additions	Heat of reaction kcal/mole*	Comments
1	2	-	Initial height of melt in crucible too low. Temperatures obtained were not dependable. Stirrer was used.
2	2	-	Frothing occurred when Li was added. Dispenser failed. Stirrer was used.
3	2	-	Stirrer stopped when Mo was added, changing the steady-state temperature of the system.
4	2	-	Lithium pellet fell on conical shield and failed to get into melt. Stirrer was used.
5	3	-	ΔH values calculated were not consistent.† Stirrer was not used.
6	3	1st − 17.83	Instantaneous reaction.
		2nd − 17.36	
		3rd − 18.21	Noninstantaneous reaction (The stirrer was not used in run 6).
7	3	-	Power could not be maintained steady. Oxidation of reactants occurred. Stirrer was not used.
8	3	-	Oxidation of reactants occurred. Stirrer was not used.
9	3	1st − 17.09	Instantaneous reaction.
		2nd − 17.14	Instantaneous reaction.
		3rd − 17.75	Noninstantaneous reaction (The stirrer was not used in run 9).

*Values corrected to ΔH 850°K.

†See "Discussion," Part II.

One probable error calculation was made. This calculation was based on addition of run 6, which was a noninstantaneous addition. This probable error was assigned to the calculated heats of reaction for all the additions made. A summary of the factors considered in such a calculation and their relative magnitudes can be found in the work on Na-Sn.

It is of interest to speculate as to the heat of reaction at 298°K. Assuming that the change in heat content of Li-Sn is equal to the change in heat content of tin plus eight-tenths of the change in heat content of the lithium, one calculates:

$$-\Delta H_{298} = 17.57 + 0.2\ (5.23)^{8} = 18.62 \text{ kcal/mole}$$

The total probable error of this value is of the order of magnitude of 1.5 kcal.

DISCUSSION OF THE WORK ON Li-Sn

It was stated in the introduction to this work on Li-Sn that the purpose of the research was to put the mathematical means of analysis previously derived to a real test. The fact that nine runs were made before two good ones were obtained is sufficient evidence that there are many obstacles to be surmounted before one can obtain good data worthy of mathematical analysis. Extensive preliminary precautions must be taken to insure good runs, and, even so, experimental errors oftentimes occur.

Heats of oxidation of the reactants are very large (e.g., 150 kcal/mole) compared to the heats one expects in these runs, and hence one must strive to remove all traces of oxygen during an experiment. Runs 7 and 8 were accompanied by oxidation, as evidenced by the frothing of the melt following lithium additions. Deterioration of the upper portion of the reaction crucible and its surrounding shield provided confirmation. Such oxidations can be partially avoided by cleaning all metal and other surfaces to remove oxide coatings prior to the time the apparatus is assembled. Following the assembly, the reaction crucible can be brought to red heat while the calorimeter is under vacuum. Adsorbed oxygen and moisture are thus removed, the little remaining being in an unreactive state. Argon can then be bled in, the vacuum removed, and the experiment continued as described under the operating procedure.

In the final runs, the stirrer was not employed. Although a more uniform temperature throughout the melt might be expected with the use of a stirrer (e.g., localized heating partially eliminated), the geometry of the apparatus was such that best results were obtained when the stirrer was not used. The comments listed in Table 8 will bear this out. To obtain reliable temperatures in the reaction crucible, a sufficient height of melt must cover the thermocouple. On the other hand, the quantities of reactants must be such that the ΔT following a lithium addition must not exceed the limits set in the derivation. Using the calorimeter and dispenser employed previously, certain restrictions were placed on the size of reaction crucible, as can be seen from the above considerations. The resulting size actually required was such that the stirrer was stopped following a Mo addition because of insufficient clearance. This produced a new steady-state temperature and made the entire run incapable of calculation.

In run 5, three additions of lithium were made and calculated. The first two additions gave quite low results, and the last addition gave a very high result compared to the final average value tabulated. Such calculated values lead one to surmise that a fraction of the lithium pellets were held up in the first two additions, and that the "hold-ups" all went in with the last addition. Such an occurrence is quite possible.

In general, the reaction rates in this research were more rapid than in the case of the Na-Sn preparations. Also the dispenser operation was much better. One would expect this to be the case since lithium, though less dense, has a higher melting point and is less subject to deformation at low temperatures than is sodium. Consequently, pellets are not as prone to get "hung-up" in the compartments of the dispenser.

Since some of the calculations for a given addition are subject to varying interpretation, pains were taken to put the probable error on the "safe" side. From the tabulated final results in Table 9 it is evident that such is the case since the actual results calculated are better than the listed probable error justifies.

Of the six additions listed in the final tabulation of results, there is no discernible trend of values for either instantaneous or noninstantaneous type reactions. This in itself lends strong support to the mathematical procedure derived, which appears to work equally well for either reaction type.

CONCLUSION (Li-Sn)

The new method of analysis of temperature-time curves has been given another test. The results for both instantaneous and noninstantaneous type reactions are well within the probable error assigned.

The heat of formation of Li-Sn was measured and found to be 17.57 ± 0.83 kilocalories per mole for the reaction at 850°K. The heat of formation was estimated as 18.62 kilocalories per mole at 298°K. The probable error is of the order of 1.5 kilocalories at this temperature. Kubaschewski and Seith[6] give a value of 16.8 ± 1.0 kilocalories at this same temperature. No other reference values are listed.

The probable error of this research is sufficiently large to make the reference value and the value obtained from this work consistent if the former value is low, and the latter is high.

DEFINITION OF SYMBOLS

Symbol	Definition
A	Area, cm^2
a	A point on the curve of Figure 6.
B	Defined as radiation heat transfer coefficient. A_1 is used as the first approximation to that quantity.
B'	Corrected value of B.
C	Integration constant; point on curve of Figure 6.
C_p	Heat capacity of system, cal/°K.
ΣC_p	Final heat capacity of system, cal/°K.
c_p	General heat capacity, cal/°K mole.
D	Convection heat transfer coefficient, hA,(kA/L), cal/min°K.
d	Prefix denoting a differential.
F	Factor defined by: $C_{p\text{alloy}} = C_{p\text{Sn}} + FC_{p\text{Na}}$.
f	Net heat transfer rate, $-(q_{1T} - q_{1t})$, cal/min.
f' plot	The plot on which the heat Q_{II} is found.
g	Acceleration of gravity.
h	Convection heat transfer coefficient, cal/°C min cm^2.
h_c	Natural convection heat transfer coefficient; in McAdams formulae, Btu/hr ft^2 °F.
ΔH	Heat of Reaction; heat of formation, cal/mole or kcal/mole.
k	Conduction heat transfer coefficient, cal/°C cm^2 min/cm.
L	Length, feet in McAdams formulae.

Symbol	Definition
ln	Natural logarithm.
P	Defined as $(4B(t')^3 + D)$; used as first approximation to this quantity.
P'	Corrected value of P.
Q	Heat; or heat required to raise alkali from the dispenser temperature to the temperature t., cal.
Q_0	Heat equivalent to the lithium vaporized, cal.
Q_I	Heat liberated by part of the noninstantaneous reaction that can be transformed to ideal instantaneous reaction and is equal to $C_p(\Delta T)$, cal.
Q_{II}	Heat liberated by reaction after "instantaneous" portion. Found from area on f' plot out to practical time limit, cal.
Q_{III}	Heat liberated after practical time limit of Q_{II}. This quantity equals $C_p(\overline{\Delta T})$.
q	Rate of heat transfer, cal/min.
q_{1t}	Rate of heat loss at temperature t, cal/min.
q_{1T}	Rate of heat loss at temperature T, cal/min.
R	Defined as $(6B(t')^2)$; used as first approximation to this quantity.
R'	Corrected value of R.
T	Any temperature, °C, °K.
T_r	Room temperature, °K.
T_1	Temperature of inside turn on molybdenum shield, °K.
T_2	Temperature of outside turn on molybdenum shield, °K.
t	Steady-state temperature before addition, °C, °K.
t'	Equilibrium temperature after addition, °C, °K.
ΔT	Temperature difference which would have been produced if the reaction had been instantaneous; or, in the Appendices, any temperature difference, °C, °K.
$\Delta T'$	$T - t'$, °C, °K.
$\Delta T''$	Smoothed temperature differences obtained from the $\ln \frac{\Delta T'}{1 + \frac{R}{P}\Delta T'}$ vs. θ plots, °C, °K.
$(\Delta T')_0$	Temperature difference, $T - t'$ at the time corresponding to θ_0, °K.
$(\Delta T')_\theta$	Temperature difference, $T - t'$ at the time corresponding to θ, °K.
$\overline{(\Delta T)}$	$(\Delta T')_{0\text{ actual curve}} - (\Delta T')_{0\text{ theoretical curve}}$, °K.
w	Weight in moles.
β	Coefficient of volumetric expansion.
ϵ	Emissivity of a given surface, no dimensions.
μ	Viscosity, in McAdams general equation, lb/hr/ft.
ρ	Density; in McAdams general equation, lb/ft.^{3}

Symbol	Definition
σ	Stefan-Boltzmann radiation constant.
θ	Time, minutes.
θ_i	Time for the instantaneous reaction, minutes.
θ_0	Reference time in the calculation of Q_{III}.

APPENDIX I

EVALUATION OF D

The "D" for the system as used in equation (7) can be represented by an equation such as this:

$$D = \Sigma hA + \Sigma kA/L.$$

Thus evaluation of all the contributing factors allows estimation of D.

Assume that:

1. Except for radiation, natural convection is the principal factor for heat loss from the sides and top of the crucible.

2. An argon atmosphere is sufficiently like one of air to justify the use of empirical equations for heat transfer in air to calculate natural convection losses.

3. Heat losses through the thermocouple well and the stirrer are by conduction only.

4. Heat losses through the zircon stand are by conduction only.

5. Natural convection heat losses are small compared to radiation losses, so that temperatures of the outside shield and base of the zircon stand can be estimated using radiation alone.

The calculation of D, using the above assumptions, follows. Calculation of temperature of the outside shield:

The emissivity, ϵ', for an oxidized molybdenum surface is 0.7.

$$\sigma\epsilon A(t^4 - T_1^4) = \sigma\epsilon A(T_1^4 - T_2^4)$$

$$\sigma\epsilon A(T_1^4 - T_2^4) = \sigma\epsilon' A(T_2^4 - T_r^4)$$

Calculating ϵ,

$$\epsilon = \frac{1}{(1/\epsilon') + (A_1/A_2)\,[(1/\epsilon') - 1]}$$

$$= \frac{1}{(1/0.7) + [(1/0.7) - 1]} = 0.538$$

Solving, using T_r as 300°K, t as 875°K, and cancelling areas, $T_1 = 780°K$, and $T_2 = 630°K$. Using the latter temperature, and an empirical equation of McAdams,[9]

$$h_c = 0.28(\Delta T/L)^{0.25},$$

we find: $\Delta T = (630 - 300) = 330°C. = (9/5)(330) = 594°F$; $L = 8.8/(12)(2.54) = 0.289$ ft; and $h_c = 0.28 (594/0.289)^{0.25}$ or $h_c = 1.89$ Btu/hr ft^2 °F. This value is for natural convection from the sides of the outside shield, and, expressed in our units, is 0.0154 g cal/min cm^2 °C.

Calculation of Natural Convection from the Top of the Crucible

Assume this to be equivalent to a horizontal plate at the temperature of the melt. McAdams[10] gives an approximate equation for air for this type of system,

$$h_c = 0.38(\Delta T)^{0.25}.$$

$\Delta T = (875 - 300) = 575°C$; $\Delta T = (9/5)(575) = 1035°F$. $h_c = 0.38(1035)^{0.25} = 2.17$ Btu/hr ft^2 °F or 0.0176 g cal/min cm^2 °C.

Calculation of T_i, the Temperature of the Inner Horizontal Face of the Zircon Stand

The k for zircon is 0.005 g-cal/sec cm^2 °C/cm, or 0.30 g-cal/min cm^2 °C/cm.

Assume conduction through the zircon wafer (0.3 cm thick) to inner horizontal face and then heat is transferred by radiation from this face to the copper stand. Take the temperature of the top of wafer as 875° K, then,

$$q = (kA/L)(875 - T_i) = \sigma \epsilon' A(T_1^4 - 300^4);$$

L = 0.3 cm.; $\epsilon' = 0.7$; substituting and solving, $T_i = 840°K$.

Calculation of Conduction Across Gap inside Stand

k = 0.035 Btu/hr ft^2 °F/ft = 0.035(60)(0.00413) = 0.0087 g-cal/min cm^2 °C/cm. Using the value for k, kA/L = (0.3)(0.3xπx5)/2.8, or kA/L = 0.504 g-cal/min °C. Since there is a very poor thermal contact where the stand meets the copper block, it is estimated that half of the above value for kA/L is effective, or kA/L = 0.252 g cal/min °C.

Calculation of Loss Out Thermocouple Well

The cross-sectional area of the molybdenum well is 0.95 cm^2. The length to the junction with the copper tube is 15 cm. The area of the copper tube is 0.30 cm^2, and its length is 25 cm. The temperature of the end of the thermocouple in the melt is 875° K, the temperature of the end of the copper tube is 300° K. The k for molybdenum is 19 g-cal/min cm^2 °C/cm, and the k for copper is 50 g-cal/min cm^2 °C/cm. Now the ratio of the ΔT's of molybdenum to copper is:

$$\Delta T_{Mo}/\Delta T_{Cu} = k_{Cu} A_{Cu} L_{Mo}/k_{Mo} A_{Mo} L_{Cu} = 50(0.30)15/19(0.95)25 = 0.50$$

The overall ΔT is (875 − 300) = 575°C. We want the equivalent length of molybdenum which would have a ΔT of 575°C under the same conditions. This equivalent length is 3(15.0) or 45 cm. Using this equivalent length, kA/L = 19(0.95)/45 = 0.401 g-cal/min °C.

Calculation of the Loss Out the Stirrer

As an approximate value, use an equivalent length of molybdenum shaft of 45 cm; k is 19 g-cal/min cm^2 °C/cm; and A is 0.495 cm^2. Then kA/L is 19(0.495)/45 = 0.210 g-cal/min °C.

Now we have the quantities necessary to evaluate D. For the runs without the stirrer, D = (0.0154)(110.5) + (0.0176)(12.6) + 0.044 + 0.252 + 0.401 = 1.702 + 0.222 + 0.044 + 0.252 + 0.401 = 2.621 g-cal/min °C.

For runs with the stirrer, D = 2.62 + 0.21 = 2.83 g-cal/min °C.

Check of assumption (2), McAdams gives an expression from which an h_c can be found for any gaseous medium,

$$\frac{h_c L}{k} = 0.548 \frac{C_p \mu}{k} \left(\frac{L^3 \rho^2 \beta g(\Delta T)}{\mu^2}\right)^{0.25}$$

For air, $C_p \mu/k$ is 0.74; for argon, 0.69. For air, ρ is α 29; for argon, α 40. For air, β is 1/T ; for argon it is 1/T also. For air, μ is 0.034; for argon, 0.042. Then the ratio of the above equation for air to argon is, assuming k's are equal,

$$\frac{\text{air}}{\text{argon}} = \frac{(0.74)(29)^2(0.042)^2}{(0.69)(40)^2(0.034)^2} = (1.07)(0.725)^2(1.233)^2 = (0.86)^{0.25} = 0.963$$

The value of 0.963 for this ratio justifies the assumption made, as the approximate equations are probably no more exact than 0.96.

APPENDIX II

EVALUATION OF F

Comparison of the heat capacities of binary alloys with their elements indicates that the molal heat capacity of the alloy is usually less than the total molal heat capacities of its constituents. Using an empirical expression for the heat capacity of an alloy,

$$C_{p_{\text{alloy}}} = C_{p_{\text{noble metal}}} + FC_{p_{\text{base metal}}},$$

and solving for the factor F, one ordinarily finds values ranging from 0.75 to 0.9. Since, in this research, a value for F is necessary to enable one to estimate the C_p of the system at various points during a run a value of 0.80 was chosen. Although this value is below the average of the calculated values, one feels justified in its use, at least qualitatively, as sodium is more electropositive than any of the other base metals investigated. Furthermore, since the proper value for F in this case is doubtful, a large probable error is assigned.* Thus, a compensation for this value of F is adequate.

---

*The value of F used in computing probable error is 0.8 ± 0.1.

APPENDIX III

SUMMARY OF CALCULATION OF PROBABLE ERRORS (Na-Sn)

Run 1, Addition 2

Value of ΣC_p[*]	24.14 ± 3.18 cal/°C.
Amount of sodium vaporized[†]	0.46 ± 0.10 g.
Value of F[‡]	0.80 ± 0.10
Value of C_p at beginning of addition 2	23.01 ± 3.20 cal / °C.
Value of ΔT for addition 2[§]	19.8 ± 2.85°C.
Value of Q_I $(C_p(\Delta T))$	455 ± 128 cal
Value of Q_0[**]	192 ± 55 cal
Value of Q_{II}[††]	624 ± 61 cal
Value of Q_{III}[‡‡]	30 ± 0 cal
(Value of $Q_0 + Q_I + Q_{II} + Q_{III}$)	5.93 ± 0.74 kcal/mole
Value of Q[§§]	4.81 ± 0.19 kcal/mole
Value of ΔH[***]	−10.74 ± 0.77 kcal/mole
Value of ΔH_{873}	−10.76 ± 0.77 kcal/mole

---

[*] This value was obtained by taking maximum and minimum reasonable values for the slope on the ln $\Delta T'$ vs. θ plot, and calculating the possible variation in ΣC_p. This variation was averaged to give the probable error.

[†] This value was obtained from a consideration of the errors in weighings and in the analysis.

[‡] For a discussion of evaluation of F, see Appendix II.

[§] This value was calculated by taking the maximum possible deviations of the slope on the ln $\Delta T'$ vs. θ plot and following the procedure outlined under "Calculation of the Heat of Reaction from Curve 3, Run 1, in Part I to give two extreme values of ΔT. The average deviation of these ΔT's from the quoted ΔT was used as the probable error.

[**] This is calculated from the probable error in vaporized sodium and the probable error in heat content values.

[††] Using the slopes mentioned in § above, the f plot calculation was carried out. The probable error reported is the average of the deviations from the quoted value.

[‡‡] The error in Q_{III} was estimated to be negligible, since Q_{III} was calculated from an exact theoretical expression.

[§§] This value was calculated from heat capacity data given by K. K. Kelley.[7]

[***] This value represents the combination of $(Q_0 + Q_I + Q_{II} + Q_{III})$ and Q.

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