

THE THERMAL DECOMPOSITION OF SOME METAL BROMATES

by

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To my parents, Fred and Jean Bancroft

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ABSTRACT

A very simple and inexpensive apparatus for thermobarogravimetric analysis was built. As the sample was heated, temperature, pressure, and weight were plotted automatically against time by a one pen recorder. The apparatus was most useful at low initial pressures and at temperatures up to 1000° C. In the study of competitive reactions and equilibria, an unique use for the apparatus is discussed.

Thermobarograms are presented of bromates that were thermally decomposed in the apparatus. The bromates decomposed to the bromide or the oxide, depending on the cation. Although the thermobarograms of strontium bromate provided some evidence for perbromate formation, this was disproved by infra-red analysis.

Free energies of decomposition and activation energies were calculated for the decompositions. The role of kinetics and thermodynamics in predicting the decomposition of bromates is discussed.

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INTRODUCTION

The Problem

The existence and usefulness of perchlorates and periodates makes the non-existence of perbromates an interesting problem, both experimentally and theoretically. Many experimental methods have been used in the attempts to make perbromate but little evidence has accumulated for the formation of perbromate. Even the theoretical reasons proposed have not satisfactorily explained the non-existence of perbromate.

In inorganic chemistry much use is made of similarities in the elements of a group in predicting whether a compound should exist. Except in the case of elements directly following the first transition series (As, Se, Br₂), an element will form analogous compounds to those directly above and below it in the group. Thus if sodium iodate and rubidium iodate exist it could be assumed that potassium iodate also exists. However, compounds of selenium, arsenic and bromine formed in their highest possible valence states do not exist or are very unstable. Thus sulfur trioxide and tellurium trioxide are stable but selenium trioxide is very unstable.

If chlorates and iodates are carefully heated, perchlorates and periodates respectively can be formed. It should follow that perbromates can be synthesized by heating bromates. Although this method has been tried with little success, it was felt that the problem warranted a more detailed study. Thus seventeen bromates were decomposed in a newly constructed apparatus in which temperature, weight and pressure were plotted automatically against time. Although a number of recording vacuum thermobalances and pressure gauges have been described, the two have never been combined. Since a plot of weight and temperature versus time is known as a thermogram, a plot of pressure, weight, and temperature versus time is therefore called a thermobarogram.

Literature Survey

Perbromates

Many attempts have been made to make perbromates. Kammerer¹ claimed to have obtained HBrO_4 , perbromic acid, by the action of bromine vapour on HClO_4 vapour, and in a smaller quantity by distillation of HBrO_3 . From his HBrO_4 many perbromates were supposedly made. In 1876 MacIvor² repeated Kammerer's experiments and found no perbromates.

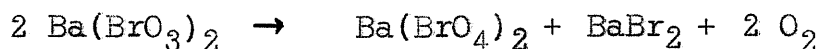
He stated that Kammerer's perbromate was probably perchlorate. Muir³ retracted his earlier observation⁴ that HBrO_4 had been formed by the action of bromine on HClO_4 . Muir also attempted to make HBrO_4 by the electrolysis of HBrO_3 but failed. Bromine water was electrolyzed by Riche⁵ without the formation of perbromate.

Rammelsburg⁶ found that perbromates were not made by heating bromates. Robertson⁷ reported that perbromates were not formed by the action of bromine on KClO_4 , by the action of bromine on NaIO_4 , or by warming KBrO_3 with PbO_2 , a very strong oxidizing agent. Fritzsche⁸ assumed that KBrO_4 and KBrO_2 were formed when solid KBrO_3 was heated. This was disproved by Potylizyn⁹ and also by Cook¹⁰. Likewise, perbromate was not formed by heating $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ ¹¹. In 1901, another unsuccessful attempt to prepare perbromates was made¹² using perchloric acid, chloric acid and chlorine dioxide on bromine.

Allison^{13,14} claimed to have detected the presence of perbromate in solutions of bromine and HClO_4 with his magneto optic method. There has been much doubt about the existence of this phenomenon even though Hughes¹⁵ and Bond¹⁶ have shown it to exist. No perbromate was isolated from these solutions.

Hackspill and Winterer¹⁷ thermally decomposed calcium, strontium and barium bromates and followed the

decompositions by measuring the pressure of oxygen evolved. They showed the possible existence of a perbromate of barium over the temperature range 265° - 300° . They postulated the following reaction:



However no plateau was formed which would indicate the formation of a compound. They interpreted the rapid decomposition to be due to the rapid evolution of oxygen from the perbromate. This interpretation does not seem to be adequately substantiated.

Two more recent efforts have been made to prepare perbromate. Decoursey¹⁸ tried many varied methods, all of which failed. The bromate was reacted with the strongest oxidizing agents - fluorine, ozone, peroxydisulfate, peroxides and superoxides. Thermal decomposition of a few bromates was also tried. This method gave some small unexplainable evidence for the formation of $\text{Ba}(\text{BrO}_4)_2$. A definite inflection point appeared when $\text{Ba}(\text{BrO}_3)_2$ was heated at 340° for less than an hour. However using "wet" analytical methods for detection, Decoursey could find no other evidence for perbromate. It is felt that Decoursey's methods of analysis were unsatisfactory. X-ray or infra red analysis could more clearly

elucidate the structural changes at the inflection point.

Rocchiccioli¹⁹ used a Chevenard thermobalance to follow the weight changes when bromates were heated. He found no discontinuities in any of the decomposition curves. Infra-red analysis of the bromates was made. This information would be very useful if any discontinuities were observed in thermograms of bromates.

Although all of the above methods have failed in the preparation of perbromate, nearly all have been used to prepare perchlorates and periodates. This apparent anomaly has been explained by a few theoretical studies. An early statement by Robertson⁷, that the interatomic vibrations are probably too strong for the molecule to hold together was based on no theoretical reasoning. He believed that since perbromate had not yet been prepared it was unstable. This, however, is not necessarily true as seen by the recent preparation of xenon and krypton compounds.

Hugus²⁰ reversed the reasoning by stating that the stability of the higher oxidation states of iodine, antimony and tellurium was abnormal rather than the absence of AsCl_5 and HBrO_4 .

Pauling²¹ stated that the non-existence of perbromate could be explained because it lies between a

stable acid with a co-ordination number of four, HClO_4 , and a stable acid with a co-ordination number of six, H_5IO_6 . However this explanation is not valid because of the existence of salts of periodic acid such as KIO_4 with a co-ordination number of four.

Nyholm²² and Dasent²³ traced the non-existence of perbromates to the firmness with which the 4s electron pair is bound in atoms such as arsenic, selenium and bromine. The ground state electronic configuration of the bromine atom is as follows: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$. In order for bromine to exist in a +7 valence state, the two 4s electrons must be shared or lost. However the build up of charge across the first transition series combined with the weak screening effect of the 3d electrons, helps to make z^* , the effective nuclear charge that the 4s electrons see, larger than the z^* that the 3s electrons see in chlorine. Nyholm cited Fig. 1 as evidence using the fifth group elements. Trace A shows the promotion energy of an $s^1 \rightarrow d^1$ transition. Trace B shows the difference between the fourth and the third ionization potential. The fourth electron is an s electron for these elements. The promotion energy for the $s^2 p^1 \rightarrow s^2 d^1$ transition is illustrated in trace C. Traces A and B show that the s electrons in arsenic and bismuth are held

FIGURE 1

Promotion energies for Group 5 elements

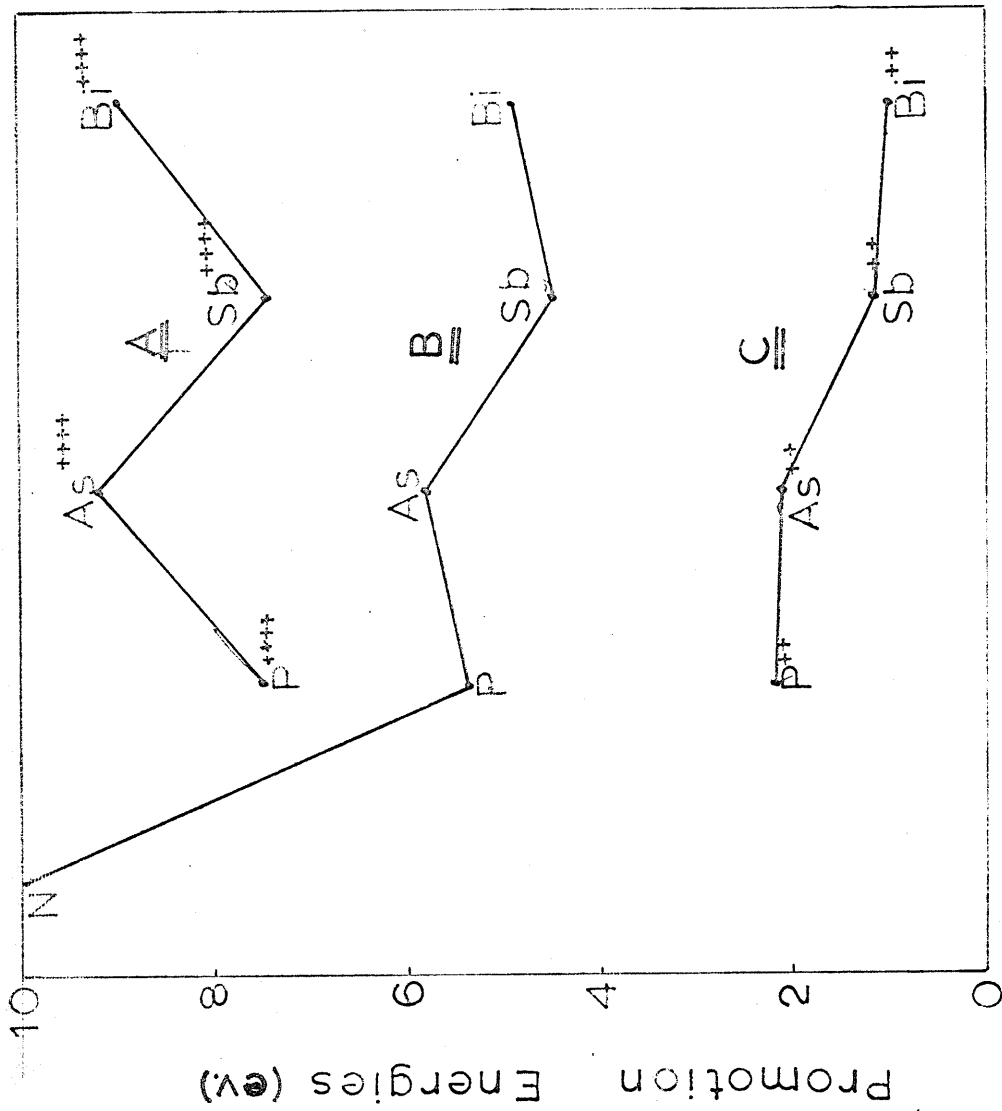


FIG. 1 PROMOTION ENERGIES FOR GROUP 5 ELEMENTS

more tightly than the s electrons in phosphorous and antimony. However as illustrated in trace C, the s electrons, which are effective shielding electrons, overcome the poor shielding of the 3d electrons. These three traces give good evidence for the relative instability of the +5 valence state of arsenic and bismuth and possibly, by extrapolation, for the non-existence of the +7 valence state of bromine.

A more recent hypothesis by Urch²⁴ made use of quantum mechanical considerations. It was suggested that the stability of the perchlorate ion is due mainly to the strong π bonding between the 3d orbitals of chlorine and the 2p orbitals of oxygen. Normalized hydrogen-like radial functions were plotted for the 3d and 4d orbitals. From this plot, the 4d orbitals of bromine would form very weak π bonds with the 2p orbitals of oxygen because of very poor overlap. Since it was assumed that the σ framework for perbromate would be similar to that for perchlorate, the absence of good π bonding would make the perbromate very unstable. That the 3d or 4d orbitals are involved in π bonding has not been verified experimentally. However group theory²⁵ shows that the d orbitals have the right symmetry properties for overlap with the lone pair orbitals on the oxygen atom. This hypothesis is certainly not con-

clusive evidence for the non-existence of perbromates.

Bromates

Table 1 lists the decomposition products and melting point of some bromates that have been studied by previous workers. It should be noted that no studies of the decomposition of the bromates of lithium, rubidium, cesium, praseodymium, yttrium or neodymium have been made. The melting points listed in this table are usually above the initial decomposition temperature and therefore are not accurately known.

Thermobarogravimetric Analysis

Methods used for weight, temperature and pressure detection will be briefly discussed in this section. Some errors in these measurements in thermobarogravimetric analysis will also be mentioned.

Thermogravimetry or T.G.A., as defined by Newkirk³², is the science or art of weighing substances while they are being heated. Thermogravimetry, when combined with such techniques as X-ray diffraction and infra red analysis, is an excellent method for determining thermal stabilities of compounds. New compounds have been detected by this method³³. Other complimentary techniques, such as differential thermal analysis (D.T.A.) and differential

TABLE 1
Decomposition Products of Some Bromates

Bromate	M.P., -°C	Decomposition Products	References
LiBrO ₃	248	-	-
NaBrO ₃	381	NaBr + O ₂	18, 19, 26, 27
KBrO ₃	434	KBr + O ₂	6, 9, 10, 18, 19, 28, 31
RbBrO ₃	430	-	-
CsBrO ₃	420	-	-
Mg(BrO ₃) ₂	200	MgO + O ₂ + Br ₂	6, 9, 29
Ca(BrO ₃) ₂	230	CaBr ₂ + O ₂	6, 17, 19
Sr(BrO ₃) ₂	240	SrBr ₂ + O ₂	17, 19, 30
Ba(BrO ₃) ₂	260	BaBr ₂ + O ₂	11, 18, 19
Zn(BrO ₃) ₂	200	ZnO + O ₂ + Br ₂	6, 19
Cd(BrO ₃) ₂	-	CdBr ₂ + CdO + O ₂ + Br ₂	26
AgBrO ₃	315	AgBr + O ₂	6, 19, 29
Co(BrO ₃) ₂ · 2H ₂ O	140	CoO + O ₂ + Br ₂	19, 26
Ni(BrO ₃) ₂	210	NiO + O ₂ + Br ₂	19, 26
Pr(BrO ₃) ₃ · 9H ₂ O	-	-	-
Y(BrO ₃) ₃	-	-	-
Nd(BrO ₃) ₃ · 9H ₂ O	-	-	-

- signifies not known

gravimetry (D.G.A.) are now being employed in conjunction with thermogravimetry to determine the temperature of phase changes, allotropic modifications and other calorific phenomena. These could occur without the loss of weight and would not be detected by thermogravimetry.

The instrument used to perform thermogravimetric analysis is a thermobalance, first used by Honda in 1915³⁴. The first thermobalances were modified analytical balances with the sample hanging from one pan into a furnace. As the sample lost weight, the change in position of a point on the balance arm was noted with an eyepiece.

The first thermobalance that recorded weight changes photographically was invented by Chevenard³⁵. Photographic paper on a rotating drum recorded changes in the position of a mirror, which in turn was due to the change in weight of the heated sample.

Different weight sensitive elements have been used. Quartz and metal springs were first used by McBain³⁶, and a cantilever rod was used by Heinrichs³⁷. The extension of the spring is directly proportional to the weight on it, if the elastic limit of the spring is not exceeded. McBain followed the weight loss with an eyepiece.

These thermobalances were made recording by

Hooley³⁸, Campbell and Gordon³⁹, and Heinrichs³⁷. An excellent review on automatic and recording balances has recently appeared⁴⁰. In many of these balances, a linear variable differential transformer (L.V.D.T.) records the weight loss automatically. The output from the transformer is directly proportional to the position of an iron core which in turn is directly proportional to the weight of the sample.

The basic L.V.D.T. consists of three coils axially spaced on a cylindrical form with a rod shaped magnetic core positioned inside the coil assembly which provides a preferred path for the magnetic flux linking the coils. When the primary or centre coil is energized with alternating current, voltages are induced in the two secondaries. The two secondary coils are connected in series opposition so that the two voltages in the secondary circuit are opposite in phase. The net output from the transformer is the difference between these two voltages. For one central position of the core, the output voltage will be zero. This is called the balance or null position.

When the core is moved from this balance point by loss of weight and contraction of the spring, the voltage induced in the coil towards which the core is moving increases, while the voltage induced in the opposite coil

decreases. This produces a differential voltage output from the transformer which with proper design varies linearly with change in core position. Motion of the core in the opposite direction beyond the null position produces a similar linear voltage but with phase shifted 180° . The output voltage is a linear function of core displacement within a range of about five mm. The linear range and sensitivity of the L.V.D.T. vary with the voltage and frequency of the input. Most of the standard L.V.D.T. types have been designed for an input voltage of 6.3 V and 60 cycles input frequency. However a lateral torque, which increases with increasing input voltage usually necessitates using a much lower input voltage. This lateral torque causes a loosely held core to strike the inside of the transformer, thus making measurement impossible unless a lower input voltage is used.

Other balances, designated null type balances have recently been used⁴¹. A sensitive element such as an L.V.D.T. detects the slightest deflection of the balance arm. An adjusting force, which may be mechanical or electrical, is applied to the beam and returns it to null position. This adjusting force, proportional to the change in mass of the heated substance, is usually recorded directly.

The temperature of the heated substance, which usually rises linearly with time, is measured by a thermocouple. This linearity is controlled by controlling the input voltage to the heating element by a motor driven variable autotransformer.

Pressure in a dynamic system has been measured in many different ways. The simplest follows the changes in position of mercury in a manometer. Low pressures due to a single gas have been measured by a precalibrated Pirani gauge⁴². The action of the Pirani gauge depends on the fact that at low pressures, the thermal conductivity of a gas is proportional to its pressure. Another useful device for pressure measurement is the Bourdon gauge^{43,44}, the action of which depends on the movement of a thin diaphragm of glass under applied differential pressure. It is extremely useful in being direct reading and it can be sealed directly to the reaction system. Because of its all glass construction, the Bourdon gauge can be used to measure pressures of corrosive gases such as bromine. Initially the position of the tip of the spoon was followed by a travelling microscope^{43,44}. Hooley⁴⁵ made this recording by following the position of the tip of the spoon with a linear variable differential transformer. The position of the tip is usually directly proportional to the differential pressure and thus the voltage output

from the L.V.D.T. is directly proportional to the differential pressure. Other devices such as the ionization gauge^{47,46} and the automatic gauge of Laidler⁴⁸ have also been used for pressure measurement in a dynamic system.

There are many problems encountered in thermogravimetry³². If the sample is being heated in air or under high pressures, convection currents will increase as the heating rate increases. This will cause the apparent weight of the sample to fluctuate. Air buoyancy due to differences of temperature in the reaction vessel will tend to give inaccurate weight readings. If the sample is heated too quickly or if the reaction is highly exothermic or endothermic, then the temperature recorded by the thermocouple will be significantly different than that of the sample. Thus heating rates should be as low as possible if accurate temperature readings are desired. Buoyancy and convection are essentially eliminated when the reaction chamber is evacuated. However, so called radiometric or aerodynamic effects^{49,50}, due mainly to molecules of gas randomly striking the sample crucible, become important, especially when micrograms are being weighed.

The effect of sample size, type of reaction chamber, size and shape of crucible and type of support for the crucible on the accuracy of the weight readings have

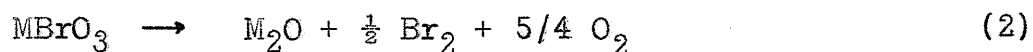
been studied³². In the majority of cases, all the errors mentioned can be eliminated, or compensated for, by modifications of the apparatus or by "blank" corrections.

Thermodynamics

Free Energy Differences

Metal bromates decompose to the metal bromide and oxygen or to the metal oxide, bromine and oxygen. The reason for this two fold mode of decomposition could possibly be justified by thermodynamics. The methods used in calculating the free energies of decomposition will be described in this section.

Markowitz⁵¹ has used thermodynamics to predict the decomposition products of metal perchlorates. As is the case with metal perchlorates, bromates decompose to leave a residue of either the oxide, the halide, or a mixture of the oxide and halide. The percentage of oxide or halide formed depends on the cation. It seems reasonable to assume that the following two reactions are competing:

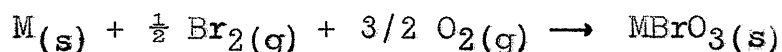


Let the free energy of decomposition of reaction (1) be

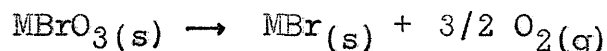
ΔF_{D1} and the free energy of reaction (2) be ΔF_{D2} . Since the free energy of formation of only potassium bromate is known⁵⁴, ΔF_{D1} and ΔF_{D2} could be calculated only for potassium bromate. However the relative importance of reaction (1) and (2) could be predicted by considering $\Delta F_{D1} - \Delta F_{D2}$. If this quantity is negative then reaction (1) should predominate; if this quantity is positive then reaction (2) should predominate. $\Delta H_{D1} - \Delta H_{D2}$ would also be useful in predicting the decomposition products. In the second part of this section the heats of formation of all the alkali bromates are determined. Then ΔH_{D1} and ΔH_{D2} can be calculated if the heats of formation of the bromide and oxide are known.

$\Delta F_{D1} - \Delta F_{D2}$ can be easily calculated knowing the ΔF_f of M_2O and MBr as follows:

For monovalent cations

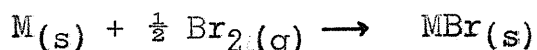


Let the free energy change in this reaction be $\Delta F_f BrO_3^-$



Let the free energy change in this reaction be ΔF_{D1}

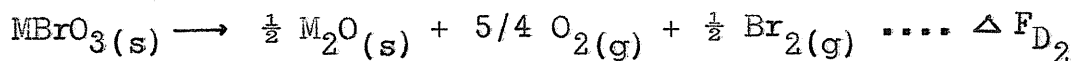
Adding the above two equations there is obtained:



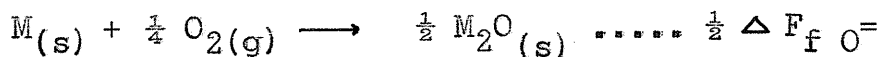
Let the free energy change in this reaction be $\Delta F_f \text{ Br}^-$

$$\text{Thus } \Delta F_f \text{ Br}^- = \Delta F_f \text{ BrO}_3^- + \Delta F_{D1} \quad (3)$$

Similarly:



Adding the above two equations:



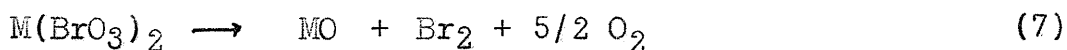
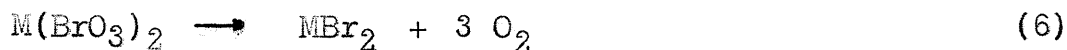
$$\text{Thus } \frac{1}{2} \Delta F_f \text{ O}^- = \Delta F_f \text{ BrO}_3^- + \Delta F_{D2} \quad (4)$$

Subtracting (4) from (3)

$$\Delta F_f \text{ Br}^- - \frac{1}{2} \Delta F_f \text{ O}^- = \Delta F_{D1} - \Delta F_{D2} \quad (5)$$

It should be noted that gaseous bromine is not the standard state for bromine. However, Smithells,⁵¹ used the ideal diatomic gas as the standard state for bromine when computing the free energy values. Thus no correction term is needed.

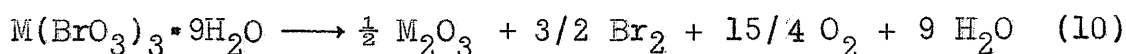
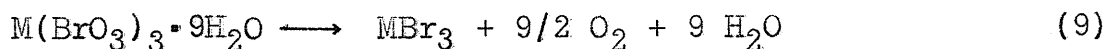
For divalent cations the following two reactions are probably competing:



Similarly in this case:

$$\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^- = \Delta F_{D6} - \Delta F_{D7}$$

For trivalent cations the two competing reactions should be:



In this case:

$$\Delta F_f \text{ Br}^- - \frac{1}{2} \Delta F_f \text{ O}^- = \Delta F_{D9} - \Delta F_{D10} \quad (11)$$

As indicated by equations (9) and (10) the bromates of trivalent cations lose their water at the same time as they decompose to the oxide or the bromide. However, the water term cancelled when $\frac{1}{2} \Delta F_f \text{ O}^-$ was subtracted from $\Delta F_f \text{ Br}^-$. Thus the water has no thermodynamic significance in $(\Delta F_{D9} - \Delta F_{D10})$. However it may be important in ΔF_{D9} or ΔF_{D10} separately.

Except for the rare earth bromides, the free energy data needed for equations (5), (8) and (11) was easily found^{52, 53, 54} (see Appendix). For the free energies of formation of neodymium, yttrium, and praseodymium bromides, it was necessary to use the average of the free energies of formation of the iodide and the chloride plus a small

correction factor (2 kcal.) as the free energies of formation of the bromides. This assumption was quite satisfactory as seen in Table 2a. In all cases the postulated values are within three kcal. of the true value. Using this assumption, the free energy of formation of the bromides was calculated at three different temperatures. The free energies of formation of the chloride and the iodide are only given in Table 2b for one temperature. (See the Appendix for the other values).

Heats of Formation of Alkali Bromates

Although the $\Delta F_{f(s)}$ and $\Delta H_{f(s)}$ values for the bromates are not known except for potassium bromate⁵⁴, $\Delta H_{f(\text{infinite dilution})}$ is known for lithium and sodium bromates⁵⁵. $-\Delta H_{f(s)}$ is defined as the heat evolved when a bromate is formed from its elements in the standard state and

$$\Delta H_{f(\text{infinite dilution})} = \Delta H_{f(s)} + S$$

where S = heat of solution.

S could be determined in a calorimeter and $\Delta H_{f(s)}$ is then known for lithium, sodium, and potassium bromates. However Morris has described a method⁵⁶ whereby the heat of formation of the bromate ion and the heats of formation of all the alkali bromates could be calculated. Once

TABLE 2a

$\Delta F_f \text{ Br}^-$ Calculated from $\frac{\Delta F_f \text{ Cl}^- + \Delta F_f \text{ I}^-}{2} + 2$ in kcal.
per Equivalent, Compared with Literature Values at 27° C.

Cation	$-\Delta F_f \text{ Cl}^-$	$-\Delta F_f \text{ I}^-$	$-\frac{\Delta F_f \text{ Cl}^- + \Delta F_f \text{ I}^-}{2} + 2$	$-\Delta F_f \text{ Br}^-$ from (51)
Ca	180.0	131.9	157.9	156.8
Cd	82.6	52.8	69.7	72.0
Cs	99.5	84.3	93.9	94.1
K	97.7	79.6	90.6	90.3
Li	91.9	66.8	81.3	80.7
Mg	141.7	90.4	118.1	119.6
Na	91.9	70.2	83.1	82.8

TABLE 2b

Calculated Values of $\Delta F_f \text{ Br}^-$ in kcal. per Equivalent for the
Rare Earth Bromides

Cation	$-\Delta F_f \text{ Cl}^-$ 27° C	$-\Delta F_f \text{ I}^-$ 27° C	$-\Delta F_f \text{ Br}^-$ 27° C	$-\Delta F_f \text{ Br}^-$ 227° C	$-\Delta F_f \text{ Br}^-$ 727° C
Nd	228.8	157.9	195.4	182.0	155.5
Y	219.0	147.3	185.1	173.9	149.5
Pr	241.0	166.3	205.6	194.7	168.6

$\Delta H_f \text{MBrO}_3$ is known for the alkali bromates, ΔH_{D1} and ΔH_{D2} could be calculated from equations (1) and (2).

$$\Delta H_{D1} = -\Delta H_f \text{MBrO}_3 + \Delta H_f \text{MBr} \quad (12)$$

$$\Delta H_{D2} = -\Delta H_f \text{MBrO}_3 + \frac{1}{2} \Delta H_f \text{M}_2\text{O} \quad (13)$$

where $-\Delta H_{D1}$ is the heat released when the bromate decomposes to the bromide and $-\Delta H_{D2}$ the heat released when the bromate decomposes to the oxide. However as seen in Table 3 which is reproduced from Markowitz⁵¹, ΔH_{D_a} and ΔH_{D_b} could not be used to determine whether reaction (a) or reaction (b) should proceed because of the large entropy term. Thus ΔH_D for the preferred reaction is still positive. However $\Delta H_{D_a} - \Delta H_{D_b}$ is very nearly equal $\Delta F_{D_a} - \Delta F_{D_b}$ and the decomposition products could be predicted using $\Delta H_{D_a} - \Delta H_{D_b}$ for perchlorates, since the entropy changes in the two modes of decomposition are nearly identical.

The method used in calculating the heats of formation of the alkali bromates will now be discussed. The lattice energy of a crystal MX is included in the following thermodynamic cycle.

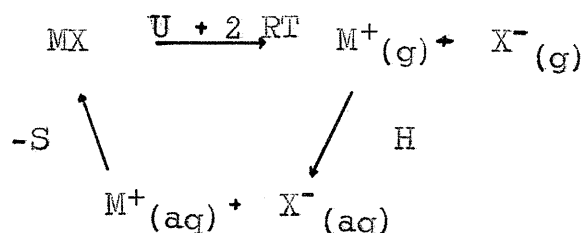
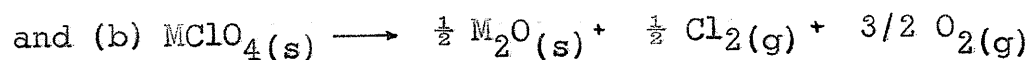
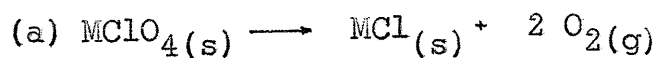


TABLE 3

Thermodynamic Changes Involved in the Decompositions of the
Alkali Metal Perchlorates at 25° C ⁵¹

via



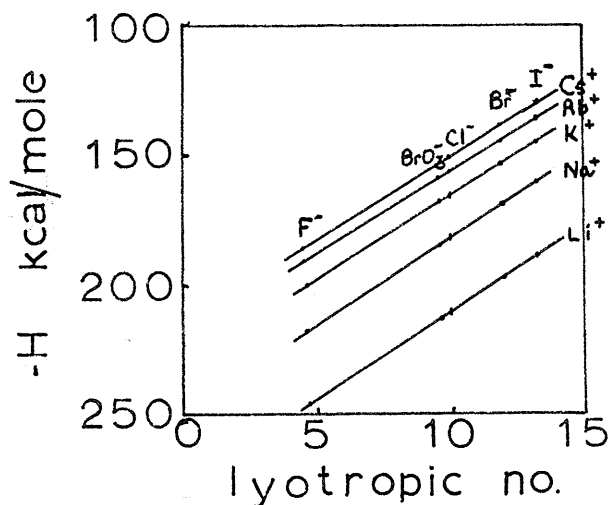
Perchlorate	ΔF° kcal/mole		ΔH° kcal/mole		ΔS° cal/mole ^o	
	by(a)	by(b)	by(a)	by(b)	by(a)	by(b)
K	-25.0	+34.2	+0.7	+61.1	+86.2	+90.2
Rb	-25.3	+38.4	+1.0	+64.4	+88.2	+87.2
Cs	-26.2	+41.3	+0.4	+65.9	+89.2	+82.5

The cycle is given in terms of enthalpies where U is the lattice energy of MX , H is the enthalpy of hydration of the two gaseous ions, and S is the standard enthalpy of solution of $MX(s)$. The $2RT$ is much smaller than U and will be neglected in this approximate treatment. Since the changes in enthalpy must equal zero for a cycle:

$$U = -H + S \quad (14)$$

Thus if H and S were known, the lattice energy could be calculated. S could be determined using a calorimeter and H could be derived from the empirical correlation between ion hydration heats and lyotropic number.

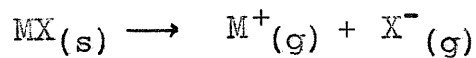
The lyotropic number as developed by Buchner, Voet and Bruins⁵⁷ is a quantitative expression of the position of an anion in the lyotropic series. It had been shown that on salting out lyophilic colloids with mixtures of sodium sulfate and other sodium salts, the amount of both salts necessary to bring about flocculation was related linearly. From graphs of the amount of different alkali salts needed to salt out the colloid, an empirical number called the lyotropic number was derived. When the lyotropic number was plotted against H , the heat of hydration, a linear relationship was obtained as seen in the following figure:



Since the lyotropic number of the bromate is known (9.55), the heat of hydration, H , of the alkali bromates could be easily calculated. Thus

$$U = -H + S$$

could now be calculated. For the reaction



U , the lattice energy, is the energy needed for the above reaction to proceed. However

$$U = -\Delta H_f \text{MX}_{(s)} + \Delta H_f \text{M}^+_{(g)} + \Delta H_f \text{X}^-_{(g)} \quad (15)$$

Rearranging equation (15)

$$\Delta H_f \text{X}^-_{(g)} = U - \Delta H_f \text{M}^+_{(g)} + \Delta H_f \text{MX}_{(s)} \quad (16)$$

Substituting (14) into (16)

$$\Delta H_f \text{X}^-_{(g)} = -H + S - \Delta H_f \text{M}^+_{(g)} + \Delta H_f \text{MX}_{(s)} \quad (17)$$

Three values of $\Delta H_f \text{BrO}_3^-_{(g)}$ could now be calculated using

the known values of H , S , $\Delta H_f M^+(g)$ and $\Delta H_f MX(s)$ for lithium, sodium and potassium bromates. The average of the three values will be taken as $\Delta H_f BrO_3^-(g)$. Once $\Delta H_f BrO_3^-(g)$ is known, equation (17) could be used to calculate $\Delta H_f MBrO_3(s)$ for all the alkali bromates.

Heats of reaction could now be calculated for reactions (1) and (2) p. 16 using equations (12) and (13). As seen in Table 3 a positive ΔH_{D1} would not necessarily suggest that reaction (1) should not proceed because of the large entropy term. However $\Delta H_{D1} - \Delta H_{D2}$ could be useful in predicting the decomposition products since the entropy changes for the two modes of decomposition should be about equal, as in the case of the perchlorates.

$\Delta H_f BrO_3^-(g)$ would also be useful in obtaining $\Delta H_f MBrO_3$ for other bromates since U could be calculated using other methods.

The Kinetics

Purely thermodynamic principles by themselves cannot determine the absolute rate of a reaction though, of course, they may impose conditions to which the kinetic results must conform. Some reactions are energetically favourable, but the rate is so slow that they effectively do not proceed. Thus two kinetic parameters E^* , the

activation energy and A, the pre-exponential factor, were calculated.

A number of investigators have obtained kinetic parameters by the analysis of thermograms^{58,59,60,61}. The first two methods^{58,59} involve either graphic or numerical differentiation of the thermogram, a procedure which is very cumbersome and subject to very large errors. Horowitz⁶⁰ has recently derived a simple integral method from which pyrolysis rate parameters (A and E*) could be easily extracted. The method is based on a combination of the reaction rate dependence on concentration:

$$\frac{dC}{dt} = -kC^n \quad (18)$$

where C = mole fraction

n = order of reaction

t = time

k = specific rate constant

and on temperature:

$$k = A e^{-\frac{E^*}{RT}} \quad (19)$$

where A = frequency factor

E* = activation energy

R = gas constant

T = absolute temperature

The assumption was made that for inorganic pyrolysis n, the order of reaction is one. Substituting k from equation (19)

into (18) and integrating:

$$\int d \ln C = \int_0^t -A e^{-\frac{E^*}{RT}} dt \quad (20)$$

$$\text{Let } \frac{dT}{dt} = q \text{ the heating rate} \quad (21)$$

$$\text{Let } C = \frac{W - W_f}{W_0 - W_f} \quad (22)$$

where W = weight of sample at time t

W_0 = weight of sample at time $t = 0$

W_f = weight of sample at the end of the pyrolysis

C varies from 1 at $t = 0$ to 0 at $t = t_f$ as the mole fraction should.

Substituting (22) and (21) into (20) and integrating

$$\ln \frac{W_0 - W_f}{W - W_f} = + \int_0^T \frac{A}{q} e^{-\frac{E^*}{RT}} dT \quad (23)$$

In general pyrolysis occurs over a fairly narrow range of temperature. A reference temperature T_s is defined such that at $T = T_s$

$$\frac{W_0 - W_f}{W - W_f} = \frac{1}{e} \quad (24)$$

where e = the base of natural logarithms.

θ is defined such that

$$T = T_s + \theta \quad (25)$$

$$\text{Then } \frac{1}{T} = \frac{1}{T_s + \theta} = \frac{1}{T_s(1 + \frac{\theta}{T_s})} \cong \frac{1 - \frac{\theta}{T_s}}{T_s} \text{ since } \frac{\theta}{T_s} \ll 1$$

Using this approximation, (23) on integration yields:

$$\ln \frac{W_o - W_f}{W - W_f} = \frac{+A}{q} \frac{RT_s^2}{E^*} e^{-\frac{E^*}{RT_s}} e^{\frac{E^*\theta}{RT_s^2}} \quad (26)$$

This expression can be simplified since at

$$T = T_s, \theta = 0 \text{ and } \frac{W_o - W_f}{W_o - W_f} = \frac{1}{e}$$

At $\theta = 0$ equation (26) becomes

$$+1 = \frac{A}{q} \frac{RT_s^2}{E^*} e^{-\frac{E^*}{RT_s}} \quad (27)$$

Substituting (27) into (26) one obtains

$$\ln \frac{W_o - W_f}{W - W_f} = e^{\frac{E^*\theta}{RT_s^2}} \quad (28)$$

Taking the natural log of both sides, equation (28) becomes:

$$\ln \ln \frac{W_o - W_f}{W - W_f} = \frac{E^*\theta}{RT_s^2} \quad (29)$$

A can now be calculated using equation (27). Thus a plot of

$$\ln \ln \frac{W_o - W_f}{W - W_f}$$

against θ should give a straight line the slope of which is

$$\frac{E^*}{RT_s^2},$$

for any first order reaction where the total number of moles

of solid is constant.

Since

$$W_o = W_f + BP_f \quad (30)$$

$$W_t = W_o - BP_t \quad (31)$$

$$\text{where } B = \frac{V M}{R T}$$

M = molecular weight of the gas evolved

Substitution of equations (30) and (31) into (29) yields:

$$\ln \ln \frac{P_f}{P_f - P} = \frac{E^* \theta}{RT_s^2} \quad (32)$$

Thus the activation energy for the decomposition could be calculated using both the weight and the pressure readings.

Nyholm has written²², "it is trite but true to say that whereas the formation of an organic compound is usually kinetically controlled, the product formed in an inorganic reaction is usually decided by the laws of thermodynamics". The thermodynamic and kinetic results for the decomposition of bromates could be a good check on this statement.

EXPERIMENTAL

Compounds Used

The following list of compounds includes those prepared and those which were used during the course of this research.

NaBrO_3 - Fischer certified reagent grade, Lot #723564.

KBrO_3 - Fischer certified reagent grade, Lot #706154

$\text{Na}_2\text{S}_2\text{O}_3$ - Baker analyzed reagent, Lot #4499.

KI - Mallinkrodt analytical reagent, Control CLNG14.

BaCl_2 - Baker and Adams reagent, Code 1408.

AgNO_3 - Johnson, Matthey and Mallory reagent grade.

$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ - Obtained from Menno Heinrichs³⁷.

AgBrO_3 - Prepared by adding 100 grams of AgNO_3 to the stoichiometric amount of hot NaBrO_3 . The precipitated AgBrO_3 was washed several times to eliminate any NaNO_3 . The AgBrO_3 was then dried under vacuum at 80°C .

$\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ - Prepared by dissolving 100 grams of BaCl_2 in water and adding the theoretical amount of NaBrO_3 . The slightly soluble $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ precipitated and the solution was cooled. The $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ was washed several times to eliminate any NaCl . The $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ was then dried under vacuum at 80°C .

The remainder of the bromates were prepared from AgBrO_3 or $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ in the following two ways:

(A) The stoichiometric amount of MCl was added to about three grams of AgBrO_3 dissolved in 500 ml H_2O with AgBrO_3 in slight excess. The AgCl was filtered and the large volume was evaporated usually at 80°C under vacuum to about 20 ml. Any excess AgBrO_3 precipitated and was filtered. The solution was then evaporated to dryness and about three to four grams of the bromate was obtained.

(B) The stoichiometric amount of MSO_4 was added to about four grams of $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ dissolved in 200 ml of hot water with $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ in slight excess. The BaSO_4 precipitated and was filtered. The solution was evaporated to about ten mls. Any excess $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ precipitated and was filtered. The solution was then evaporated under vacuum and about four grams of the bromate was obtained.

LiBrO_3 - Prepared from AgBrO_3 and LiCl , British Drug House reagent.

RbBrO_3 - Prepared from AgBrO_3 and Fischer Scientific RbCl #770266 purified.

CsBrO_3 - Prepared from AgBrO_3 and Fischer Scientific CsCl #771586 purified.

$\text{Mg}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ - Prepared from $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ and May and Baker #58968 $\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ reagent.

- $\text{Ca}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ - Prepared from AgBrO_3 and #G93062 May
and Baker CaCl_2 reagent.
- $\text{Co}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ - Prepared from $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ and
Mallinkrodt reagent grade $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ #CLNS18. This
was dried at 45°C .
- $\text{Ni}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ - Prepared from $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ and Fischer
#712889 $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ reagent.
- $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ - Prepared from $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ and
Mallinkrodt reagent grade ZnSO_4 Control #CKKX8.
- $\text{Cu}(\text{BrO}_3)_2$ - Prepared from $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ and May and
Baker $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Control #G52965. This was dried
at 45°C .
- $\text{Eu}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ - Prepared from AgBrO_3 and Lindsay EuCl_3
LT0321 Code 1023.
- $\text{Dy}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ - Prepared from AgBrO_3 and Lindsay DyCl_3
LT0523 Code 1735.
- $\text{Gd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ - Prepared from AgBrO_3 and Lindsay LT0504
Code 9399.
- $\text{Pr}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ - Prepared from AgBrO_3 and Lindsay PrCl_3
LS1113 Code 7499.
- $\text{Ho}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ - Prepared from AgBrO_3 and Lindsay HoCl_3
LT0507 Code 1635.
- $\text{Sm}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ - Prepared from AgBrO_3 and Lindsay SmCl_3
LT0412 Code 833.

$\text{Er}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ - Prepared from AgBrO_3 and Lindsay ErCl_3
LP0812 Code 1335.

$\text{Y}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ - Prepared from AgBrO_3 and Lindsay YCl_3
LR1129 Code 1135.

$\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ - Prepared from AgBrO_3 and Lindsay NdCl_3
LT0606 Code 6499.

An attempt was also made to synthesize $\text{Be}(\text{BrO}_3)_2$ and $\text{Fe}(\text{BrO}_3)_3$. The $\text{Be}(\text{BrO}_3)_2$ solution was evaporated at 20°C under vacuum. The $\text{Be}(\text{BrO}_3)_2$ decomposed with the evolution of bromine when the concentration of the solution was about 0.5 Molar. The $\text{Fe}(\text{BrO}_3)_3$ decomposed at a concentration of 0.1 M even in acid solution.

Methods of Analysis

All the bromates were analyzed for bromate purity by the potentiometric method of Britton and Britton⁶². About 0.1 gram of bromate was dissolved in 75 mls of water and 8 mls of concentrated H_2SO_4 . A 0.1 N KI solution was made and used as the titrant. A typical titration curve is shown in Fig. 2. The great advantage of this method was the very small amounts of bromate that were needed in the analysis. The results of the analysis of most of the bromates are shown in Table 4.

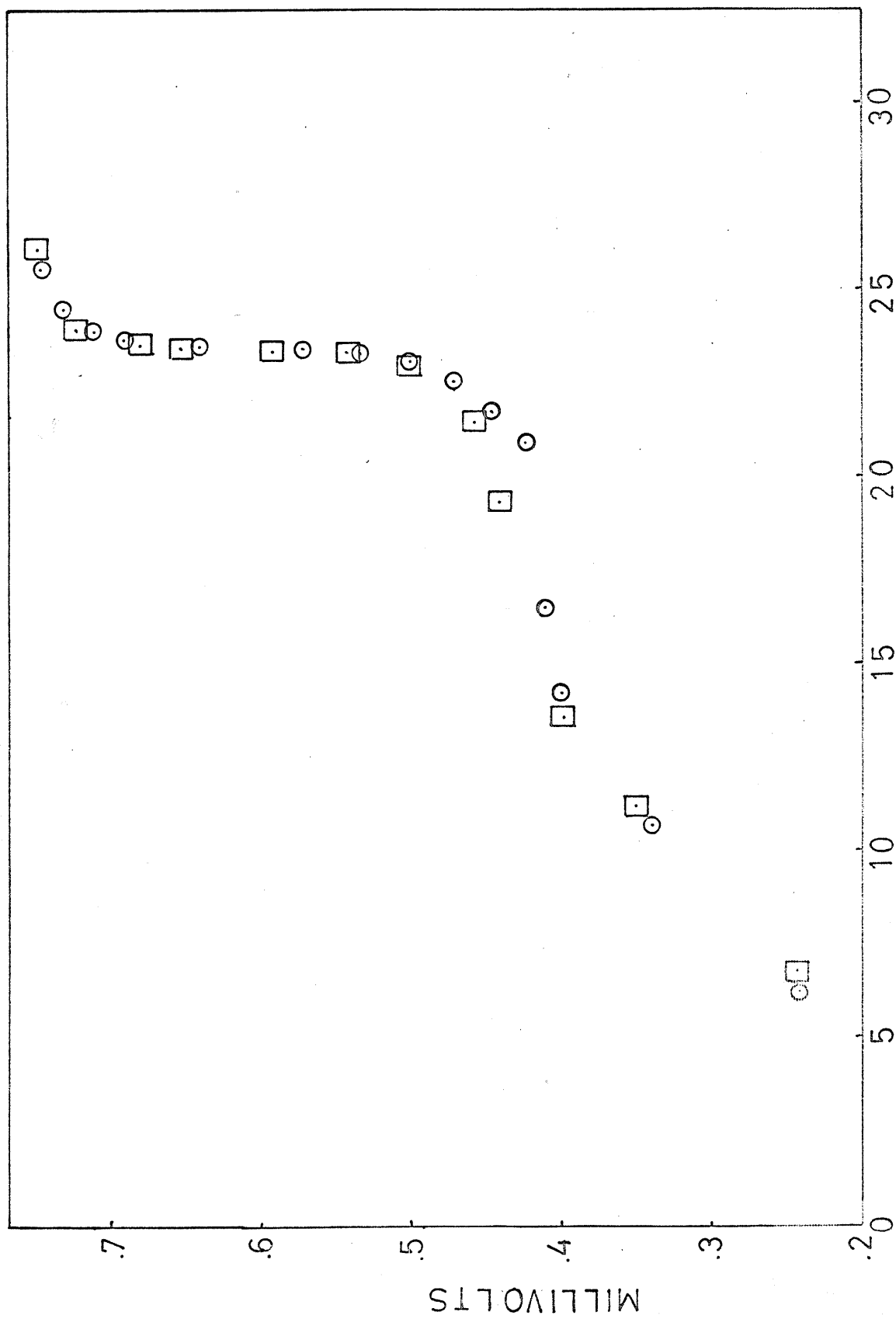
Admittedly, the above results show in a few cases

TABLE 4
 Analysis of the Bromates by the Method of
 Britton and Britton⁶²

Bromate	% Bromate	
	#1	#2
$\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$	97.9	96.7
$\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$	100.0	100.3
$\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$	98.8	98.6
$\text{Rb}(\text{BrO}_3)$	95.6	98.7
$\text{Ni}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$	98.8	99.6
$\text{Cs}(\text{BrO}_3)$	98.1	99.7
$\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$	98.1	98.5
$\text{Co}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$	97.7	94.7
$\text{Ca}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$	99.1	98.7
$\text{Mg}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$	98.4	99.2
LiBrO_3	99.5	100.0
$\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$	99.3	100.5
AgBrO_3	99.5	99.2
$\text{Y}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$	100.6	99.6

FIGURE 2

Analysis of $\text{Ca}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ potentiometrically

FIG. 2 ANALYSIS OF .0628 GRAMS $\text{Ca}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$

that either the bromates were impure or that the method was inaccurate. However recrystallization of a few of the bromates did not improve the purity. Since the samples were only 60 to 100 mg, an error in weighing of 0.5 mg is 0.5% to 0.7% in the final result. The weighing error probably constitutes the major source of error.

Those bromates that were made from $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ were tested for the presence of barium ion with H_2SO_4 ; those that were made with AgBrO_3 were tested for the presence of silver ion with HCl . None of the bromates was contaminated with silver or barium ions. The only other impurity could be the oxide or the bromide. A small amount (less than 0.5%) of bromide was found in bromates of zinc rubidium and cobalt. Kashoulis⁶³ noted that a small amount of LiCl had very little effect on the rate of decomposition of LiClO_4 . As will be seen in the results, a small amount of bromide added to strontium and barium bromates, had little effect on the rate of decomposition.

After the bromates were decomposed, the gases evolved and the residue were analyzed. For those bromates that liberated solely oxygen, the analysis was simple. The oxygen evolved was measured in a gas burette and the bromide residue was analyzed potentiometrically using 0.025 N AgNO_3 as the titrant (see Fig. 3). One of the results is redundant but

FIGURE 3
Analysis of CsBr residue

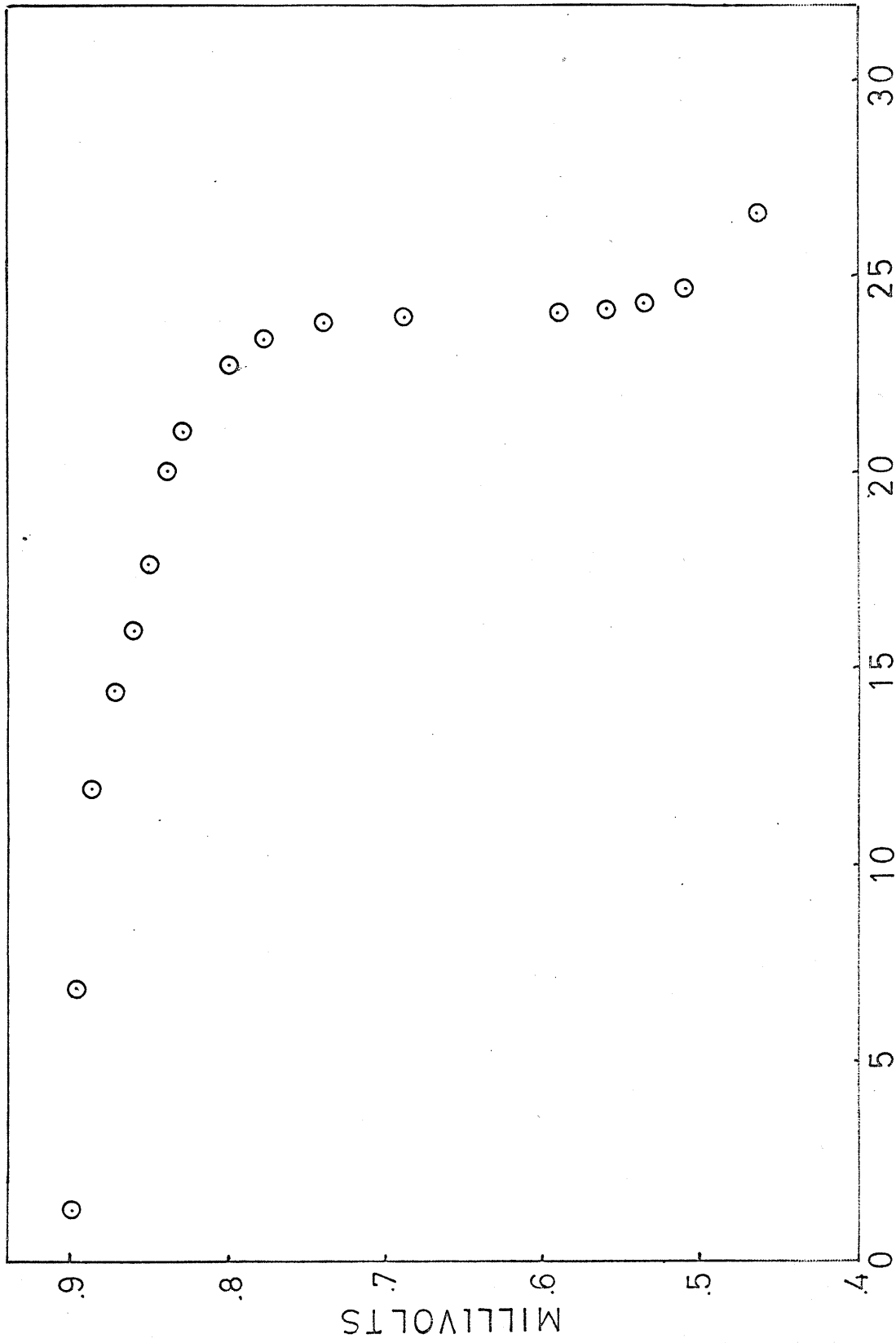


FIG. 3 ANALYSIS OF .125 GRAMS CsBr

is a good check on the other.

When both bromine and oxygen were evolved, the analysis problem became more difficult. The bromine evolved was trapped using liquid nitrogen, and the oxygen which still has an appreciable vapour pressure at -196°C , was pumped into the gas burette and measured. The bromine was then condensed into a flask which contained 1:1 acetic acid. The bromine was determined by addition of KI and titration of liberated iodine with $\text{Na}_2\text{S}_2\text{O}_3$. Bromine tended to be absorbed in the system and also reacted with any mercury vapour that was present. Thus the bromine results were always low. For the analysis of the residue, the platinum crucible was added to 50 ml water and the insoluble oxides were filtered. The filter paper was burned off and the oxide dried at about 500°C . The bromide was again determined potentiometrically using AgNO_3 . The bromine and oxide determinations were discontinued in later experiments because of the inaccuracies involved and because only two out of four determinations are necessary.

The Apparatus

The essential apparatus used in these experiments is shown in Fig. 4. Evacuation was accomplished through L and M. The system was evacuated to less than one micron Hg

FIGURE 4
The apparatus

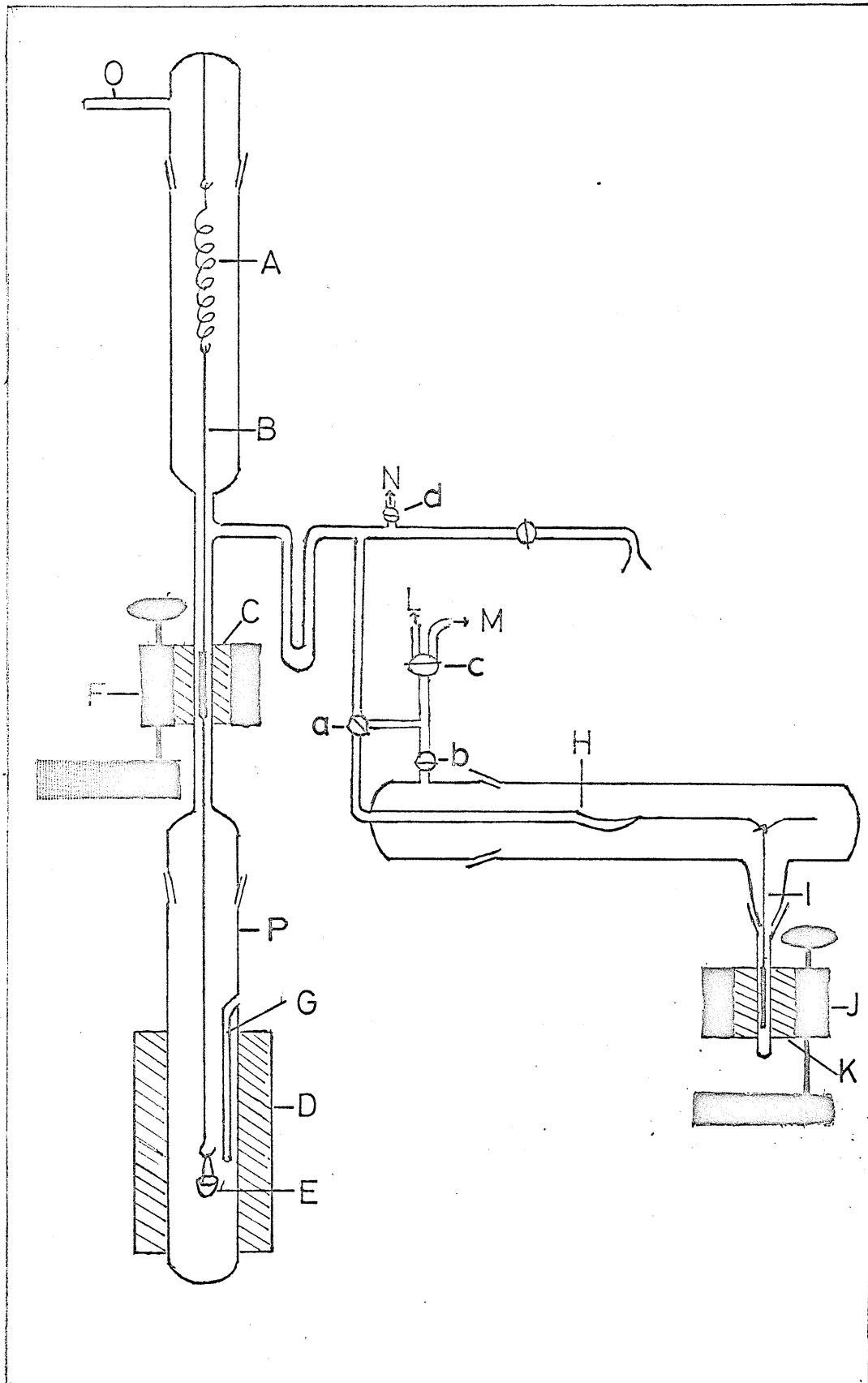


FIG. 4 THE APPARATUS.

pressure by a mercury diffusion pump backed by a rotary oil pump. The residual pressure was measured with a McLeod gauge. The entire apparatus in Fig. 4 was tightly clamped.

The temperature sensitive element was an iron-constantin thermocouple calibrated at 0°C and 100°C . This thermocouple was lowered into a well G so that the tip of the thermocouple was almost directly above the sample. The furnace D was a #73-S 210 watt Hevi-Duty electrical heating unit. Except for temperatures below 100°C , linearity in the time-temperature plots was obtained when the voltage across the furnace was varied linearly. A very simple motor and gear box drive was used to turn a #116 U Powerstat. The output from this variable autotransformer was fed into another variable autotransformer which controlled the maximum temperature. By selecting suitable gear combinations and maximum temperatures, heating rates from 60°C per hour to 500°C per hour could be obtained.

The thermobalance using a #175ES-L L.V.D.T. (C) from Schaevitz Engineering was essentially the same as that described by Hooley³⁸. A quartz spring A, purchased from Worden Laboratory, having a sensitivity of 1 cm/gram was the weight sensitive element. The L.V.D.T. was mounted in a fibre block F with a finely threaded screw so that the transformer could be vertically adjusted. A lever arm O was used



for fine horizontal adjustments of the core. The core, plated with rhodium to resist the action of corrosive gases, was held by a 1 mm diameter quartz rod (B). A circular platinum pan (E), one cm in diameter and 1 cm in depth, was in turn held by a 1 mm diameter quartz rod.

The pressure gauge using a 100SS-LT L.V.D.T. (K) from Schaevitz Engineering was essentially the same as that described by Hooley⁴⁵. The core of the transformer was held by a 1 mm diameter quartz rod, which was hanging from the tip of the spoon. The spoon held a differential pressure of 30 cm of Hg and had a sensitivity of 0.1 mm movement of the tip for 1 cm Hg differential pressure. The gauge was calibrated using a mercury manometer and a ballast (M). All stopcocks in the line were greased with Kel-F to resist corrosive gases.

The demodulator circuit⁶⁴ for the weight transducer is shown in Fig. 5. An identical circuit was used for the pressure transducer. The A.C. input to the L.V.D.T. as measured by the voltmeter V was 2 V for the weight L.V.D.T. and 1.25 V for the pressure L.V.D.T. The A.C. output, which depends on the position of the core (see introduction p. 12) was amplified by a transistor and rectified. The output from the rectifier was bucked by a 40 mv. voltage from a potentiometer circuit so that the L.V.D.T. and amplifier were operated over their linear ranges. Any voltage

FIGURE 5

The demodulator circuit

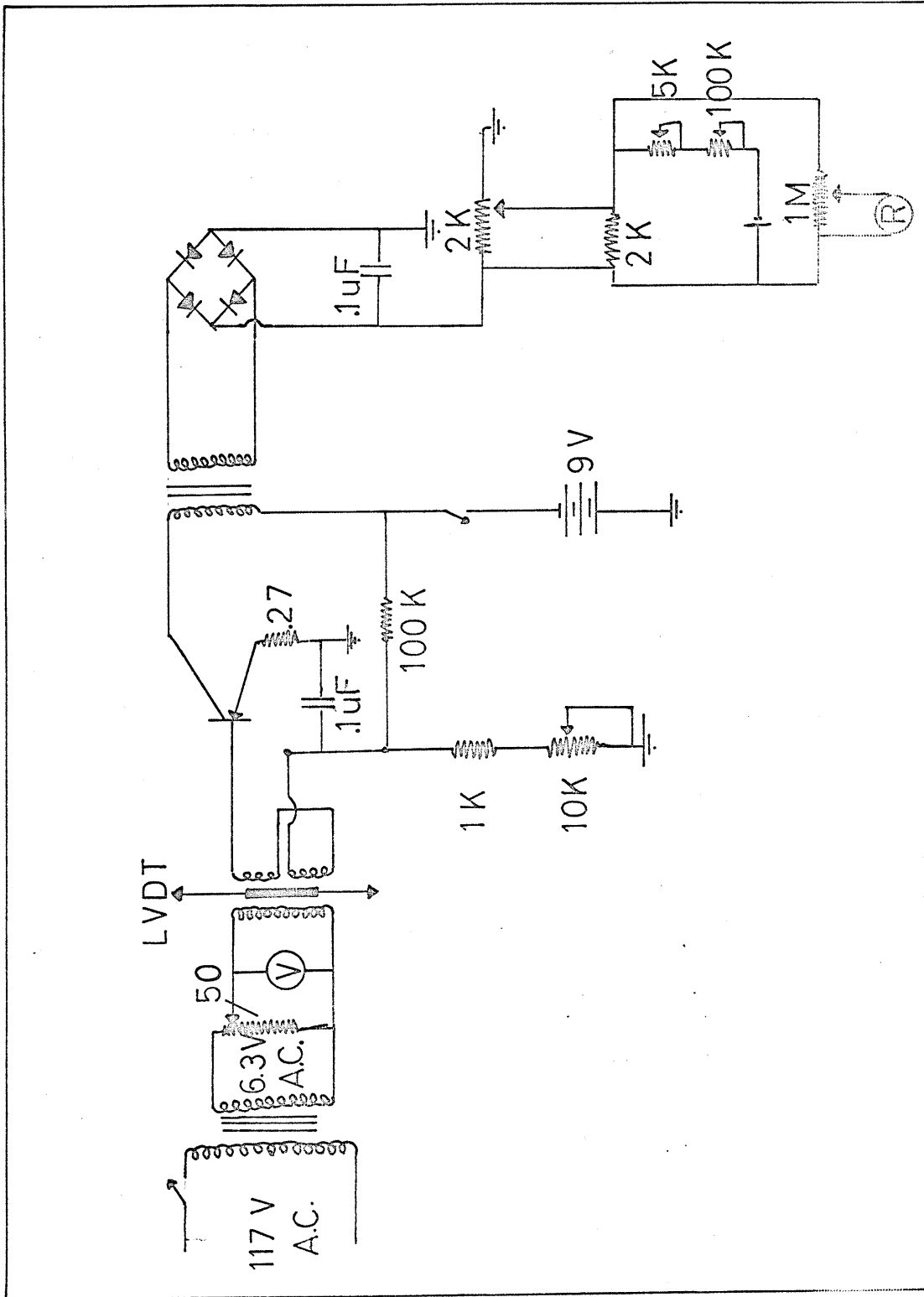


FIG. 5 THE DEMODULATOR CIRCUIT

exceeding 40 mv. was divided by the 1 Mohm resistor. This fraction of the amplified output from the weight and pressure transducers along with the unaltered output from the thermocouple were fed to a M.P. #4A606 switching device from Davis Automatic Controls Ltd. and thence to the 25 mv. scale on a single pen Photovolt #43 recorder. In this way temperature, weight and pressure were recorded by the same pen, which was switched every twenty seconds.

A Typical Experiment

Calibration

The lower female joint P was removed along with the furnace. With the pen of the recorder set at zero, ten milligram weights were dropped onto the platinum pan. The sensitivity on the recorder was usually set at about 0.5 mg/division where one division was one hundredth of full scale. Thus a weight change of 50 mg would span the whole 10 inches of chart paper.

The initial step in calibrating the spoon gauge was to evacuate both sides of the spoon to less than one micron pressure. With stopcocks a and c open and b closed air was let in through a two liter ballast via M. The resultant differential pressure on the spoon was measured

by an open mercury manometer. The sensitivity on the chart was adjusted by the potentiometer circuit to twenty divisions/cm of mercury pressure. Thus a differential pressure on the spoon of 5 cm would span the chart. The pressure and weight transducers were recalibrated about every two or three experiments. In general, the calibration remained constant.

Operation

The platinum pan, containing 50-150 mg of the ground sample, was attached to the quartz rod. The lower female joint P was then positioned and clamped. The heater was then slid over the glass tube and clamped. The iron constantin thermocouple was then placed in position in the well. If the core was not perfectly centred, the lever arm O was rotated. By adjusting the vertical position of the L.V.D.T. with F, the weight reading was set at about 22.5 mv. on the chart. The pressure reading was set at about 2.5 mv. by adjusting the vertical position of the pressure L.V.D.T. with J. Since the unaltered output from the thermocouple was fed directly to the recorder, the initial temperature setting was about 0.75 mv. depending on the room temperature.

The system was usually evacuated for over an hour.

The residual pressure, as measured by a McLeod gauge was always less than one micron. Stopcocks b, c, and d were now closed and the actual experiment was started.

The furnace was turned on and the motor on the gear box drive began to turn the first variable autotransformer. For most experiments the autotransformer turned one revolution in eleven hours which gave a heating rate of 1° C/min. A faster heating rate resulted in splattering for most bromates. The temperature of the furnace then began to rise and the thermobarogram was plotted automatically. When the motor driven autotransformer had completed one revolution and the maximum temperature had been reached, a micro switch shut off the recorder, furnace and the motor that turned the autotransformer. Thus experiments could be performed overnight.

RESULTS

The Thermobarograms

The thermobarograms of all the bromates and calcium oxalate are shown in Fig. 6-30. Table 5 summarizes the results of these decompositions and Table 6 shows the accuracy of the pressure and weight measurements. The theoretical and thermobalance readings coincided well except in the following two general cases:

1. When splattering occurs. This splattering was troublesome with lithium, sodium and potassium bromates and was very difficult to eliminate even at the lowest heating rates. Although weight readings were inaccurate, pressure readings were still accurate in these cases.

2. Bromates which liberated water, oxygen and bromine simultaneously. The water and bromine tended to be absorbed by the core, making the weight and pressure readings too low. The absolute pressure readings were really useless because water is a non-ideal gas. However relative pressure readings as seen by comparison with the weight readings are still accurate.

Except for the above two cases the difference between the theoretical and thermobalance readings was less than 3% of the total weight loss or pressure increase.

TABLE 5
Decomposition Data for the Bromates and Calcium
Oxalate Monohydrate

Figure	Compound	Weight of Sample gms	T _s °C ± 2°	Heating rate °C/min	Temper- ature Range °C ± 2°	% Br ⁻ in Residue wt. %
6	CaC ₂ O ₄ ·H ₂ O	0.133	160	2	104-180	
7	CaC ₂ O ₄ ·H ₂ O	0.126	154	3	101-170	
8	CaC ₂ O ₄ ·H ₂ O	0.137	-	8	150-485	
9	LiBrO ₃	0.084	251	1	236-256	
10	LiBrO ₃	0.085	214	constant	214	90
11	NaBrO ₃	0.112	343	1	298-368	100
12	KBrO ₃	0.114	390	1	366-395	100
13	RbBrO ₃	0.137	403	3	328-416	100
14	RbBrO ₃	0.129	406	1	335-410	100
15	CsBrO ₃	0.155	366	2.5	265-388	100
16	CsBrO ₃	0.155	355	1	258-385	100
17	Mg(BrO ₃) ₂	0.060	316	1	245-329	5
18	Ca(BrO ₃) ₂	0.095	256	1	245-270	100
19	Sr(BrO ₃) ₂	0.100	265	1	248-275	100
20	Sr(BrO ₃) ₂	0.095	273	1	257-280	100
21	Ba(BrO ₃) ₂	0.119	317	1	267-328	100
22	Ba(BrO ₃) ₂	0.118	324	1	276-330	100

TABLE 5 continued

Figure	Compound	Weight of Sample gms	T _s		Heating rate °C/min	Temper- ature Range		% Br in Residue wgt. %
			°C	2°		°C	2°	
23	AgBrO ₃	0.161	272		1	212-292	100	
24	Co(BrO ₃) ₂ ·2H ₂ O	0.055	110		1	73-115	3	
25	Ni(BrO ₃) ₂	0.067	195		2	168-221	7	
26	Zn(BrO ₃) ₂	0.055	190		1	160-205	1	
27	Cd(BrO ₃) ₂	0.072	299		1	240-310	2	
28	Nd(BrO ₃) ₃ ·9H ₂ O	0.052	220		1	207-227	20	
29	Pr(BrO ₃) ₃ ·9H ₂ O	0.058	202		1	188-210	36	
30	Y(BrO ₃) ₃ ·9H ₂ O	0.054	214		1	172-227	15	

TABLE 6

Operation of the Balance and Pressure Gauge

Figure	Compound Decomposed	Total wgt loss in mgms		Pressure gain in cm Hg	
		By Thermo-balance	Theoretical	By Gauge	Theoretical
6	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	15.8	16.4	1.7	1.7
7	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	10.8	10.9	1.6	1.6
8	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	45.0	43.2		
9	LiBrO_3	splattering		3.9	3.95
10	LiBrO_3	31.0	31.5	4.0	4.1
11	NaBrO_3	41.0	36.7	5.0	5.6
12	KBrO_3	splattering		5.1	5.1
13	RbBrO_3	28.5	28.9	4.0	4.0
14	RbBrO_3	31.0	30.8	5.4	5.2
15	CsBrO_3	29.5	28.6	4.1	4.1
16	CsBrO_3	30.0	29.4	4.7	4.7
17	$\text{Mg}(\text{BrO}_3)_2$	36.0	36.9	2.4	2.4
18	$\text{Ca}(\text{BrO}_3)_2$	34.0	30.0	4.2	4.2
19	$\text{Sr}(\text{BrO}_3)_2$	26.5	26.5	3.6	3.7
20	$\text{Sr}(\text{BrO}_3)_2$	25.5	24.9	3.6	3.6
21	$\text{Ba}(\text{BrO}_3)_2$	29.5	28.5	4.1	4.1
22	$\text{Ba}(\text{BrO}_3)_2$	29.0	28.4	4.1	4.2
23	AgBrO_3	32.0	31.7	4.8	4.8
24	$\text{Co}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$	32.0	35.6	adsorption	

TABLE 6 continued

Figure	Compound Decomposed	Total wgt loss in mgms		Pressure gain in cm Hg	
		By Thermo-balance	Theoretical	By Gauge	Theoretical
25	$\text{Ni}(\text{BrO}_3)_2$	35.0	36.1	2.3	2.4
26	$\text{Zn}(\text{BrO}_3)_2$	32.0	31.1	2.2	2.0
27	$\text{Cd}(\text{BrO}_3)_2$	40.0	41.2	2.7	2.6
28	$\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$	not reliable		adsorption	
29	$\text{Pr}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$	33.0	34.4	adsorption	
30	$\text{Y}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$	not reliable		adsorption	

FIGURES 6-30
The thermobarograms

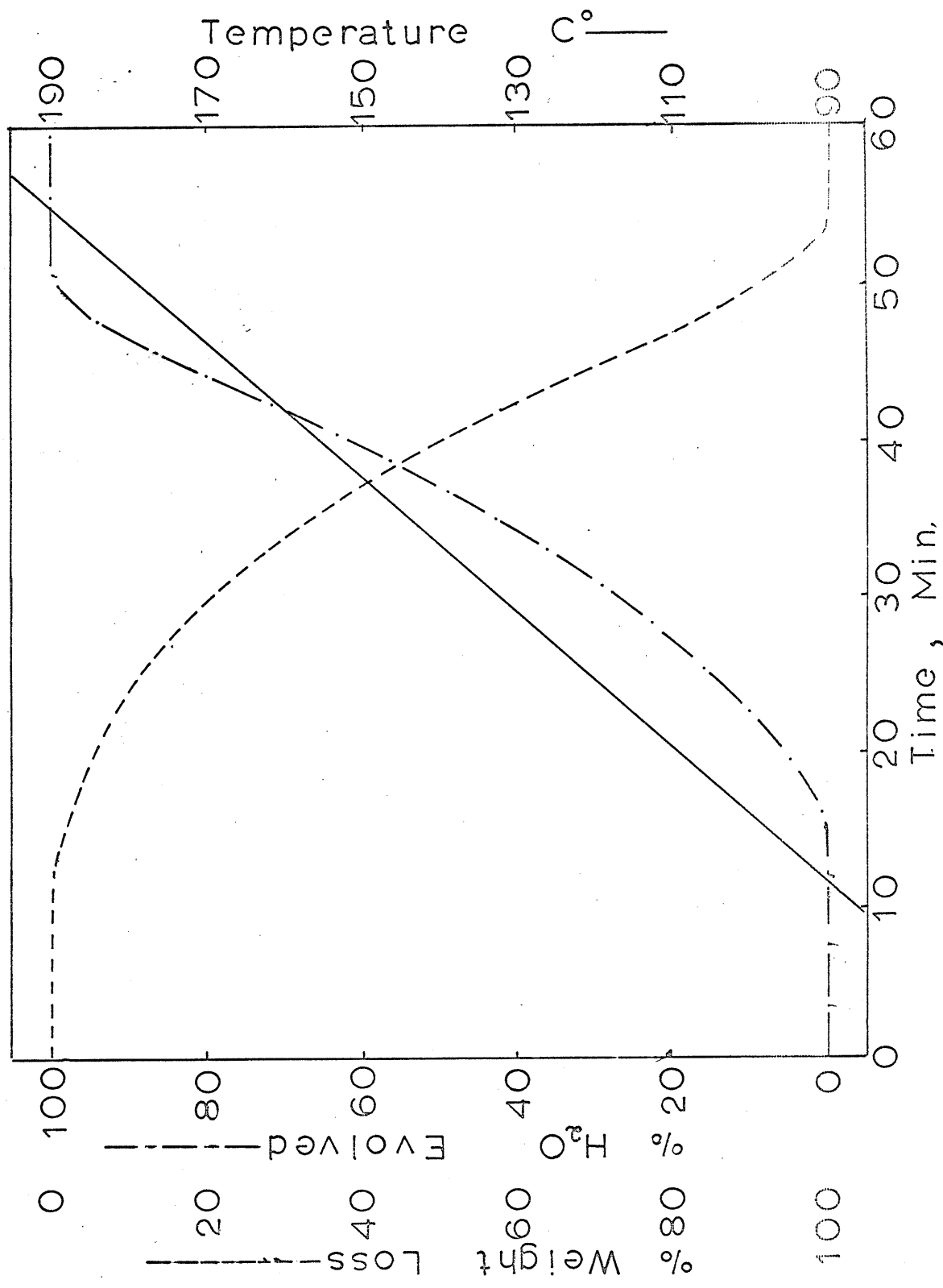


FIG. 6 $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$

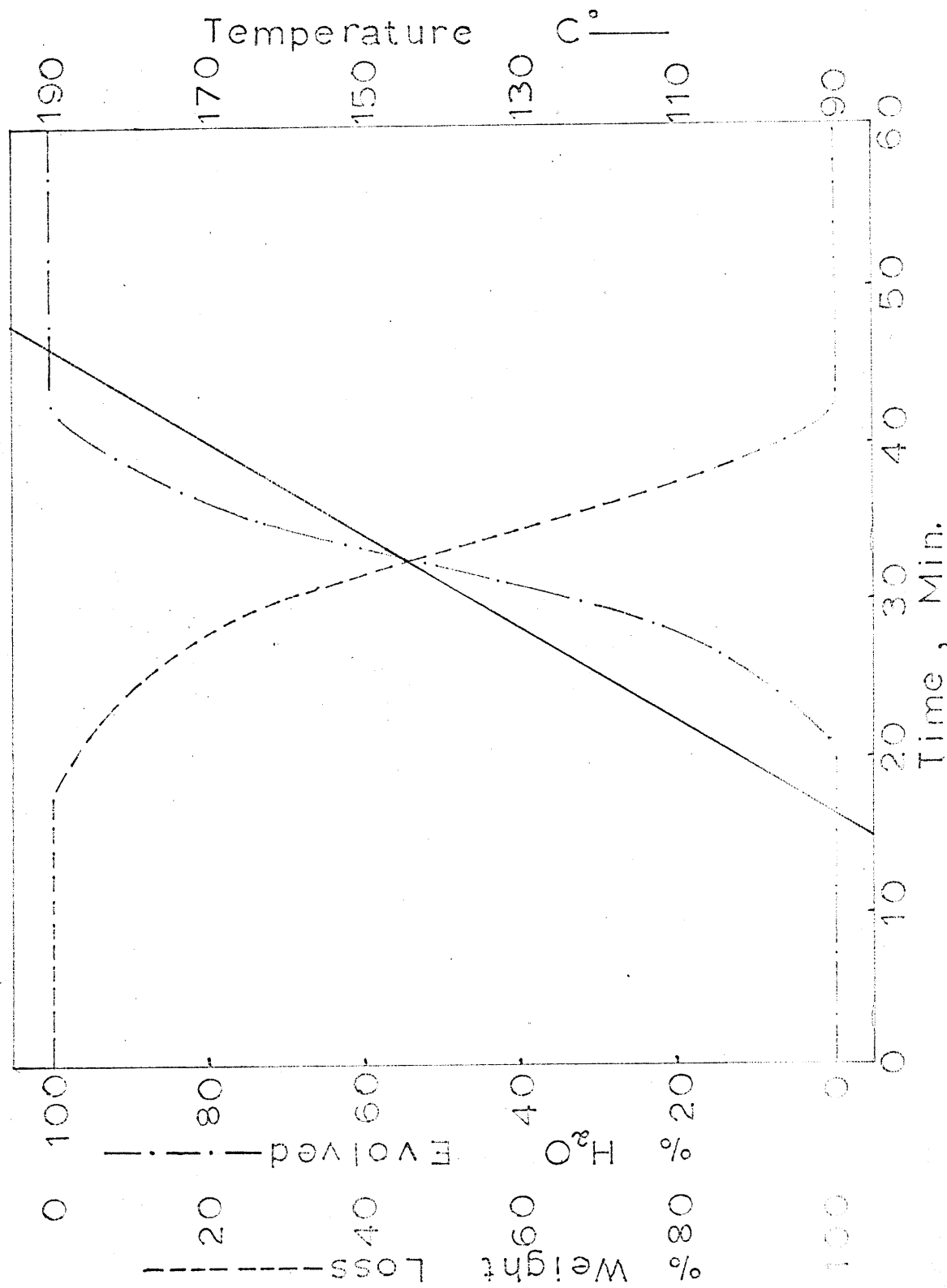


FIG. 7 $\text{CaCO}_3 \cdot \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$

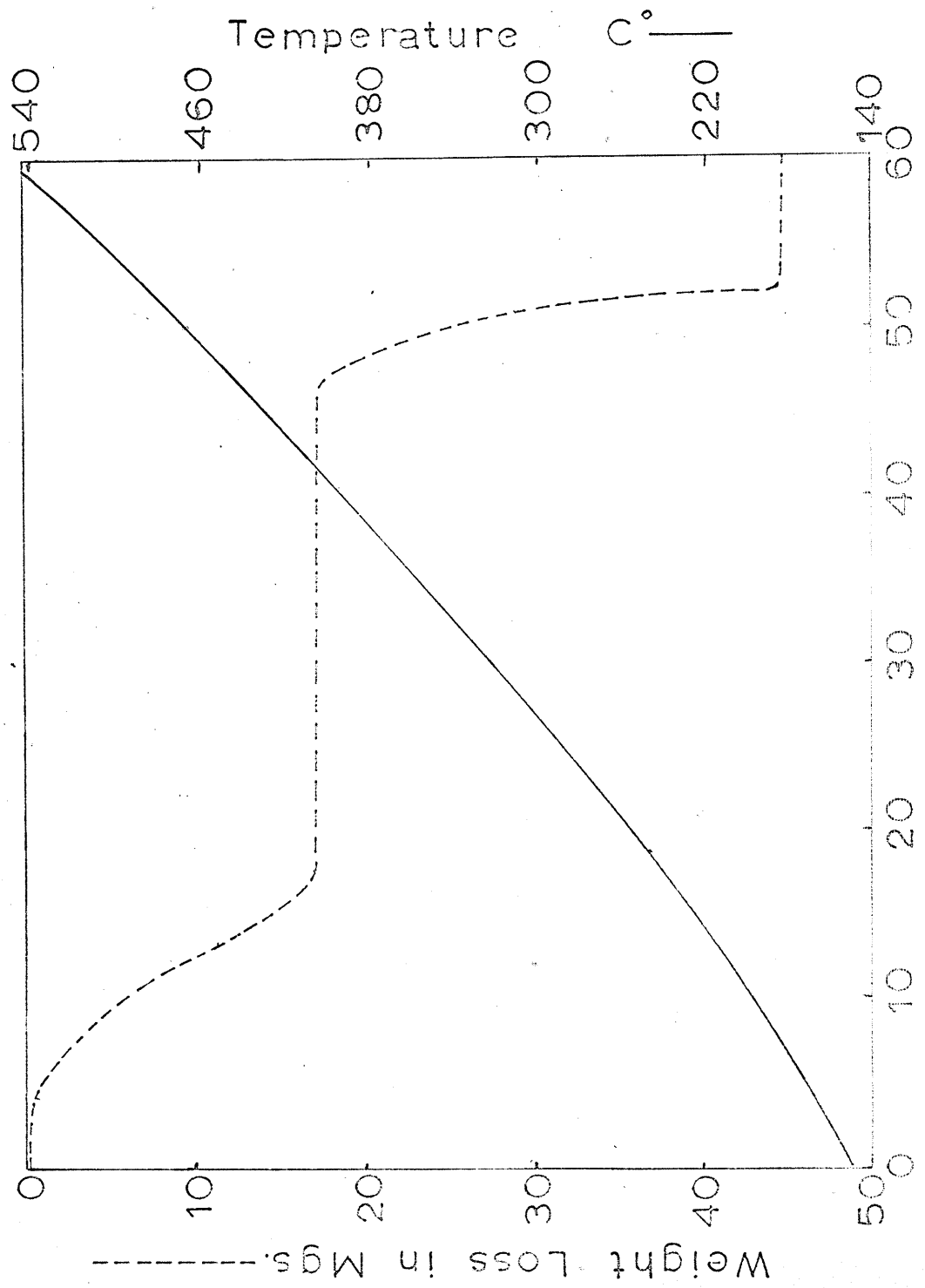
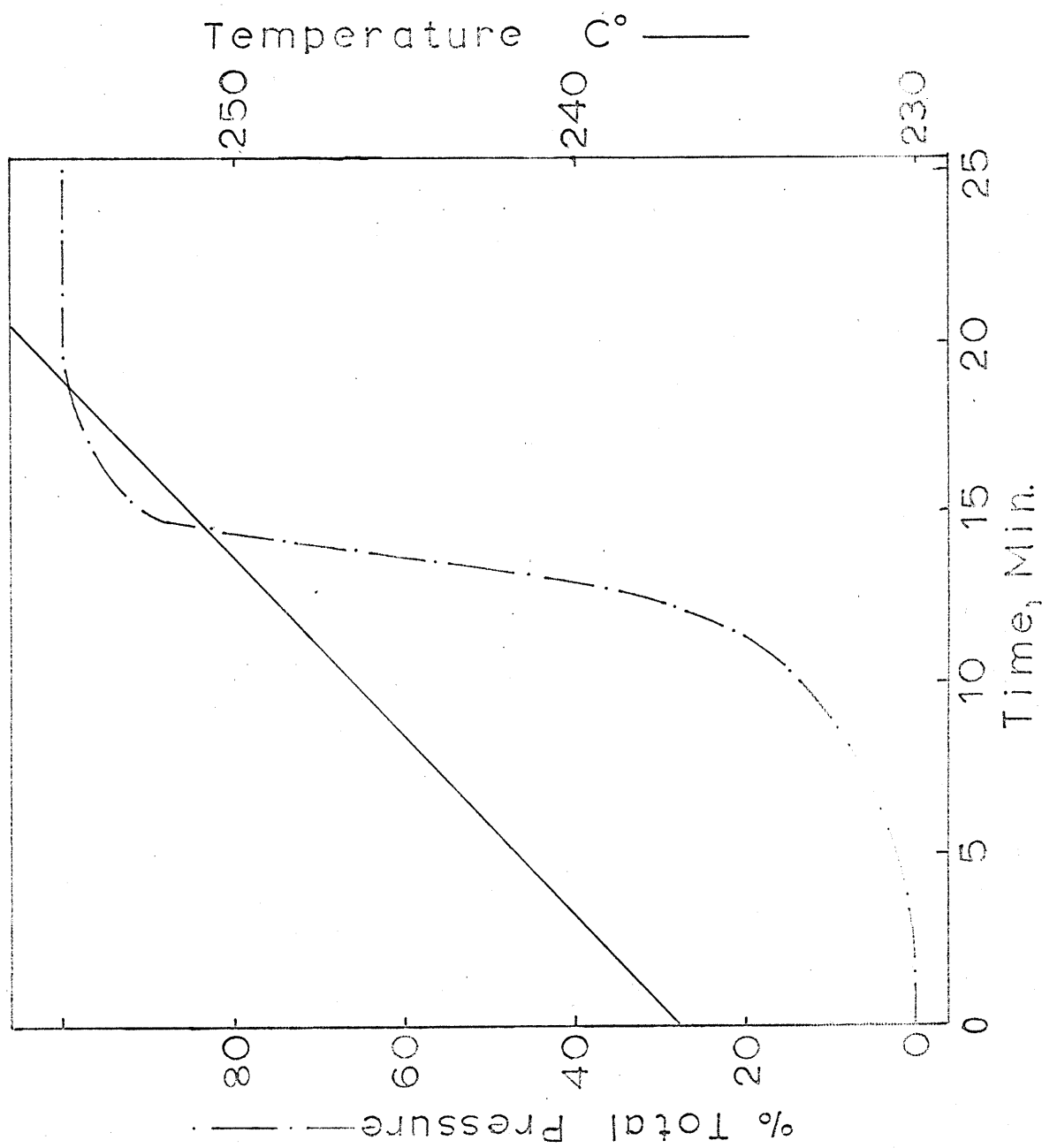
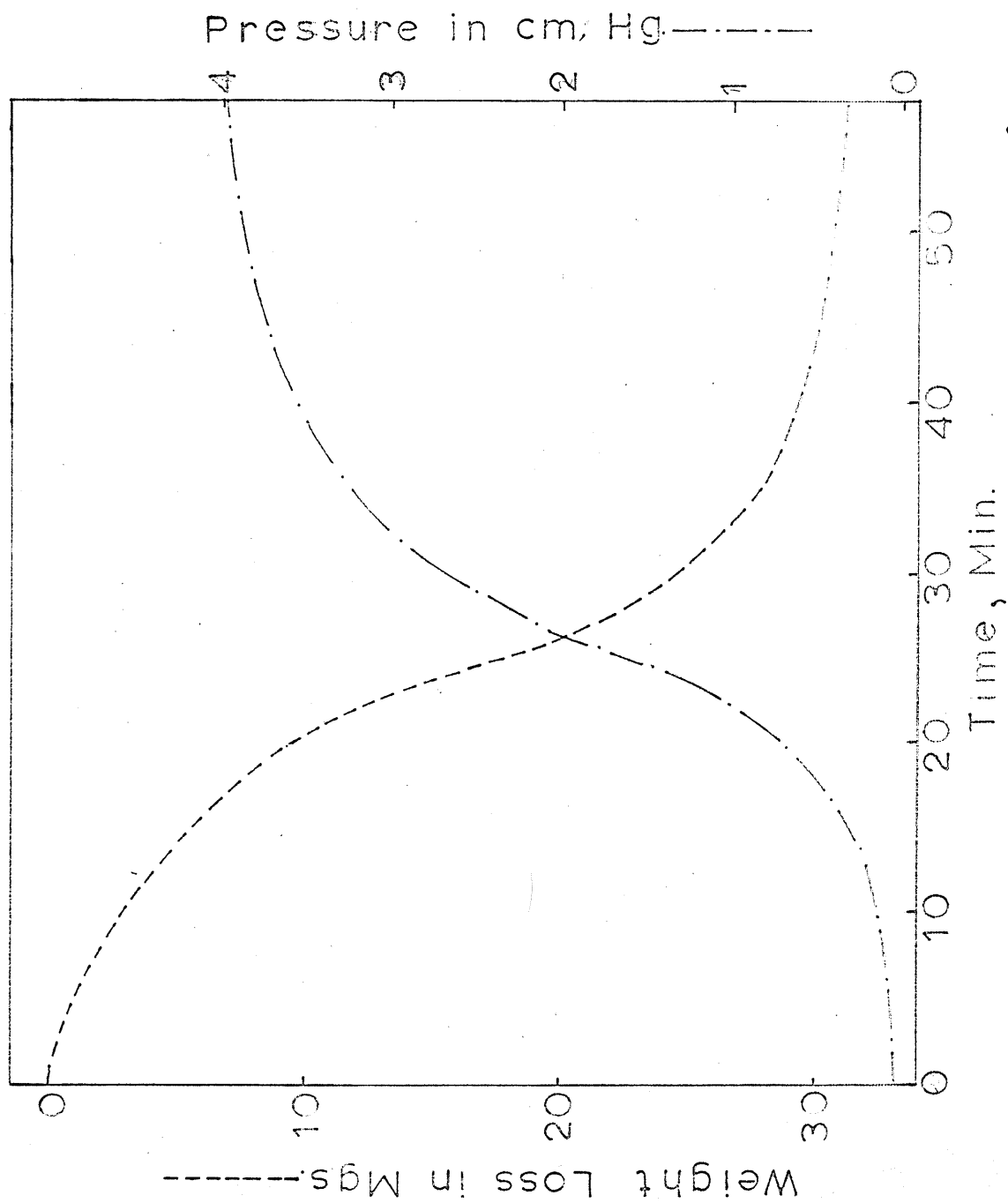


FIG. 8 DECOMPOSITION OF $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaCO}_3$

FIG. 9 DECOMPOSITION OF LiBrO_3

FIG.10 DECOMPOSITION OF LiBrO_3 AT 214°C

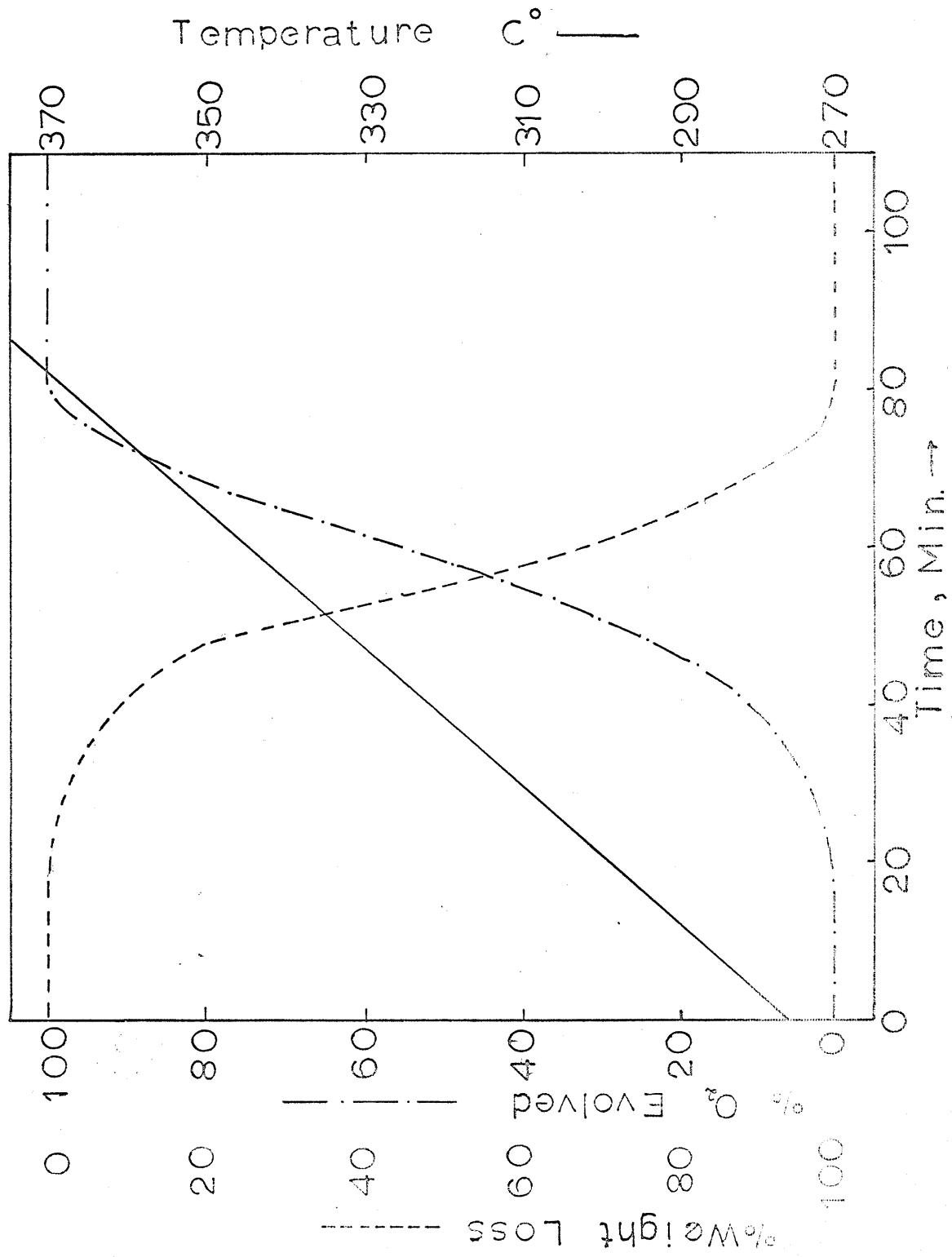


FIG.11 DECOMPOSITION OF NaBrO_3

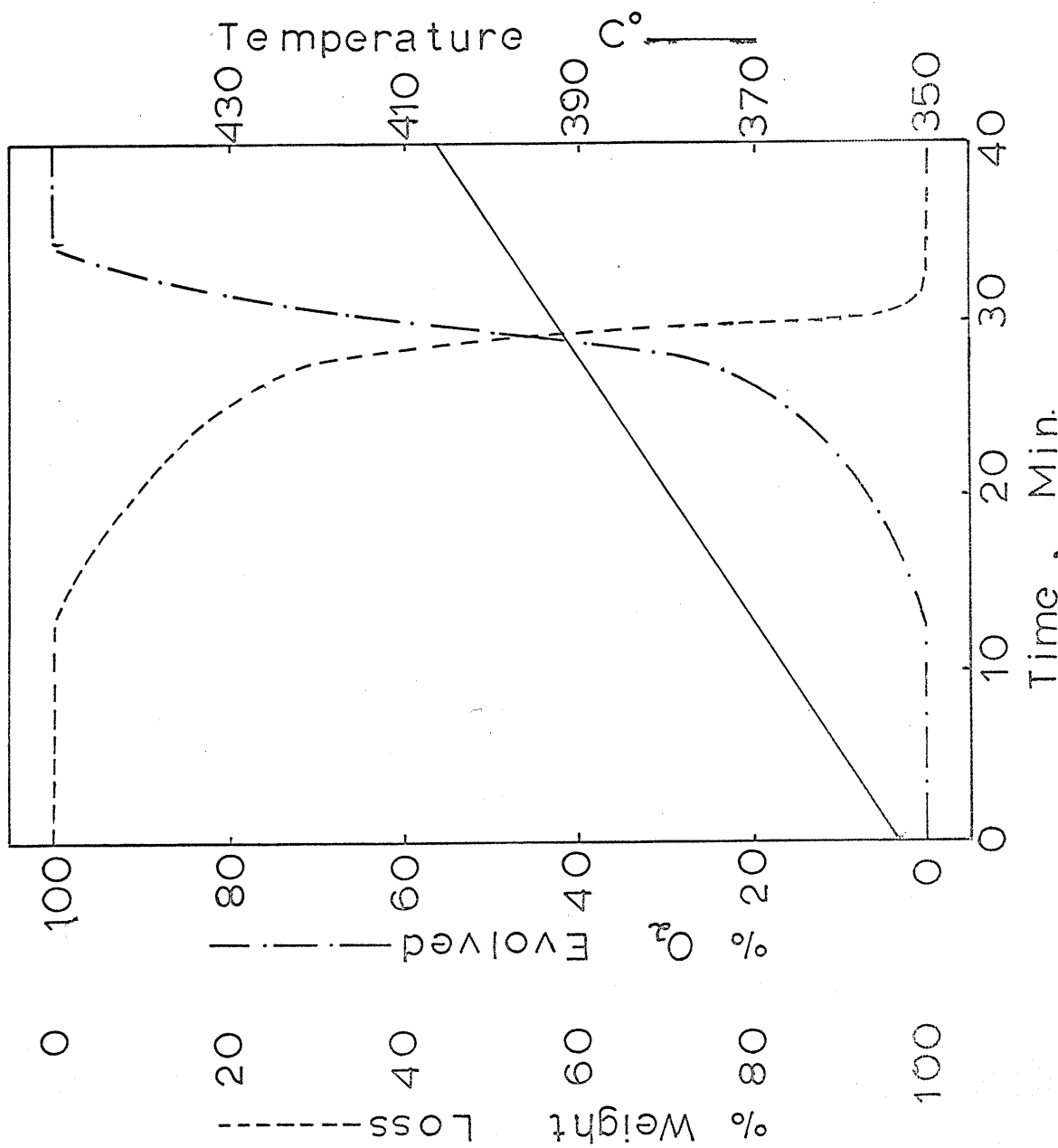


FIG. 12 DECOMPOSITION OF KBrO_3

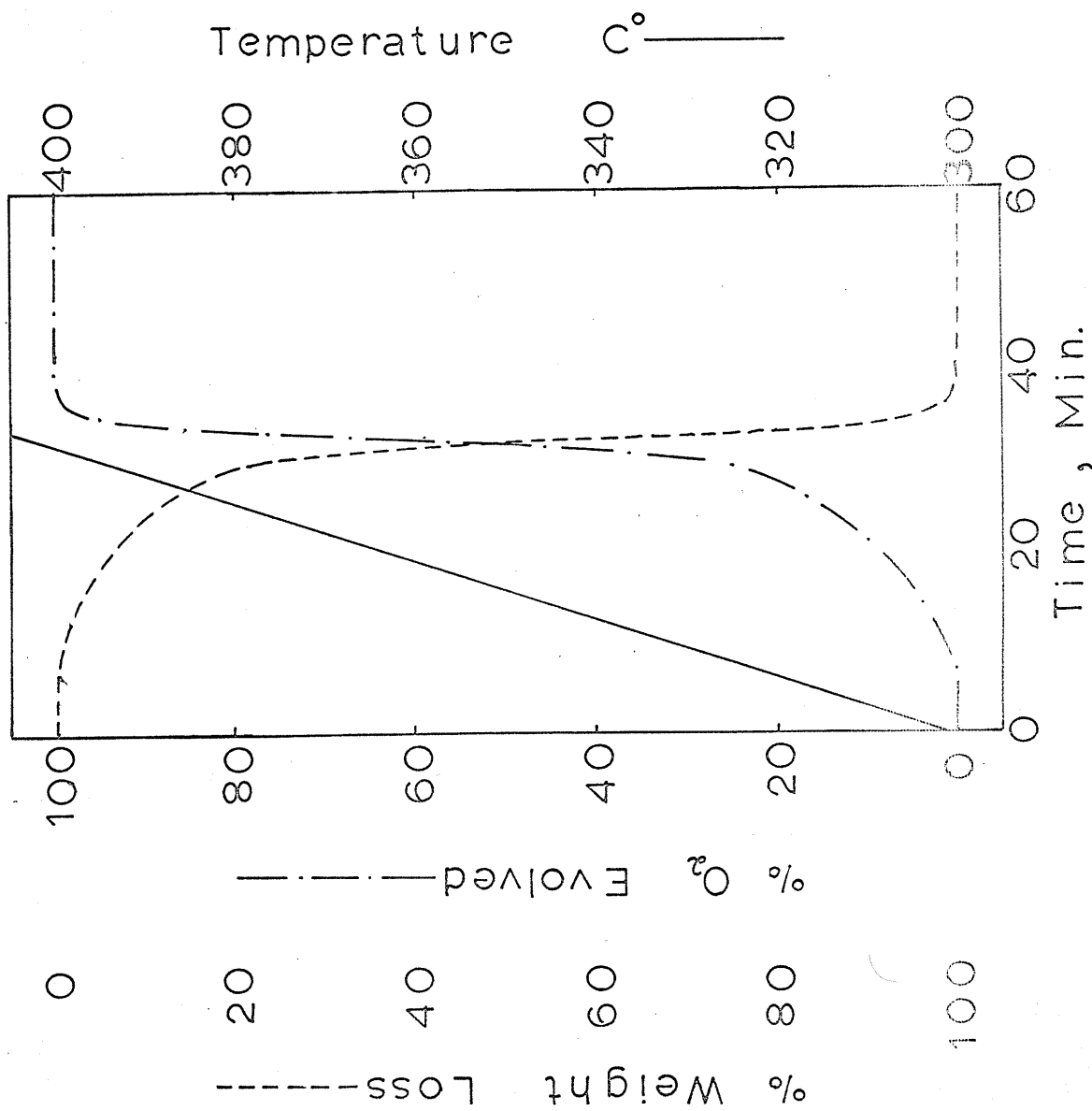


FIG.13 DECOMPOSITION OF RbBrO_3

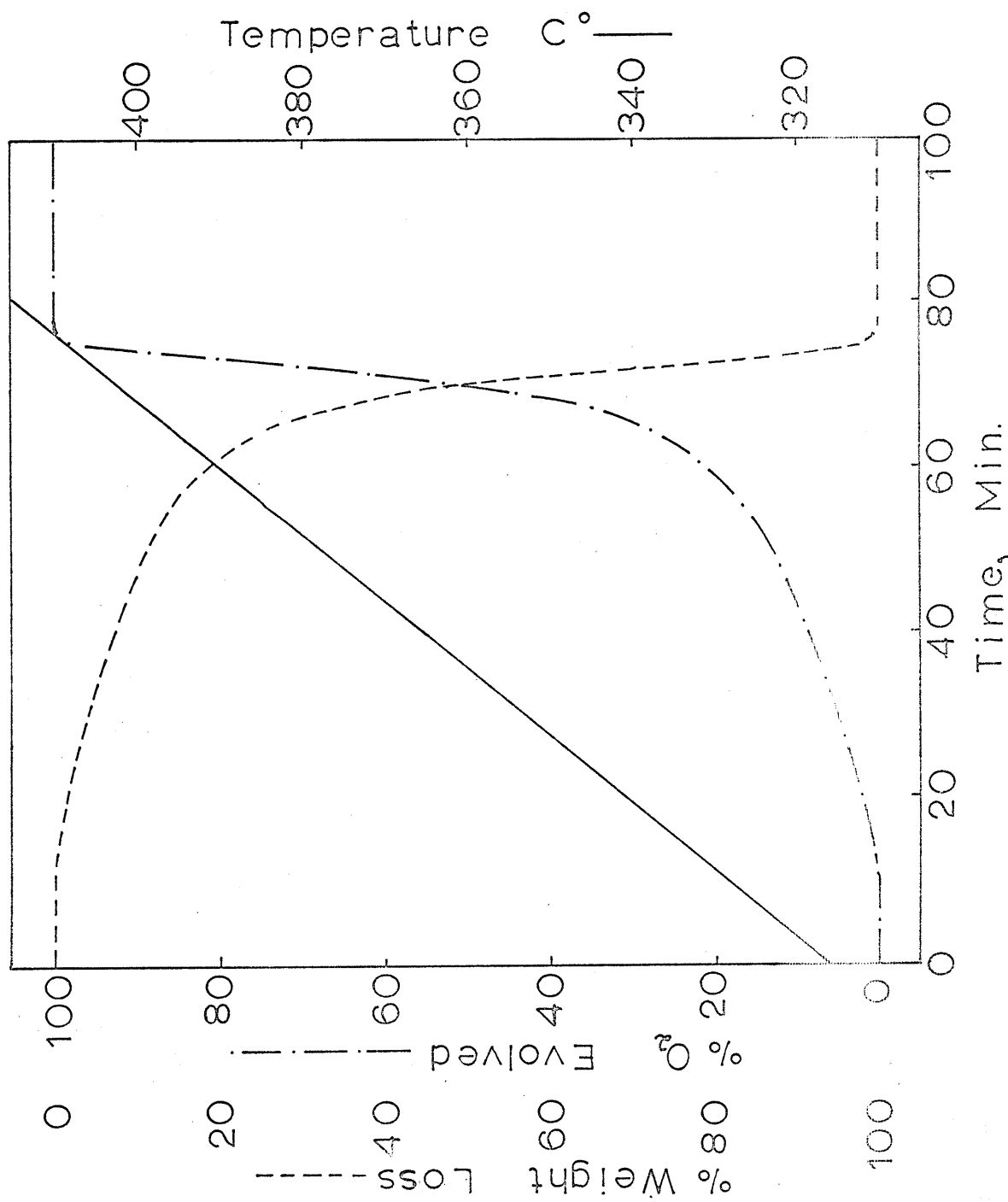


FIG.14 DECOMPOSITION OF RbBrO₃

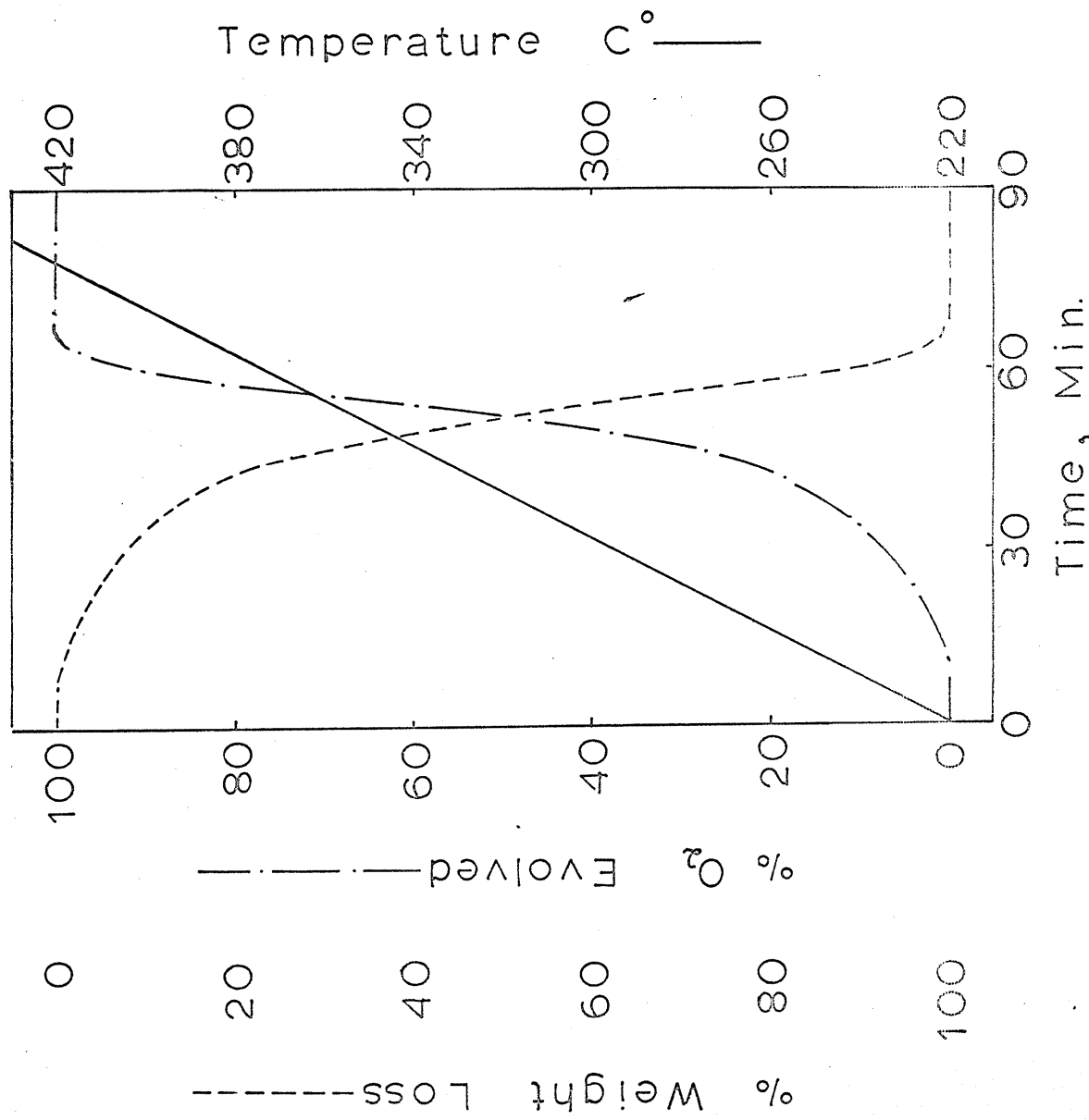
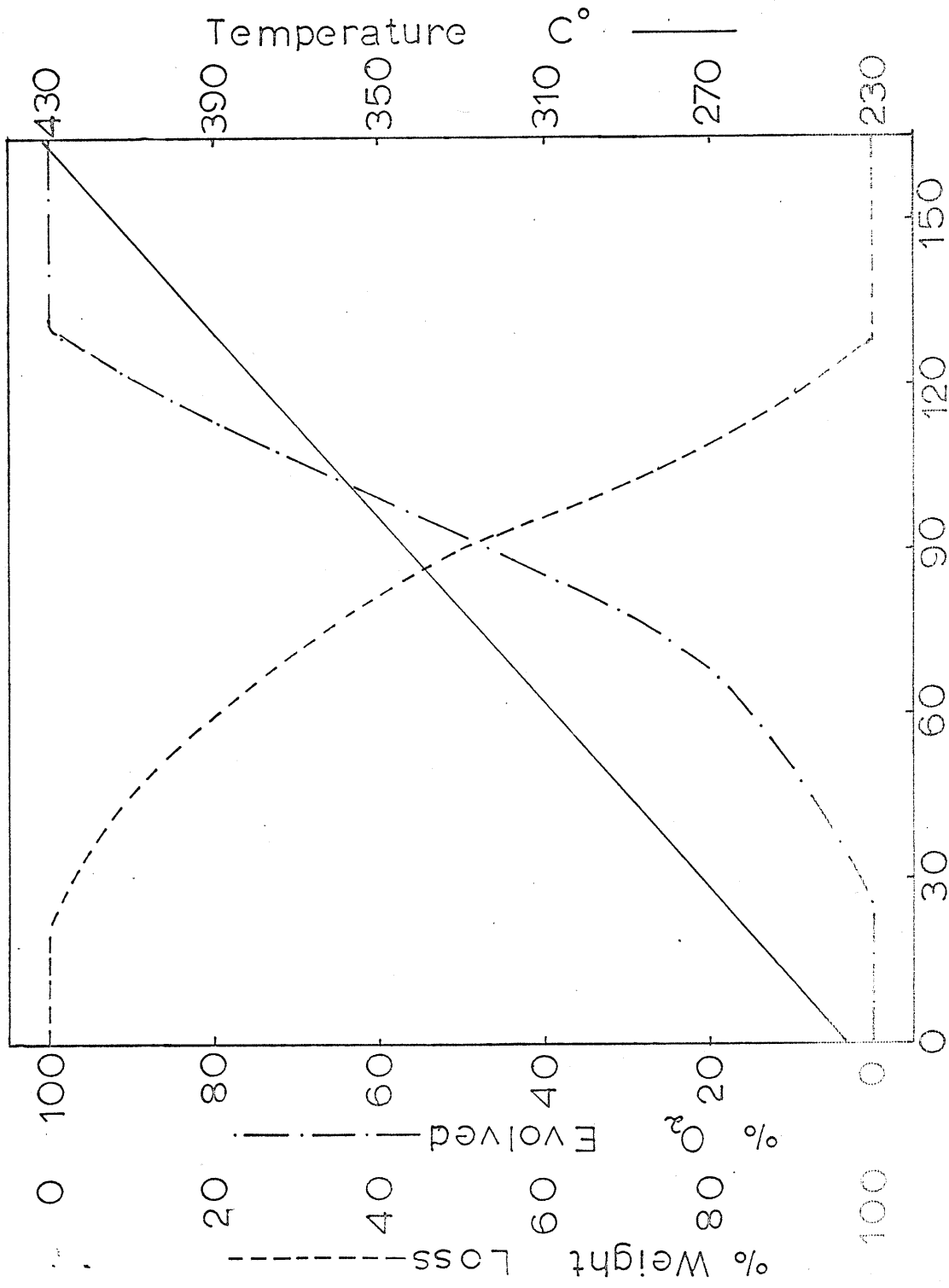


FIG.15 DECOMPOSITION OF CsBrO_3

FIG.16 DECOMPOSITION OF CsBrO_3

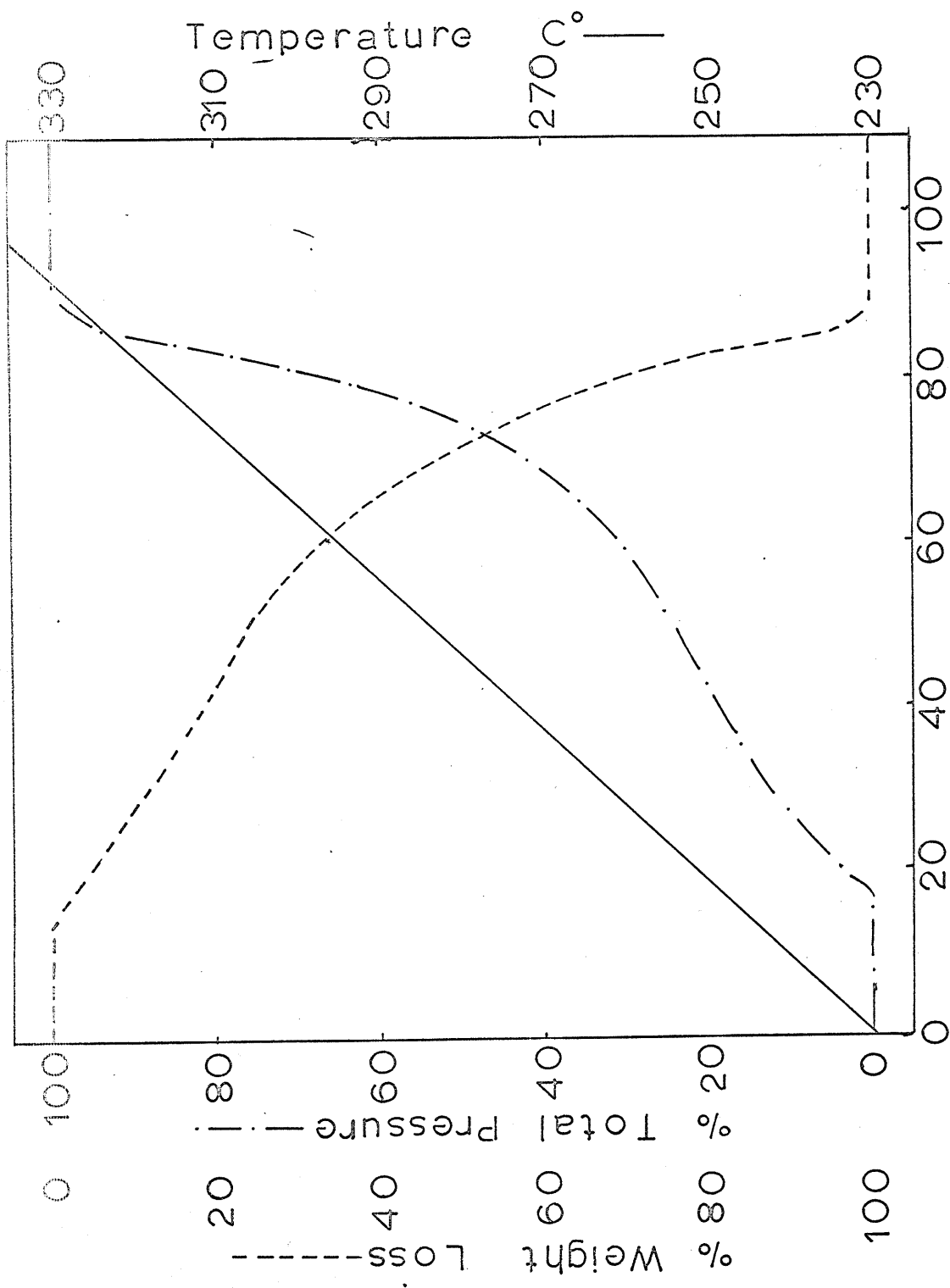


FIG. 17 DECOMPOSITION OF $Mg(BrO_3)_2$

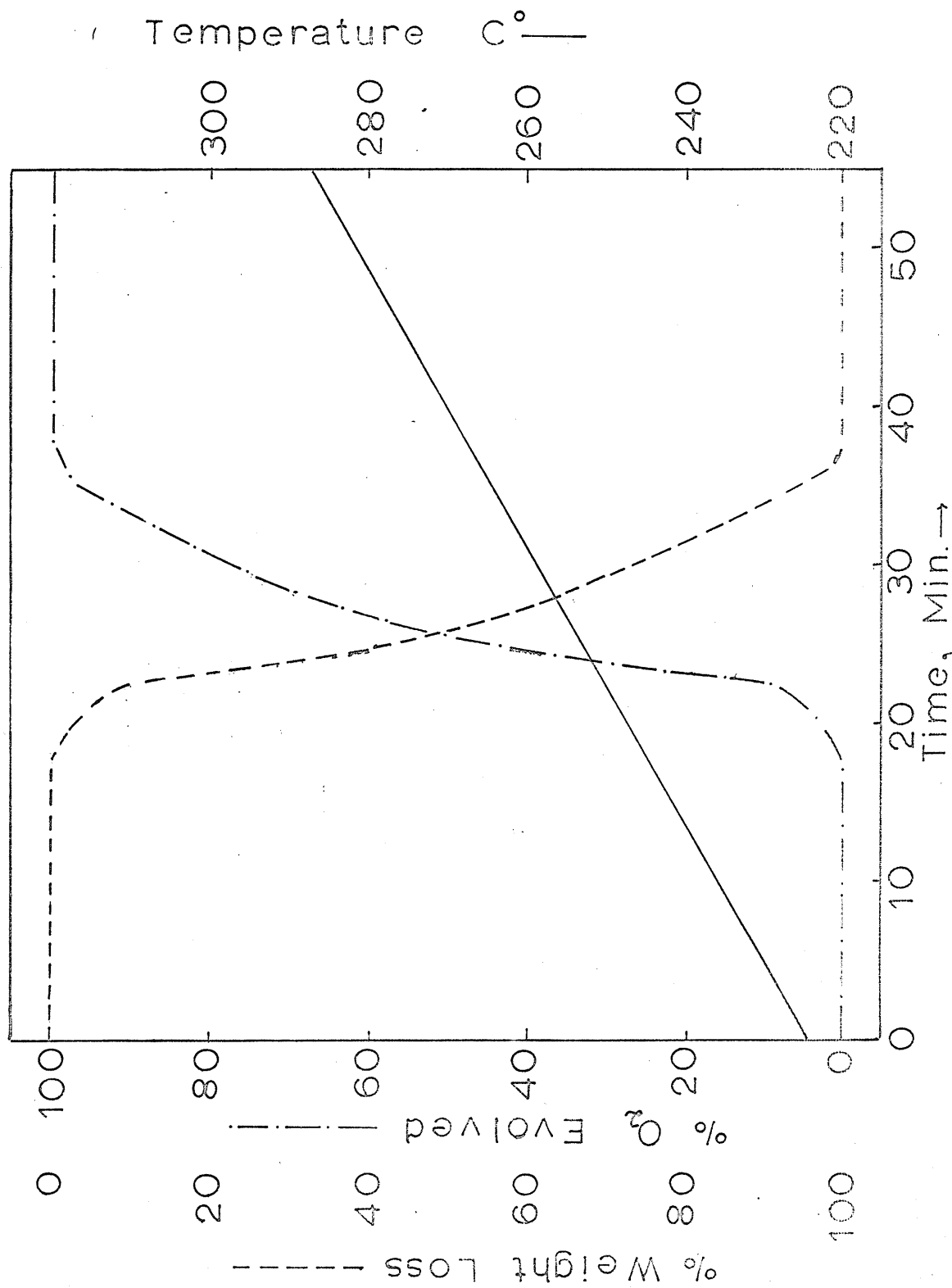


FIG 18 DECOMPOSITION OF $\text{Ca}(\text{BrO}_3)_2$

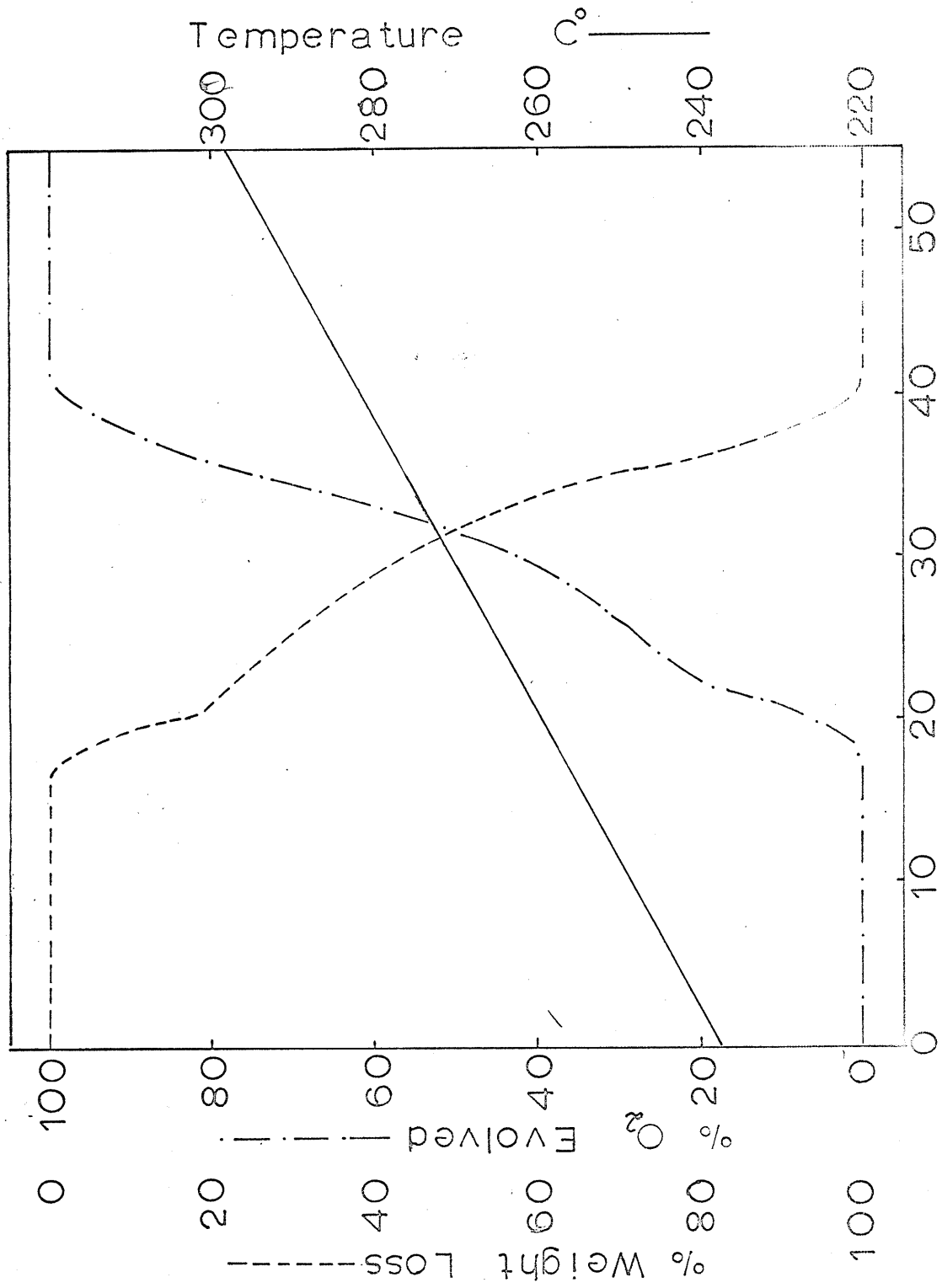


FIG. 19 DECOMPOSITION OF $Sr(BrO_3)_2$

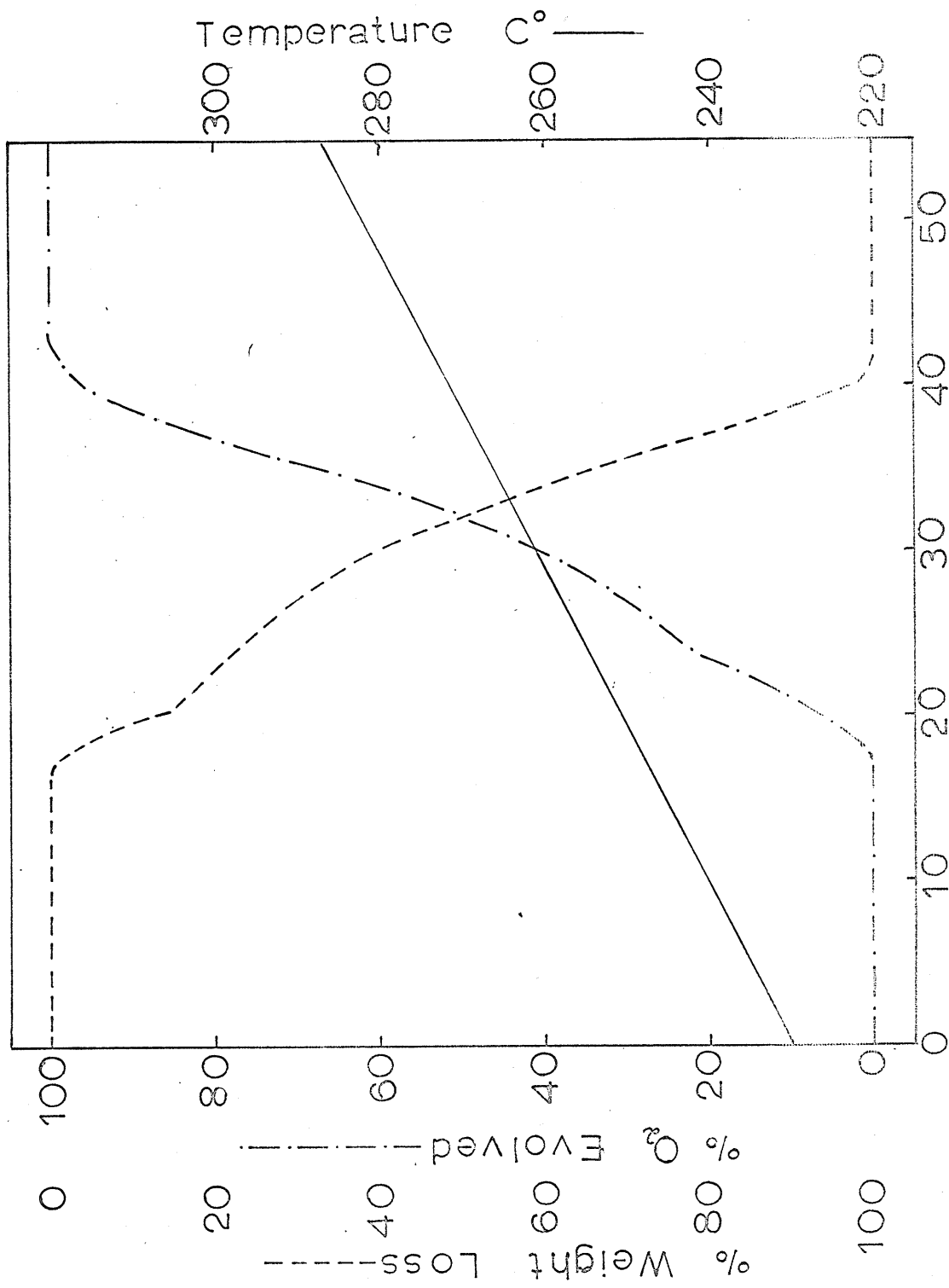
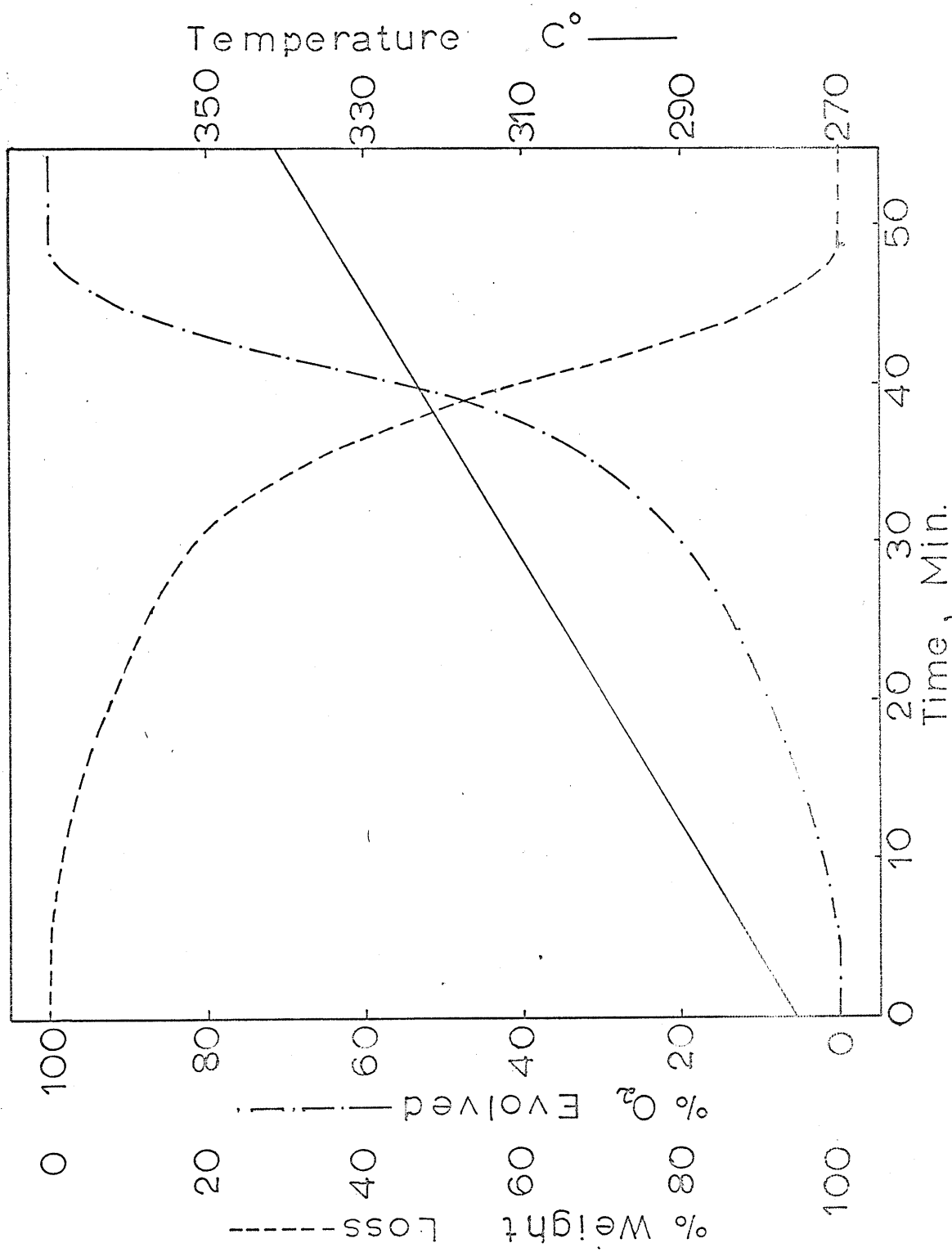


FIG. 20 DECOMPOSITION OF Sr(BrO₃)₂

FIG. 21 DECOMPOSITION OF $\text{Ba}(\text{BrO}_3)_2$

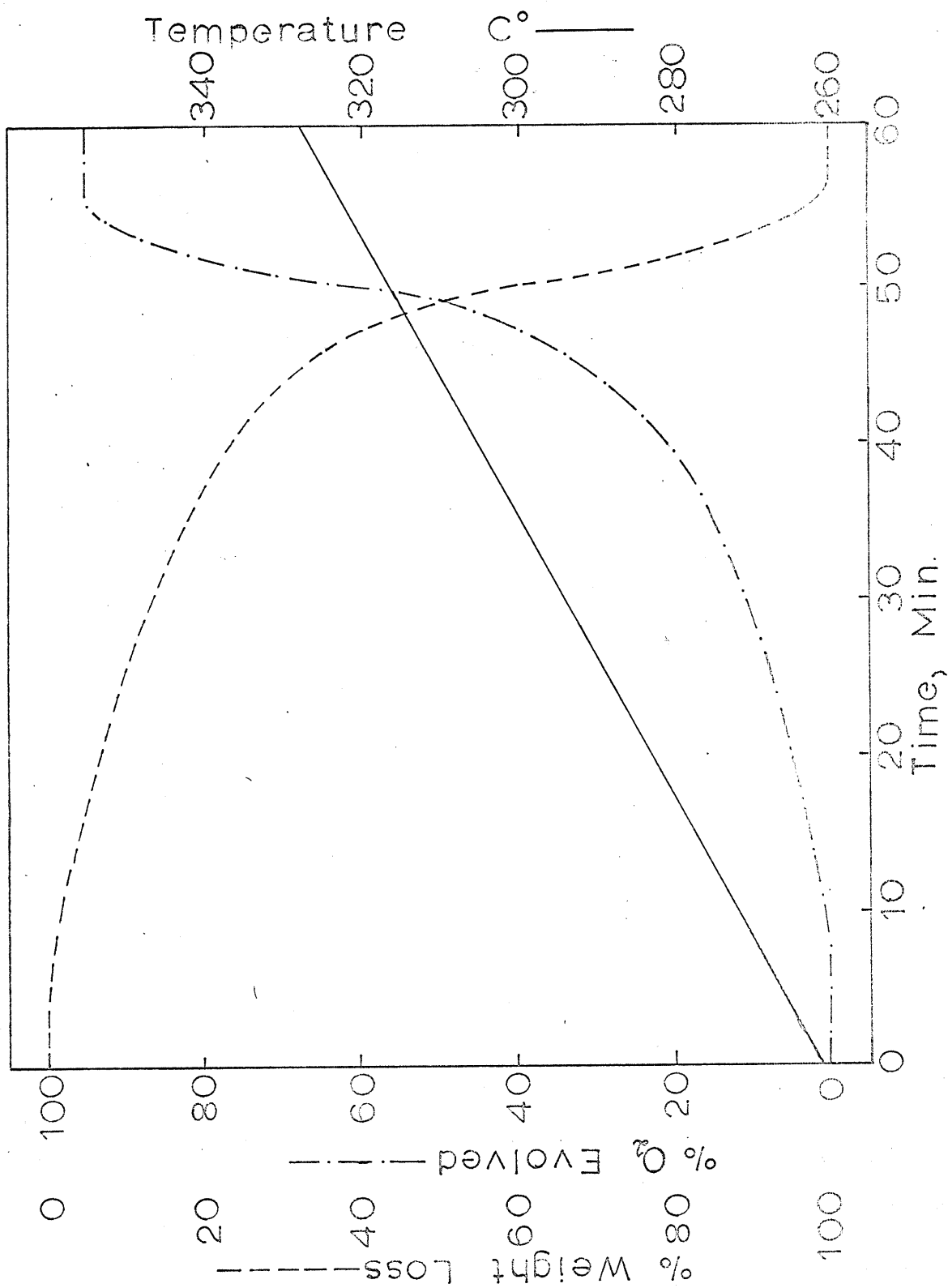
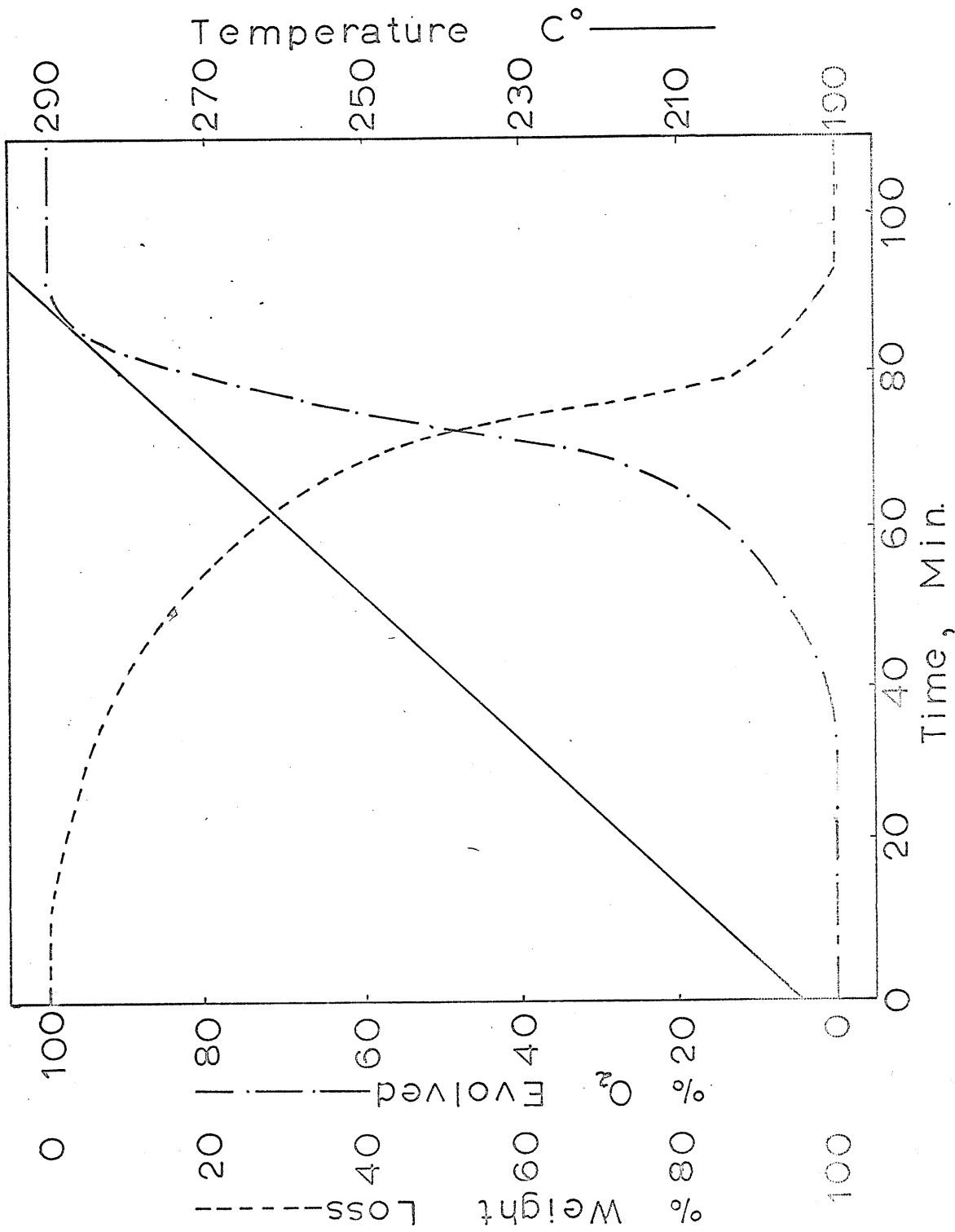


FIG. 22 DECOMPOSITION OF $\text{Ba}(\text{BrO}_3)_2$

FIG. 23 DECOMPOSITION OF AgBrO_3

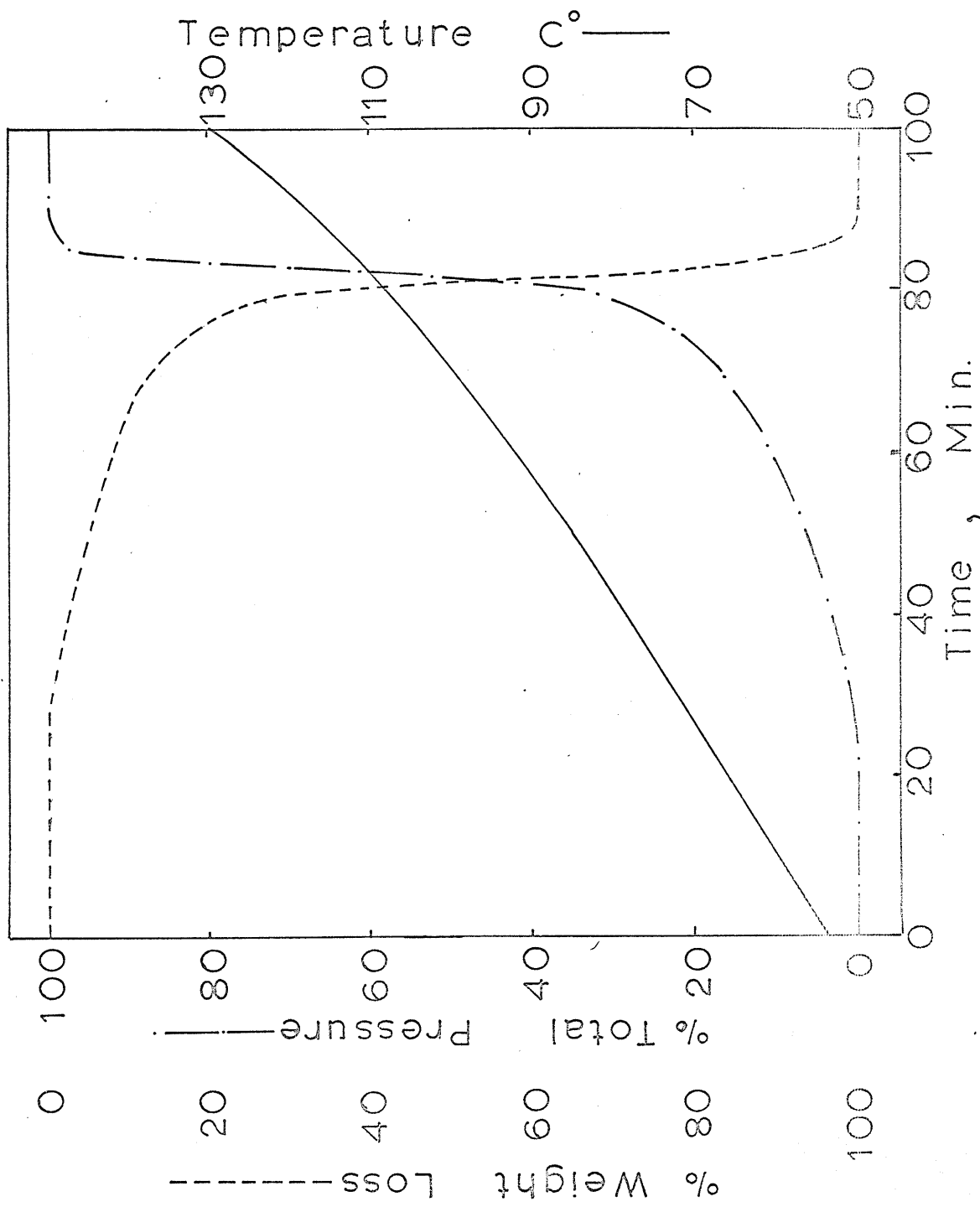


FIG. 24 DECOMPOSITION OF $\text{Co}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$

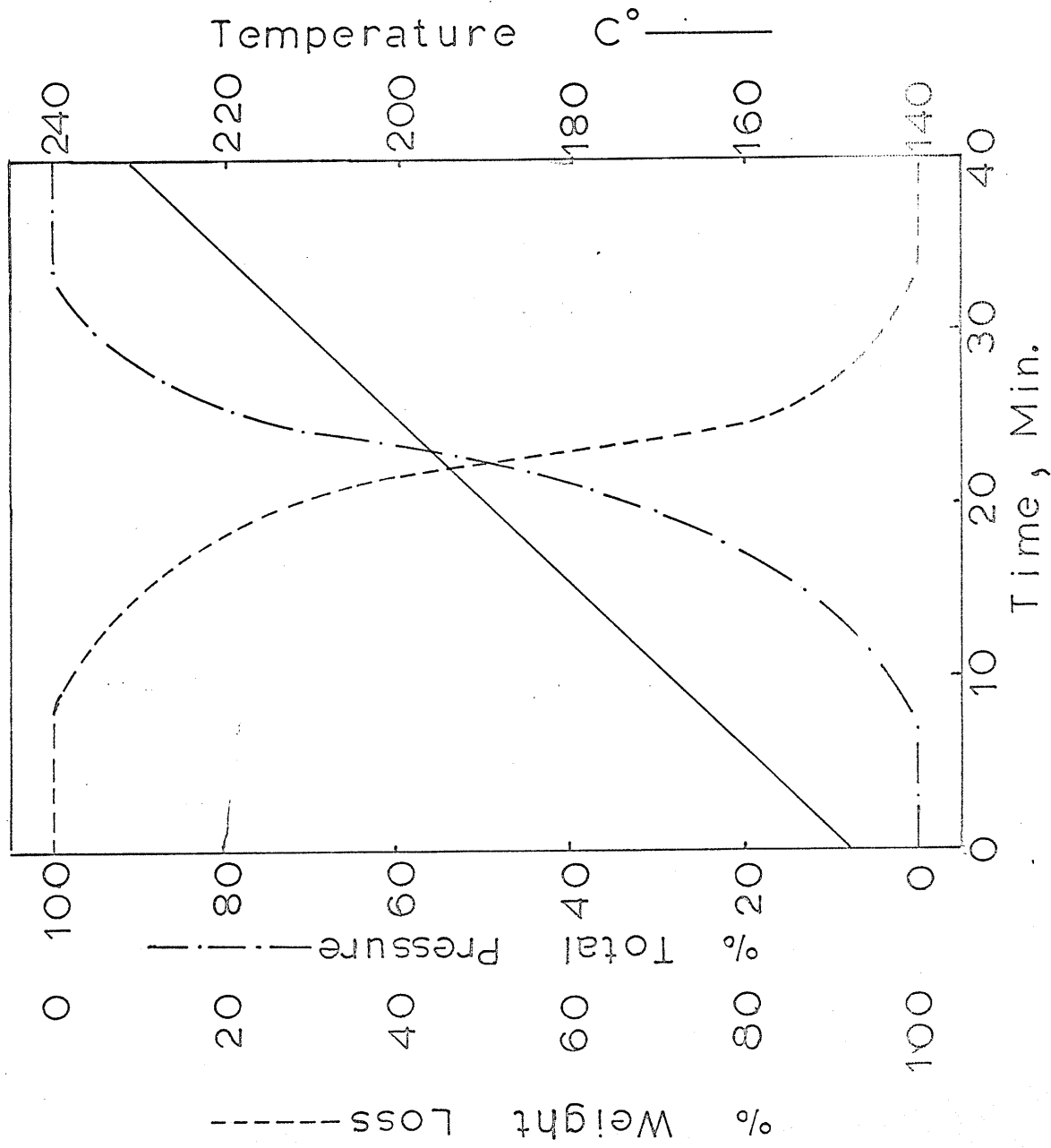


FIG. 25 DECOMPOSITION OF $\text{Ni}(\text{BrO}_3)_2$

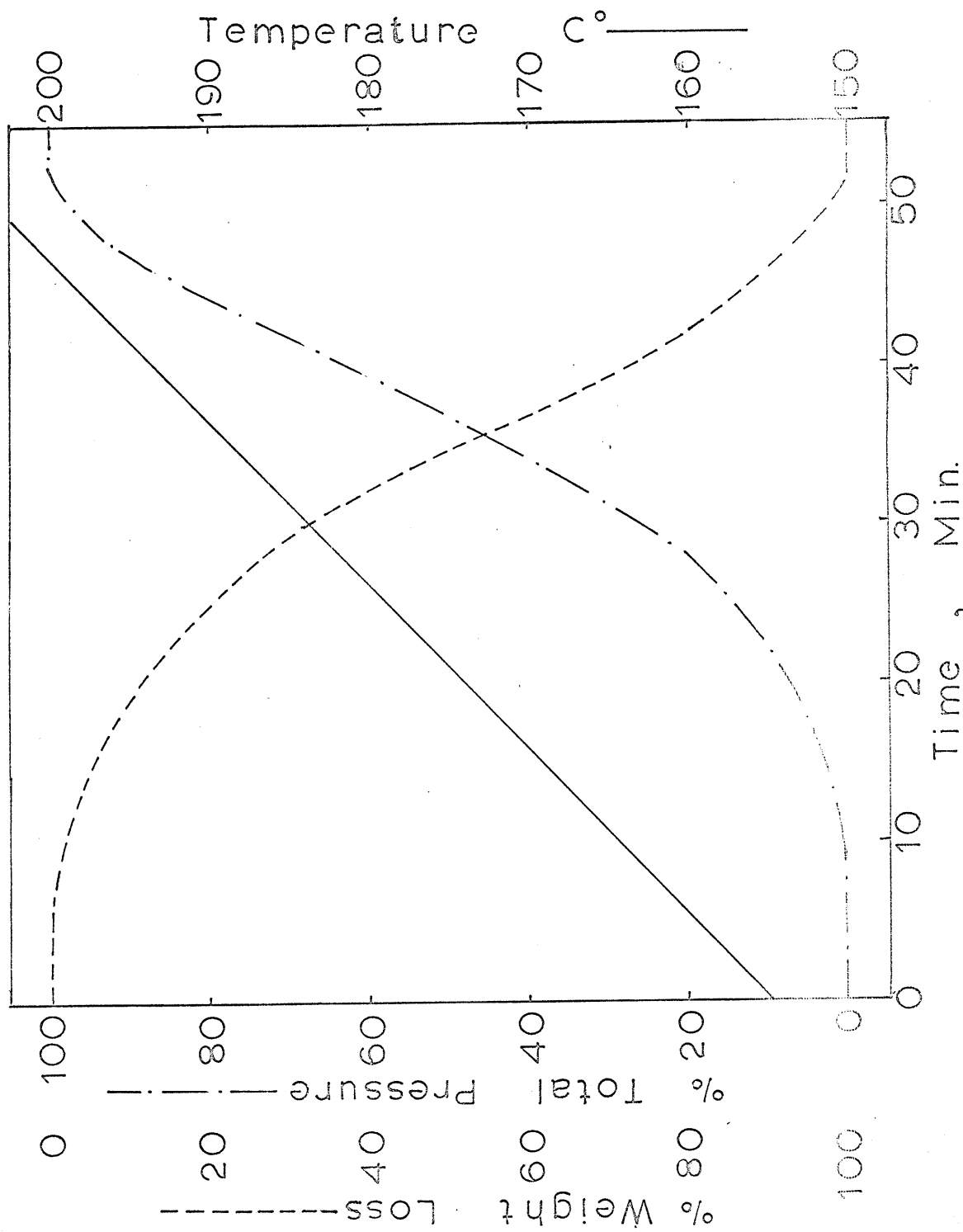


FIG. 26 DECOMPOSITION OF $\text{Zn}(\text{BrO}_3)_2$

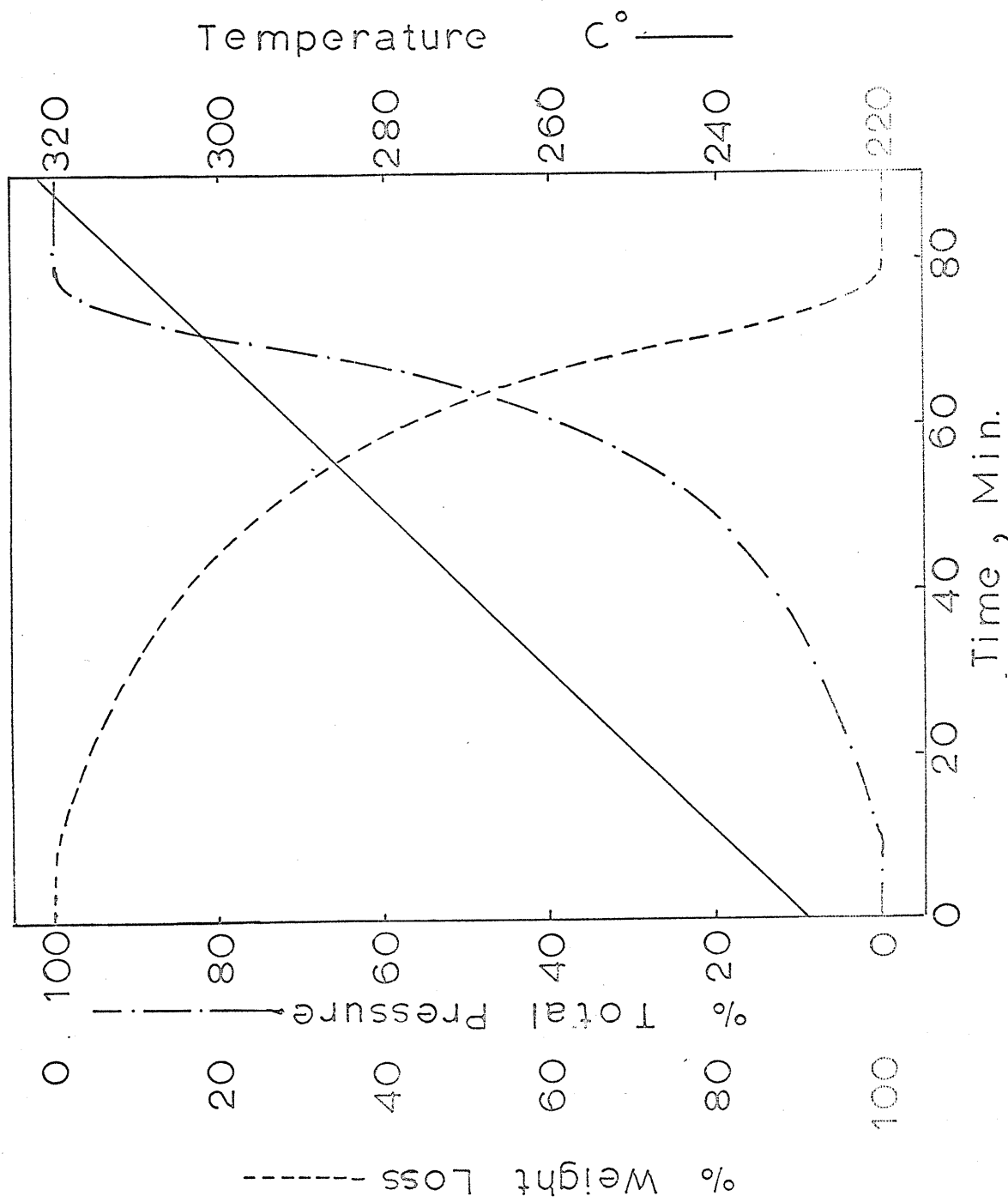


FIG. 27 DECOMPOSITION OF $\text{Cd}(\text{BrO}_3)_2$

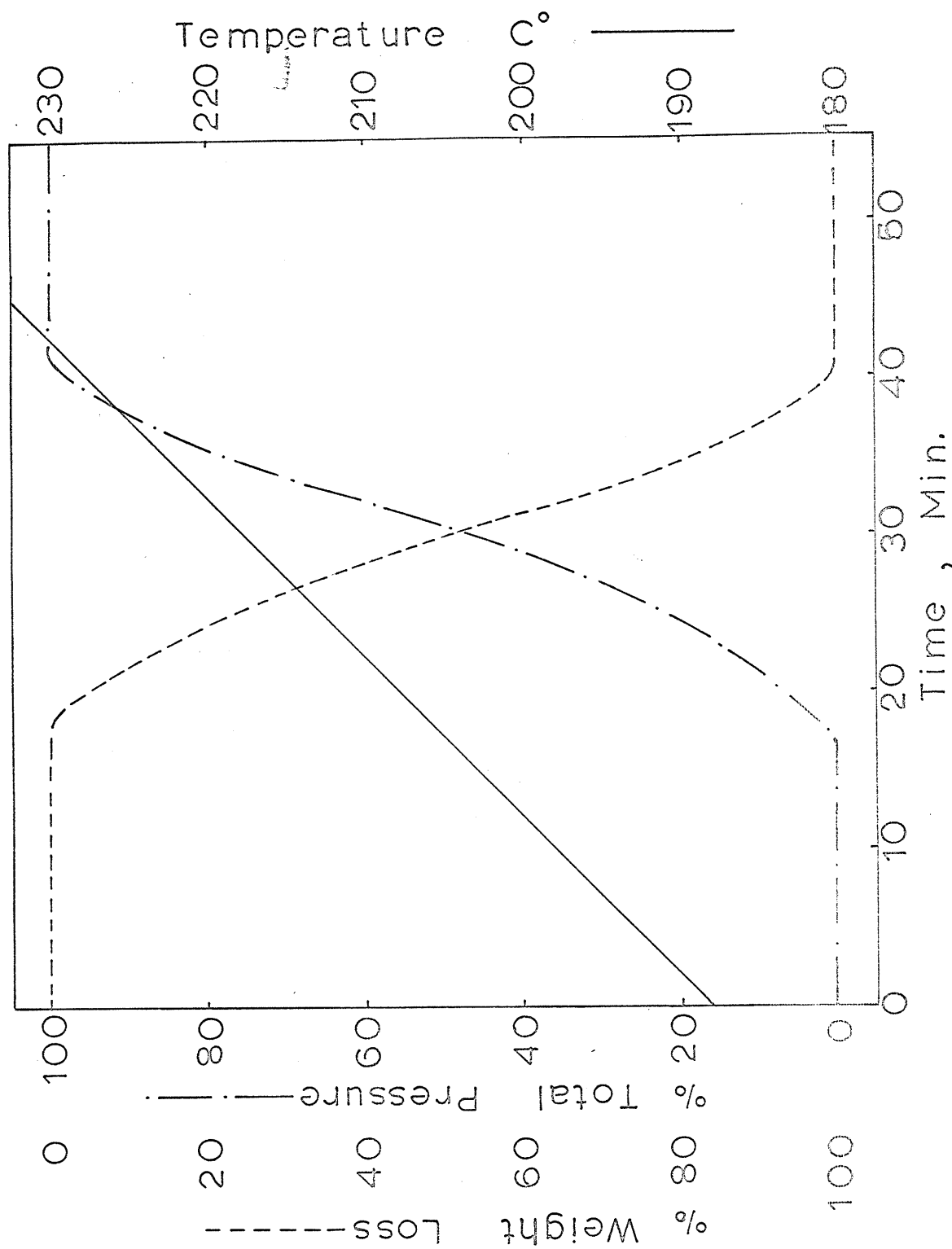


FIG. 28 DECOMPOSITION OF $\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$

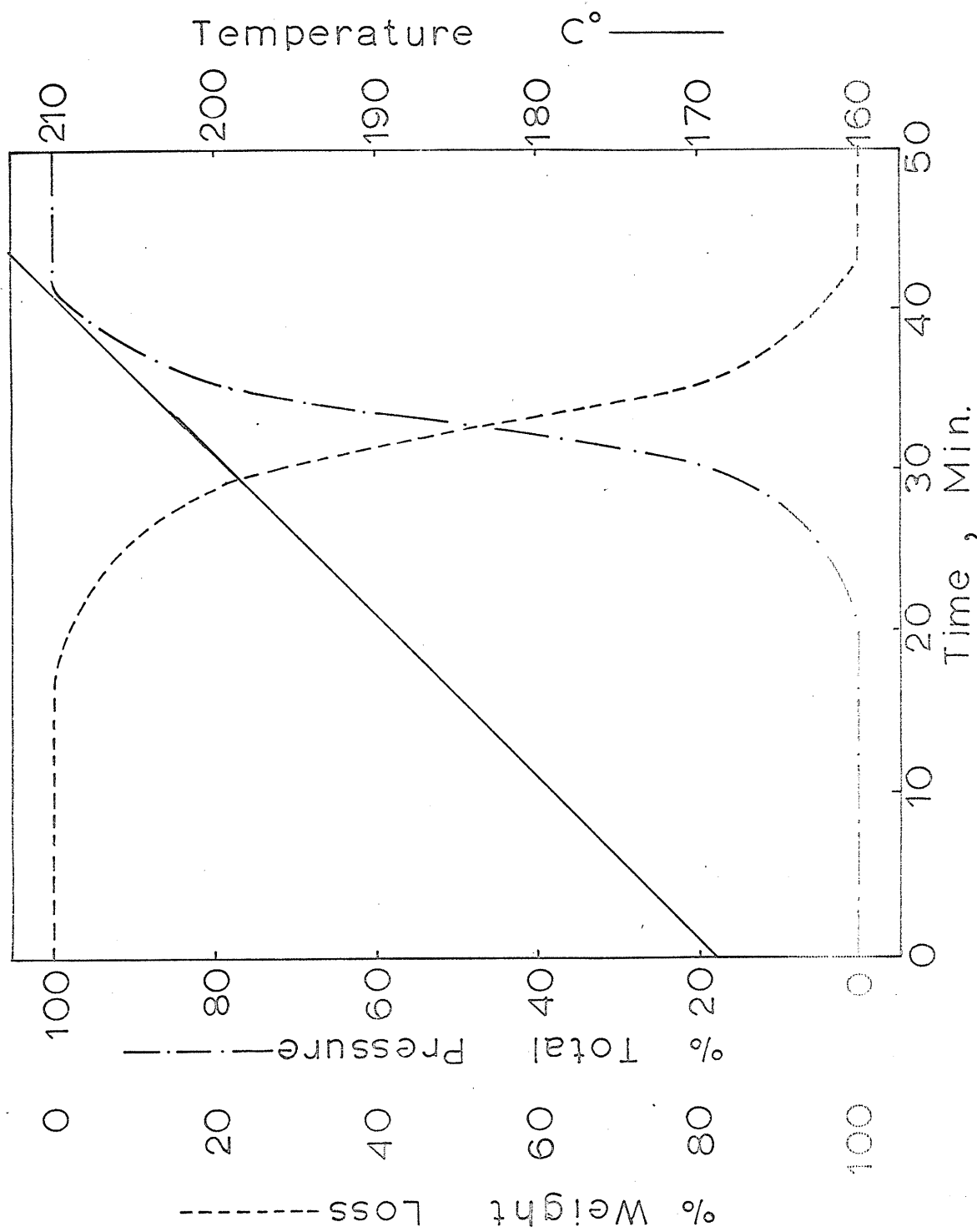


FIG. 29 DECOMPOSITION OF $\text{Pr}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$

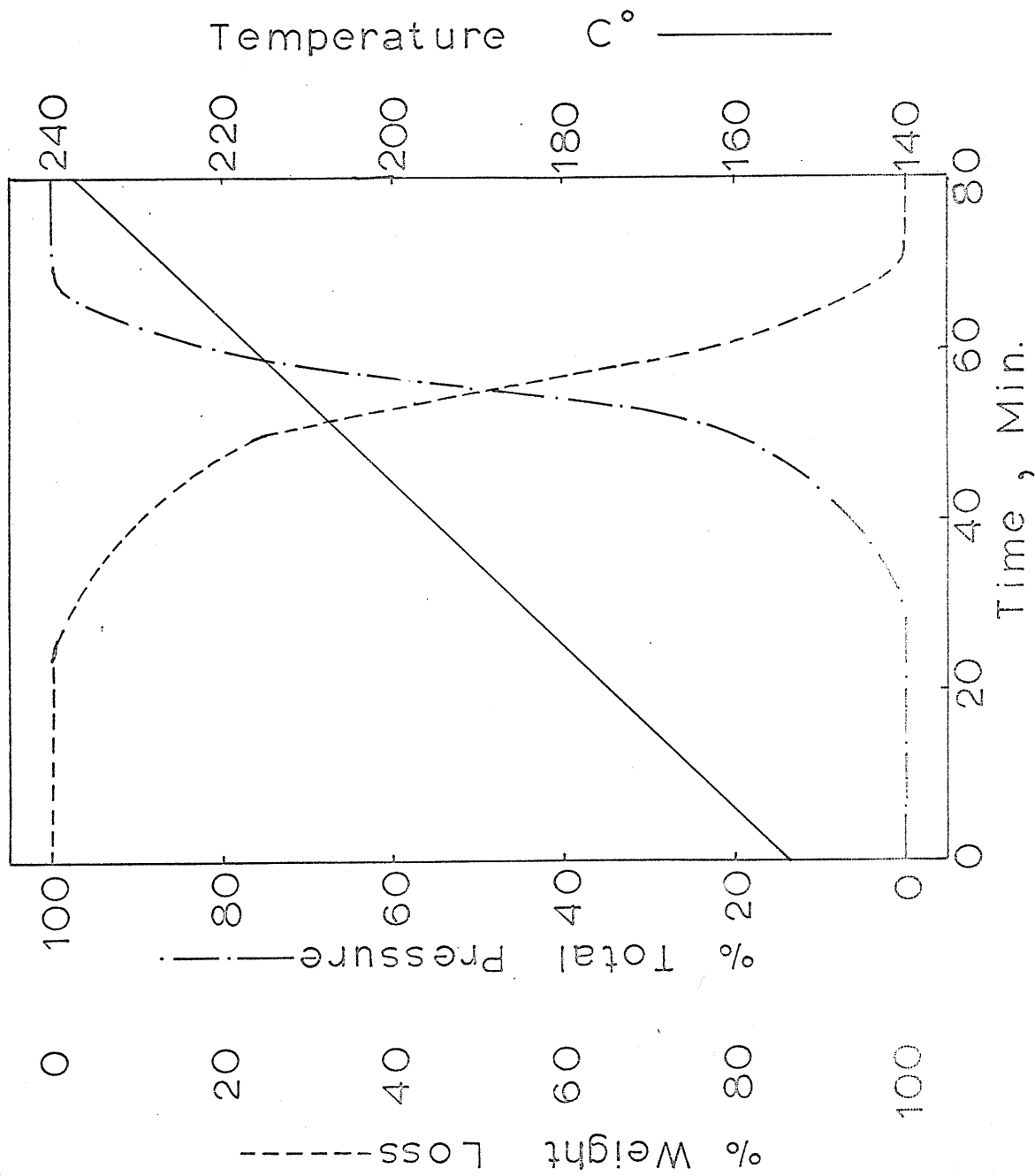


FIG. 30 DECOMPOSITION OF $Y(BrO_3)_3 \cdot 9H_2O$

Even though most of the bromates crystallize as hydrates, every attempt was made to completely dehydrate these bromates before decomposition to the bromide or oxide. Contrary to the work of Rocchioccioli¹⁹, the bromates of zinc and nickel were completely dehydrated before decomposition to the bromide or oxide ensued. However cobalt evolved two water molecules with bromine and oxygen as Rocchioccioli noted. Rocchioccioli decomposed the bromates under atmospheric pressure. The water is evolved at a much lower temperature under vacuum. This is probably the reason why anhydrous bromates of zinc and nickel were obtained in this work.

As seen in Table 5 the heating rate is nearly always equal to 1° C/min except for a few experiments. The percentage of bromate that decomposed to the bromide or oxide is also shown in Table 5. This percentage was determined by the analysis methods as described on p. 37 T_s as defined in the introduction is the temperature at which $\frac{W_o - W_f}{W - W_f} = \frac{1}{e}$.

The thermobarograms shown in Fig. 6-30 were plotted from the original thermobarograms. The original decomposition curves were in most cases not as smooth as the ones shown due to instability in the input voltage and the

radiometric effect. For convenience the weight and pressure readings were plotted as percentages of the totals. The time chosen as $t = 0$ was completely arbitrary and had no significance even when activation energies were calculated.

Thermodynamic Results

Table 7 shows the thermodynamic data, $\Delta F_{D1} - \Delta F_{D2} = \Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^-$ at different temperatures and at T_s . As described in the introduction, a negative value of $(\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^-)$ per equivalent indicates that the bromate should decompose to the bromide, and a positive value indicates that the oxide should be the decomposition product. $(\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^-)_{\text{equiv}}$ at $T = T_s$ was calculated from a linear interpolation of the other three values or in a few cases an extrapolation. Thus this free energy difference was evaluated at some common temperature to all the decompositions.

Table 8 shows the data necessary to calculate the ΔH_f of the alkali bromates at 298° C. Table 9 lists the calculated heats of formation of the alkali bromates along with the heats of formation of the oxide and bromide⁵² and the heats of decomposition to both the oxide and bromide. As noted in the introduction p. 26

TABLE 7

Free Energy Differences ($\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^-$) equivalent

Bromate	% Br ⁻	($\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^-$) equivalent			in kcal
		27° C	227° C	727° C	T _s ^o *
LiBrO ₃	90	-13.8	-12.9	-11.3	-11.6
NaBrO ₃	100	-36.2	-35.2	-32.8	-34.6
KBrO ₃	100	-51.8	-50.2	-46.9	-49.1
RbBrO ₃	100	-55.8	-54.9	--	-54.1
CsBrO ₃	100	-59.1	--	--	-51.5
Mg(BrO ₃) ₂	5	16.9	18.4	22.6	19.2
Ca(BrO ₃) ₂	100	-12.6	- 9.9	- 4.9	- 9.6
Sr(BrO ₃) ₂	100	-34.2	-30.7	-26.2	-30.2
Ba(BrO ₃) ₂	100	-49.0	-43.4	-38.8	-42.9
Zn(BrO ₃) ₂	1	2.9	5.2	4.9	5.0
Cd(BrO ₃) ₂	2	-16.9	-14.1	- 8.5	-13.5
Co(BrO ₃) ₂ ·2H ₂ O	3	- 1.4	1.3	5.4	- .1
AgBrO ₃	100	-19.2	--	--	-15.1
Ni(BrO ₃) ₂	7	.8	2.7	8.4	2.5
Nd(BrO ₃) ₃ ·9H ₂ O	20	9.0	14.0	18.0	14.0
Y(BrO ₃) ₃ ·9H ₂ O	15	18.9	17.8	24.2	17.7
Pr(BrO ₃) ₃ ·9H ₂ O	36	4.5	9.1	19.4	8.9

*from linear interpolation or extrapolation of the other three values.

--not known.

Note See Appendix for values of $\Delta F_f \text{ Br}^-$ and $\Delta F_f \text{ O}^-$

TABLE 8

Data for the Calculation of ΔH_f for the
Alkali Bromates in kcal per mole

Bromate	H [*]	S [†]	U = -H + S	ΔH_{fM}^{\ddagger}	$\Delta H_{fMX(s)}^{\circ}$	$\Delta H_{fMX(s)}^{\#}$ (inf, dil.)	$\Delta H_{fMX(s)}^{\times}$
KBrO ₃	-167	9.8	176.8	123.0	-80.7	-69.6	-79.4
LiBrO ₃	-212	0	212	162.8	-76.1	-77.8	-77.8
NaBrO ₃	-186	6.9	192.9	146.0	-73.8	-68.7	-75.6
RbBrO ₃	-160	11.5	171.5	118.3	-76.6		
CsBrO ₃	-153	14.2	167.2	110.1	-80.5		

* H from lyotropic numbers

† S determined in a calorimeter

‡ ΔH_{fM} from reference 54

ΔH_f (inf. dil.) from reference 55

° $\Delta H_{fMX(s)}$ from equation (17)

× $\Delta H_{fMX(s)}$ from $\Delta H_{fMX}(\text{inf. dil.}) + S$

$\Delta H_{fX(g)} = -26.9$ kcal/mole - an average value calculated
using equation 16 for lithium, sodium and
potassium bromates.

TABLE 9

ΔH_{D1} and ΔH_{D2} for the Decomposition of Alkali Bromates.
at 25° C in kcal/mole

Bromate	ΔH_f^* MBrO ₃ (s)	ΔH_f^+ Br ⁻	ΔH_f^\ddagger O ⁼	ΔH_{D1}	ΔH_{D2}
LiBrO ₃	-76.1	-83.6	-142.4	- 7.5	4.9
NaBrO ₃	-73.8	-86.0	- 99.4	-12.2	24.1
KBrO ₃	-80.7	-93.7	- 86.4	-13.0	37.5
RbBrO ₃	-76.6	-93.0	- 78.9	-16.4	37.1
CsBrO ₃	-78.3	-94.3	- 75.9	-16.0	4.0

* ΔH_f MBrO₃(s) from Table 8

† ΔH_f Br⁻ from reference 52

‡ ΔH_f O⁼ from reference 52

ΔH_{D1} and ΔH_{D2} could not be used to determine whether reaction (1) or (2) should proceed because of the large entropy term. However $\Delta H_{D1} - \Delta H_{D2}$ is very closely equal to $\Delta F_{D1} - \Delta F_{D2}$. Thus $\Delta H_{D1} - \Delta H_{D2}$ could be used to predict the decomposition products since the entropy changes, although large, are nearly identical for the two modes of decomposition.

If entropies were known, free energies of decomposition could be calculated. In addition, the value of $\Delta H_f \text{ BrO}_3^-(g)$ calculated should be very useful in obtaining $\Delta H_f \text{ MBrO}_3(s)$ for other bromates, since the calculated values for sodium, potassium and lithium are close to the literature values.

The Kinetics

Table 10 lists the kinetic parameters E^* and A for the bromates and calcium oxalate monohydrate. Fig. 31 and 32 are typical plots of θ vs. $\ln \ln \frac{W_0 - W_f}{W - W_f}$ from which E^* is extracted. The two E^* values calculated from Fig. 31 for the decomposition of calcium oxalate monohydrate (Fig. 6 and 7) were in excellent agreement with those calculated by Freeman and Carroll⁵⁸ (22 kcal), Horowitz and Metzger⁶⁰ (20.2 kcal) and Coats and Redfern⁶¹ (21.2 kcal). An example of the plot of $\ln \ln \frac{W_0 - W_f}{W - W_f}$ vs. θ for the bromates is seen

TABLE 10

Kinetic Parameters E^* and A for the Decompositions

Compound	Heating Rate $^{\circ}\text{C}/\text{min}$	E^* kcal/mole	A min^{-1}
LiBrO_3	1	277^{D}	8.0×10^{115}
NaBrO_3	1	84^{W}	1.1×10^{29}
KBrO_3	1	118^{D}	1.8×10^{38}
RbBrO_3	3	54^{W}	7.8×10^{16}
RbBrO_3	1	49^{W}	4.3×10^{14}
CsBrO_3	2.5	33^{W}	2.4×10^{10}
CsBrO_3	1	26^{W}	4.4×10^7
$\text{Mg}(\text{BrO}_3)_2$	1	20^{W}	8.5×10^5
$\text{Ca}(\text{BrO}_3)_2$	1	288^{W}	4.0×10^{119}
$\text{Sr}(\text{BrO}_3)_2$	1	68^{W}	8.1×10^{26}
$\text{Sr}(\text{BrO}_3)_2$	1	65^{W}	2.1×10^{25}
$\text{Ba}(\text{BrO}_3)_2$	1	52^{W}	1.9×10^{18}
$\text{Ba}(\text{BrO}_3)_2$	1	52^{W}	1.1×10^{18}
$\text{Cd}(\text{BrO}_3)_2$	1	38^{W}	2.5×10^{13}
$\text{Ni}(\text{BrO}_3)_2$	2	46^{W}	9.6×10^{20}
AgBrO_3	1	45^{W}	1.2×10^{17}
$\text{Zn}(\text{BrO}_3)_2$	1	46^{W}	8.1×10^{20}
$\text{Co}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$	1	21^{W}	8.5×10^{10}
$\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$	1	91^{W}	8.7×10^{39}

TABLE 10 continued

Compound	Heating Rate °C/min	E* kcal/mole	A min ⁻¹
Y(BrO ₃) ₃ ·9H ₂ O	1	47 ^w	1.8 x 10 ²⁰
Pr(BrO ₃) ₃ ·9H ₂ O	1	133 ^w	1.4 x 10 ⁶¹
CaC ₂ O ₄ ·H ₂ O	2	20.6 ^w	3.3 x 10 ⁹
		21.0 ^p	
CaC ₂ O ₄ ·H ₂ O	3	20.9 ^w	1.1 x 10 ¹⁰
		21.2 ^p	

w - from weight readings

p - from pressure readings

in Fig. 32. These two plots are from decompositions of $\text{Ba}(\text{BrO}_3)_2$ at the same heating rates (Fig. 21 and 22). An excellent straight line was obtained for the first part of the reaction but there was deviation near the end of the decomposition. Most of the bromates showed the same type of kinetic plot. For all the decompositions except those of calcium and lithium bromates, a straight line kinetic plot was obtained for over the first two-thirds of the decomposition. In the case of lithium and calcium decompositions linearity in the kinetic plot was obtained over about one-half of the decomposition.

FIGURE 31

Plot of θ vs $\ln \ln \frac{W_0 - W_f}{W - W_f}$ for the decompositions of

$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (see Figures 6 & 7)

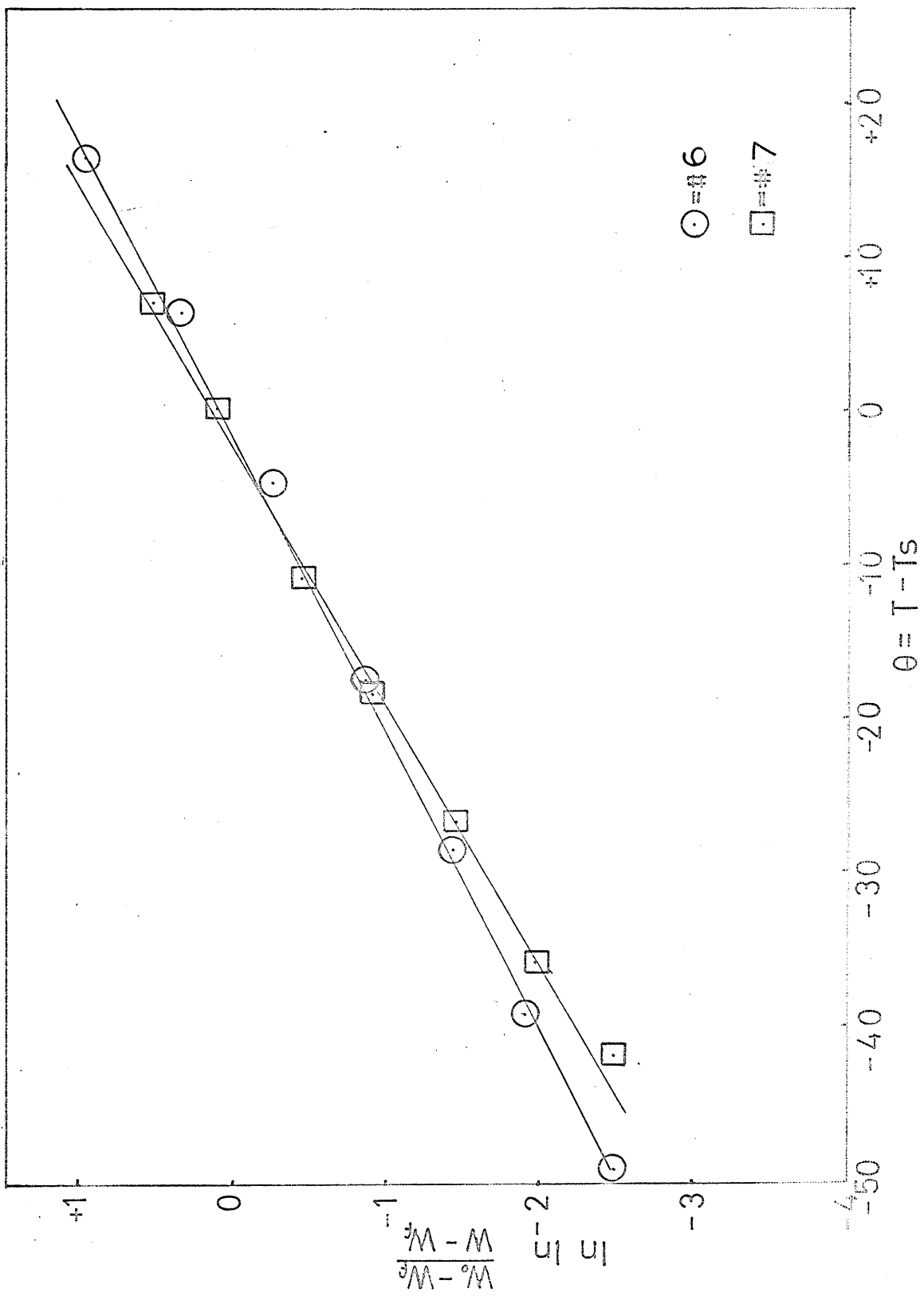
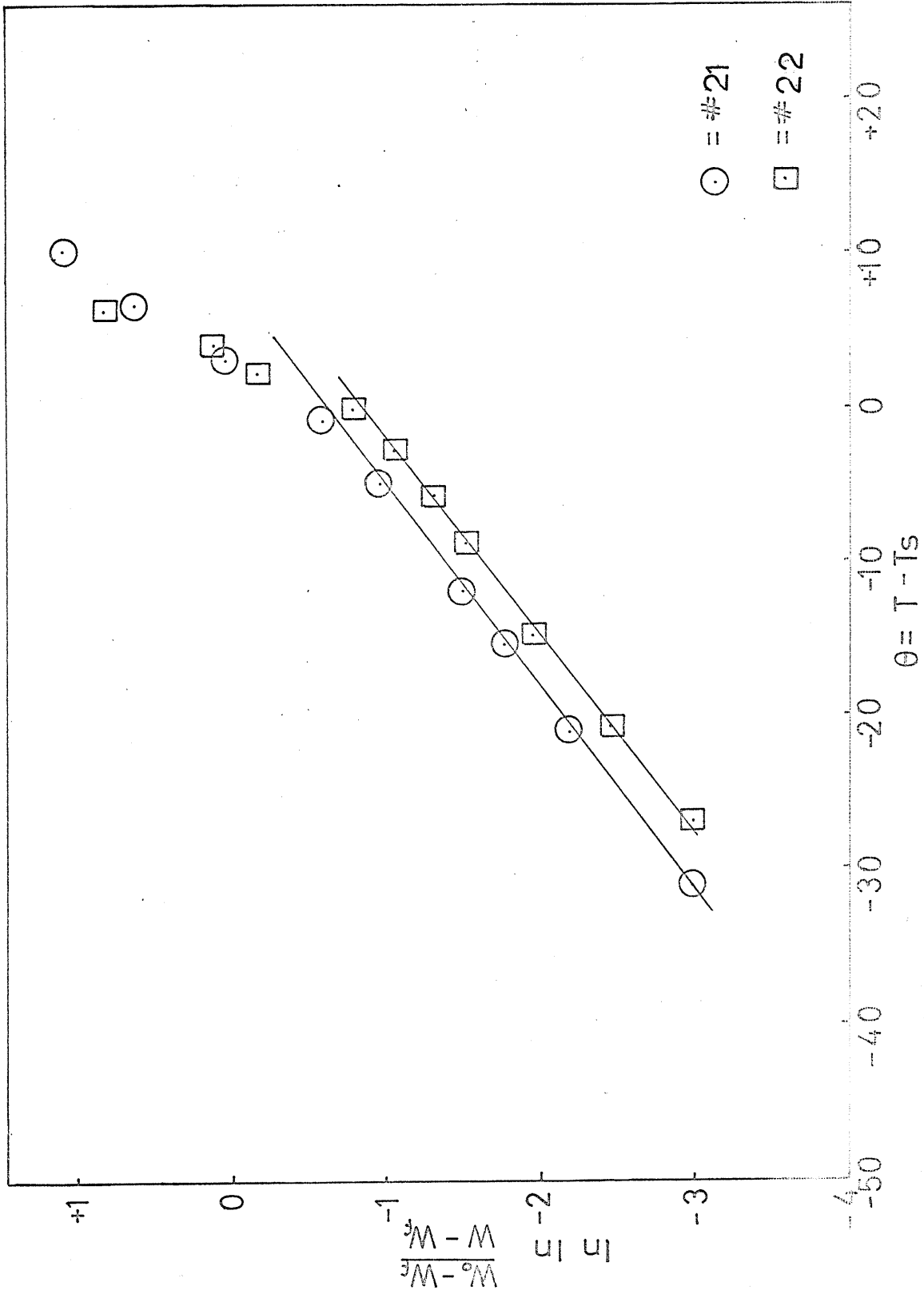


FIGURE 32

Plot of θ vs $\ln \ln \frac{W_0 - W_f}{W - W_f}$ for the decompositions of

$\text{Ba}(\text{BrO}_3)_2$ (see Figure 21 & 22)



DISCUSSION

The Balance and Its Uses

To check the performance of the thermobalance and to check the accuracy of the temperature measurement, calcium oxalate was heated to 500°C (Fig. 8) under atmospheric pressure. The first plateau, after the evolution of water, began at about 240°C . The second plateau, after the evolution of carbon monoxide, began at 485°C . This contrasts with 230°C and 435°C reported by Heinrichs³⁷ and compares well with 235°C and 485°C reported by Newkirk³². When calcium oxalate monohydrate was heated under very low initial pressures (Fig. 6 and 7), the water was evolved at a much lower temperature than when heated at atmospheric pressure. However, the activation energies calculated both from the pressure and weight readings were in excellent agreement with that calculated by previous workers. The above results suggest two things:

1. that the temperature being recorded was close to the true temperature of the sample if it is assumed that the temperatures recorded by Newkirk are accurate and

2. that the recorded weight and pressure readings were accurate, since the activation energy agreed with the previously determined values.

Fig. 33 shows the decomposition of $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$. One and one-half molecules of water were evolved between 60° and 90° C and the other half molecule was evolved at a much higher temperature. Finally the anhydrous bromate decomposed to give cadmium oxide, bromine and oxygen with a trace of cadmium bromide.

Two important features are illustrated by the thermobarogram of $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$. The first is that not only the weight but also the pressure remained constant over the long plateau from 90° C to 200° C. This would not be expected ordinarily, but the heated volume of about 50 ml was small in comparison with the total volume (400 ± 2 cc.). The second consequence provides a unique use for the apparatus. If only one gas is evolved in the decomposition, the weight and the pressure readings are redundant although one is a good check on the other. However as seen in the thermobarogram of $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$, the pressure reading is not redundant, because water, although a very non-ideal gas, constituted a much greater percentage of the total pressure than of the weight loss.

A better example is illustrated by Fig. 10, the decomposition of LiBrO_3 at constant temperature. Lithium bromate, like all bromates could decompose to the bromide and/or the oxide. The following two reactions were thus

FIGURE 33

The decomposition of $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$

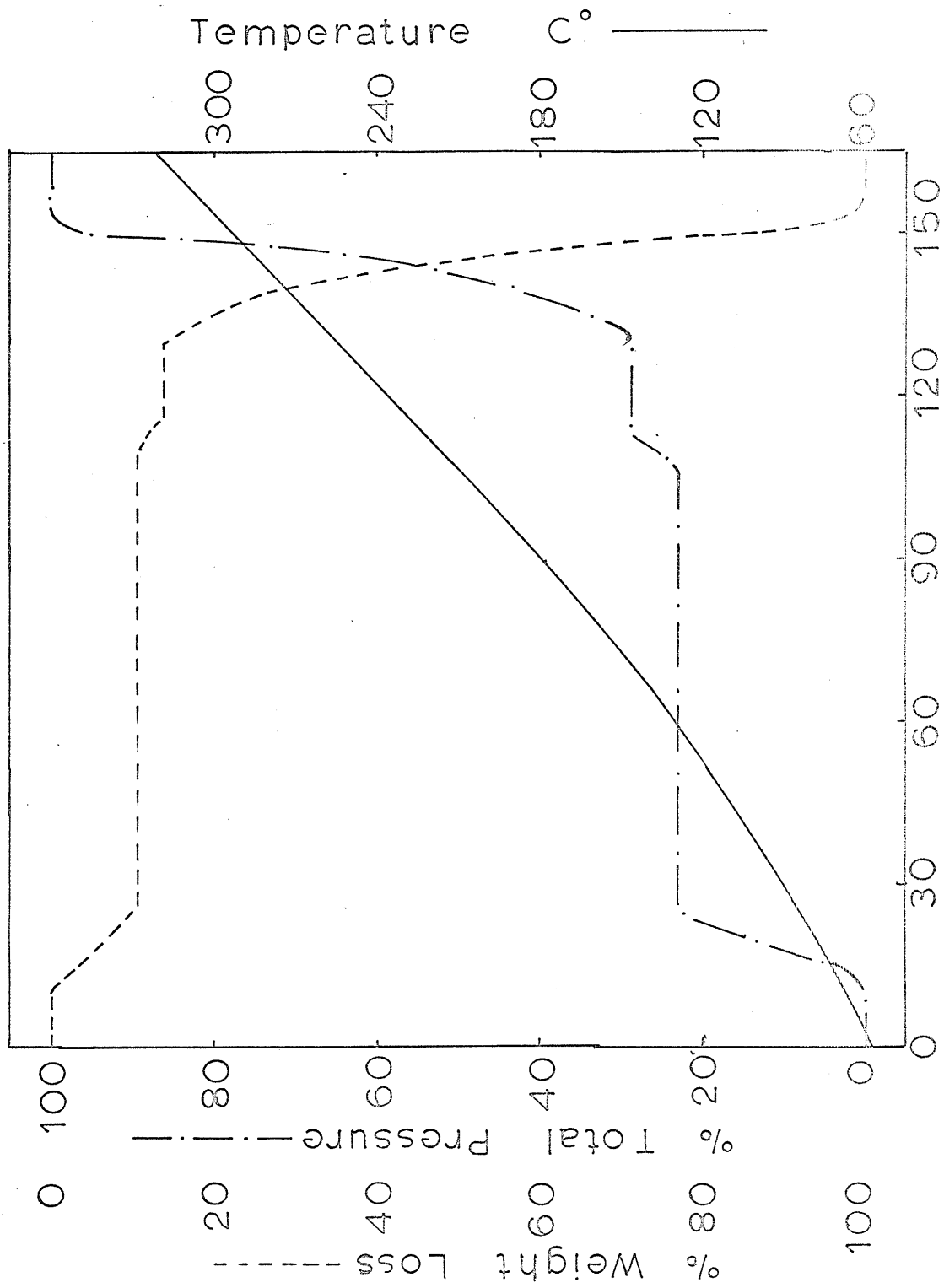


FIG. 33 DECOMPOSITION OF $\text{Cd}(\text{BrO}_3)_2 \cdot 2 \text{H}_2\text{O}$

competing:



The total pressure in the system due to lithium bromate decomposing to both the bromide and oxide could be expressed as:

$$\begin{aligned} P_t &= 3/2 P_1 + 5/4 P_2 + \frac{1}{2} P_2 \\ &= 3/2 P_1 + 7/4 P_2 \end{aligned} \quad (33)$$

where $3/2 P_1$ is the pressure due to decomposition by reaction(1)

and $7/4 P_2$ is the pressure due to decomposition by reaction (2).

Since at low pressures

$$PV = nRT$$

$$\text{the weight loss} = \Delta W = \frac{PVM}{RT} \quad (34)$$

where $V = .4$ liters

$$R = .0821 \text{ liter-atmos } ^\circ\text{C}^{-1} \text{ mole}^{-1}$$

$$\text{M.W.} = M = 160 \text{ for Br}_2 \text{ and } 32 \text{ for O}_2$$

$$\text{Let } X = \frac{V}{RT}$$

where X is a constant

$$\text{Then } \Delta W = 48XP_1 + 80XP_2 + 40XP_2 \quad (35)$$

Substituting the value for X into equation (35)

$$\Delta W = 1.04 \times 10^{-2} P_1 + 2.60 \times 10^{-2} P_2 \quad (36)$$

where P is in cm Hg and ΔW is in grams.

Equations (33) and (36) are two equations with two unknowns.

Solving:

$$P_1 = 71.9 \Delta W - .50 P_t \quad (37)$$

$$P_2 = 1.25 P_t - 83.8 \Delta W \quad (38)$$

Thus if the weight loss and pressure were known at any time, the number of moles of bromide and oxide present at that time could be calculated using P_1 and P_2 and substituting into $n = \frac{PV}{RT}$.

If 0.0739 grams of lithium bromate decomposed entirely to the bromide, the weight loss would be 25.9 mg and the pressure rise 3.76 cm. If 0.0739 grams of lithium bromate decomposed entirely to the oxide, the weight loss would be 65.3 mg and the final pressure 4.38 cm. The observed weight loss was 31.9 mg and the final pressure 3.95 cm. Obviously then decomposition to both the bromide and oxide had occurred.

From Fig. 10, the number of moles of lithium bromide and oxide at different times during the course of the reaction were calculated using equations (37) and (38) and were plotted separately in Fig. 34. It is very interesting to note that the lithium oxide is formed initially and then no more bromine is liberated. The slight loss of lithium oxide

FIGURE 34

The analysis of Figure 10

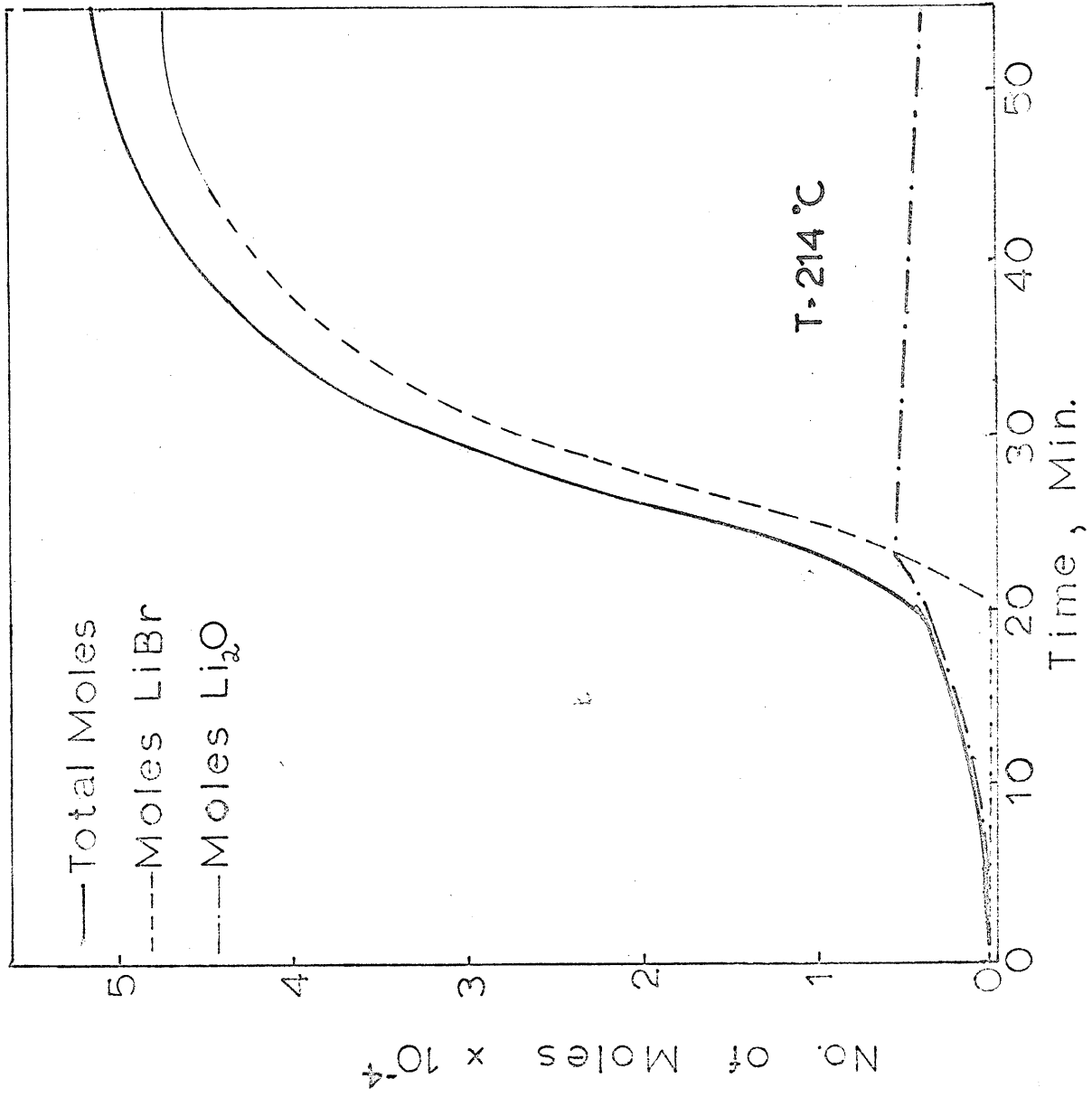
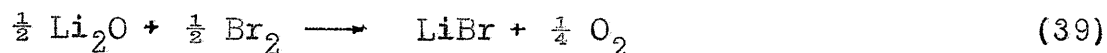


FIG.34 ANALYSIS OF FIG.10

as the reaction proceeds is probably due to experimental error but could be due to the reaction:



since $(\Delta F_f \text{Br}^- - \Delta F_f \text{O}^{2-})_{\text{equiv}}$ is -11 kcal. Lithium oxide, prepared from lithium carbonate did not react with bromine at 250° C which seems to rule out the possibility of reaction (39) proceeding. This will be discussed in more detail in a later section. If lithium bromate did not have to be heated at constant temperature to prevent splattering, activation energies for the bromate decomposing to the bromide and the bromate decomposing to the oxide could have been calculated.

The bromates of magnesium, nickel, zinc, cadmium, cobalt and the rare earths also decomposed to oxide and the bromide. However the above method was not used for the first four of the bromates mentioned because of the very small amount of bromide formed. For cobalt and the rare earths, the method could not be used because a third gas, water, was evolved while the bromates decomposed. Equations (33) and (36) would then become two equations with three unknowns.

As was illustrated by the decomposition of lithium bromate, the use of pressure and weight readings became very useful. This method could be used if a compound decomposes by either of two competing reactions provided two different

gases having appreciably different molecular weights are evolved. The decomposition of such compounds as chlorates, perchlorates, iodates and periodates could be studied in this way.

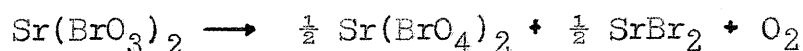
Although several articles have been written on the errors that are introduced into thermogravimetry at low pressures^{49,50} very little error was introduced by these so-called aerodynamic effects in this investigation. As seen in Table 6, the error in the weight and pressure readings was never more than 3% except when splattering or absorption by the core became important. However, the balance does not seem suitable for atmospheric or high pressure work, although the pressure gauge would still function as a differential detector. For high pressure work and for the elimination of adsorption by the core in the decomposition of hydrated rare earth bromates, the sample would have to be above the core. Most of the high pressure thermobalances now made have the sample above the core of the linear variable differential transformer.

The Search for Perbromate

As seen in Fig. 9-30, only strontium bromate shows a distinct discontinuity in the decomposition curve. However the magnesium bromate thermogram Fig. 17 shows a tendency

for the weight and pressure readings to level off. This tendency, although not evident on the original large thermobarograms, became noticeable in the condensed graph. Thus for magnesium, Fig. 17 was not taken as evidence for perbromate formation.

If the reaction proposed by Hackspill and Winterer¹⁷ occurred for strontium bromate i.e.



then the perbromate would form until one-third of the total oxygen had been liberated. The break in the decomposition curves at about one fifth of the total oxygen evolved could be due to the tendency toward perbromate formation. Because this appeared promising, the strontium bromate was decomposed at constant temperature, Fig. 35. A tendency for the weight and pressure readings to level off was observed but no plateau was formed. Another identical experiment was performed, except at point b the sample was removed from the furnace and an infra red spectrum was taken using a potassium bromide pellet. The spectrum was found to be identical to that of the anhydrous bromate (Fig. 36, trace C). Trace B in Fig. 36 shows the spectrum of strontium bromate monohydrate and trace A the spectrum of the pure potassium bromide pellet. By analogy with the chlorate and perchlorate, and the iodate and periodate, a small shift should be observed

FIGURE 35

The thermobarogram of $\text{Sr}(\text{BrO}_3)_2$ at constant temperature

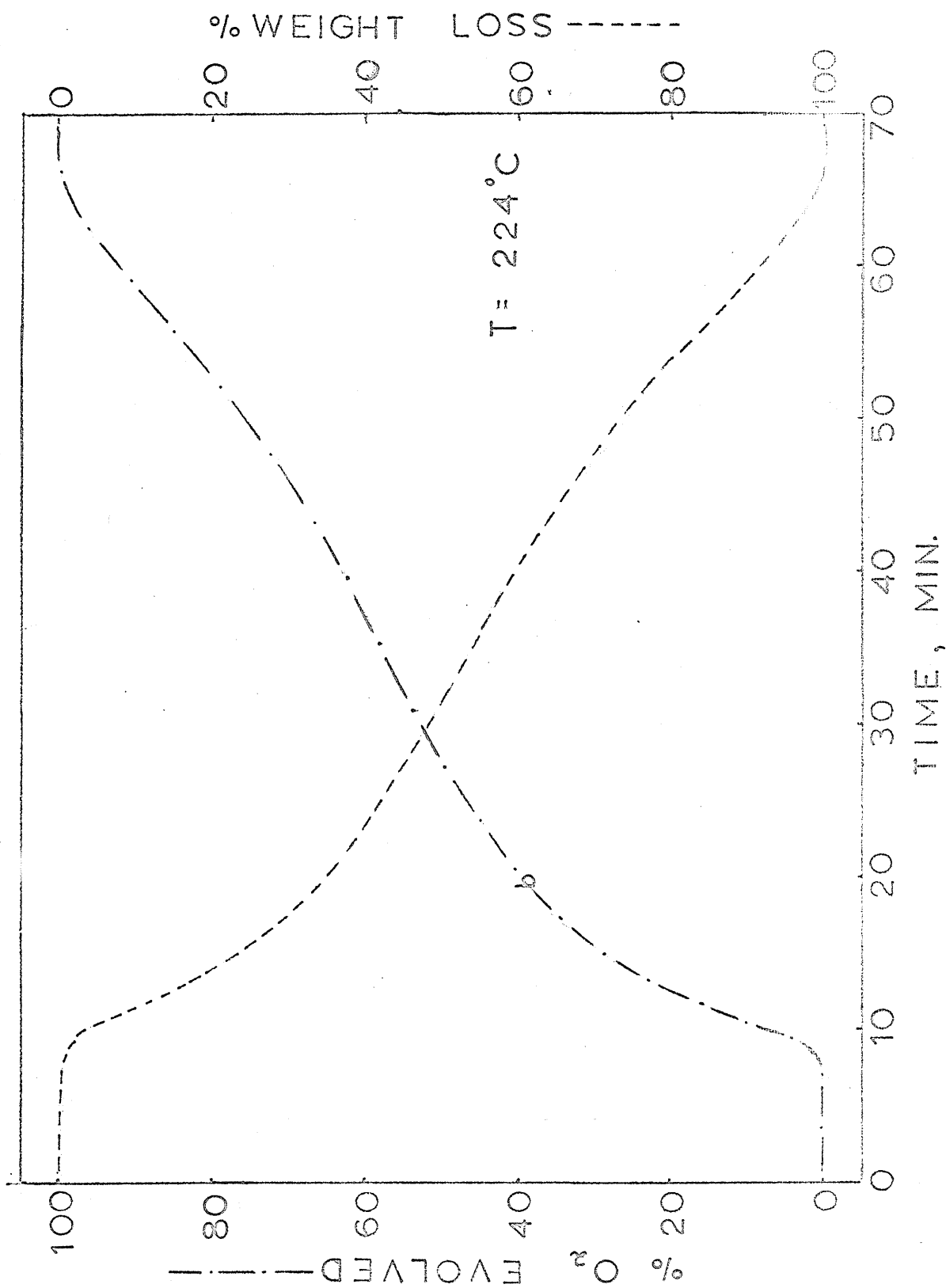


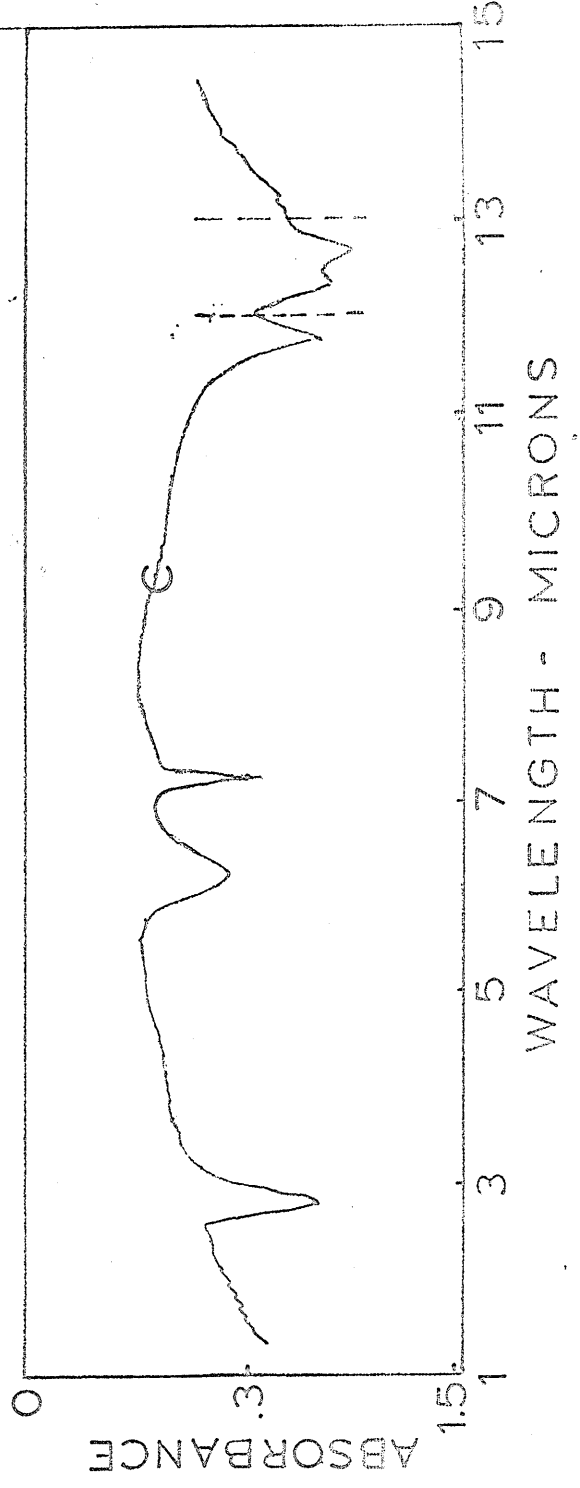
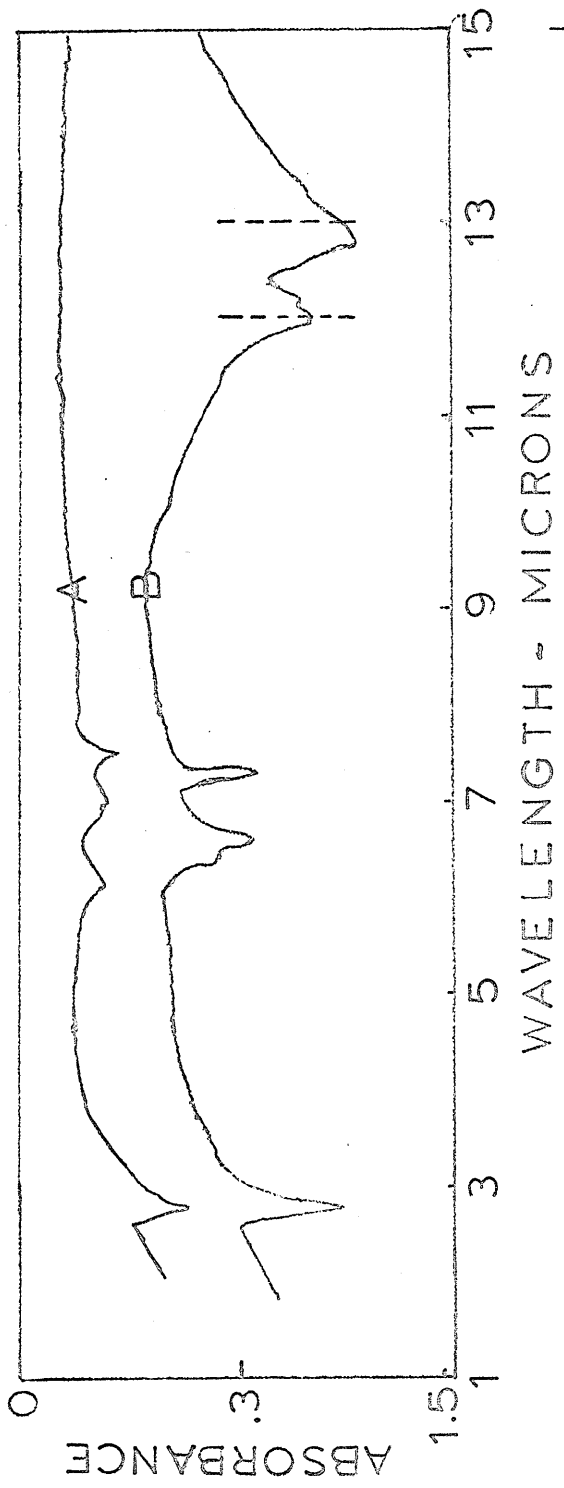
FIGURE 36

The infra red spectra of:

A) KBr

B) $\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$

C) SrBrO_3 before decomposition and
at point b on Fig. 35.



in the two peaks at 11.80 and 12.65 microns if perbromate was formed⁶⁵. However no shift was observed. It is possible, but not probable, that the structure of the sample changed when cooled or when the potassium bromide disc was made under high pressure. Ideally, infra red spectra should be taken as the sample is being heated. In this way, the structural changes of the sample could be followed continuously.

This discontinuity in the decomposition of strontium bromate was not observed by either Hackspill and Winterer¹⁷ or Rocchioccioli¹⁹. It is possible that some small impurity other than bromide in the strontium bromate could cause this. However Hackspill and Winterer and Rocchioccioli decomposed the strontium bromate under atmospheric pressure. In addition, much higher heating rates were used - 150° C per hour in comparison to 60° C per hour used in this study. This higher heating rate could easily obliterate the discontinuity.

The Thermobarograms

Except for the decompositions of calcium and strontium bromates, the thermobarograms are typical of autocatalytic decompositions i.e. the rate of decomposition increases as more product is formed. The decomposition of barium bromate

is typical of this type. These curves are qualitatively similar to the thermogram of Hackspill and Winterer¹⁷. There is no indication of a discontinuity or a plateau in contrast to Decoursey's thermobarogram¹⁸. Barium bromate was also decomposed at five different constant temperatures. However no discontinuity or plateau was observed in any of them. The thermobarograms of calcium and strontium bromates are not typical of usual solid state decompositions, either exothermic or endothermic⁶⁶. The products in these decompositions appear to inhibit the decompositions. However the thermobarogram of calcium bromate in this study is qualitatively similar to the thermogram of Rocchioccioli. It should be noted in Fig. 19 and 22 that 2.5 mole % strontium bromide and barium bromide were added to the strontium and barium bromates respectively. This had little effect on the rate of these decompositions. Thus the bromide impurities in some of the bromates should have little effect on the rate of decomposition.

Jach has reported^{27,28} melting during the decomposition of sodium and potassium bromate. Melting is due to a eutectic formation between the bromide and bromate which lowers the normal melting point of the bromate. Melting, although not characteristic of inorganic solid state decompositions⁶⁷, also probably occurred in the decomposition of

lithium bromate. In this study, melting was very likely the cause of splattering in the decompositions of lithium, sodium, and potassium bromates. Differential thermal analysis could detect the onset of melting in all the bromates.

To explain the different types of decomposition curves would require a detailed study at constant temperatures of each of the bromates using different catalysts or inhibitors. However some speculation will be undertaken here to suggest possible types of decomposition for the bromates. In the majority of cases studied the thermobarograms could be interpreted in terms of a three stage process⁶⁸: (1) a slow initial reaction occurring on the surface of the crystals (2) formation of nuclei of the new phase B (either oxide or bromide) and (3) a reaction occurring at the interface between phase A (the bromate) and phase B which then proceeds by an advance into the medium (the envelope mechanism). All of the bromates except strontium and calcium probably decompose in the above fashion. For calcium and strontium bromates, where the initial rate of decomposition is fast, the initial surface reaction probably does not occur, and the nuclei of the new phase B must commence to grow within a short time interval over the whole surface.

In solid reactions there are very many complications.

Thus the solid may crack under the strains created by the formation of the new solid phase and reaction may take place as follows:

(1) reaction at crystal defects close to a surface. This may then be followed by radial growth, so that one defect could lead to the decomposition of many molecules.

(2) reaction along dislocation lines possibly followed by expanding cylinders. As noted before, melting may occur. Jach^{27,28} postulated that melting speeds up the decomposition rates and may cause the decompositions to proceed autocatalytically.

The strontium bromate decomposition perhaps begins at crystal defects followed by the ordinary "envelope mechanism". Although there is no evidence for the above statement concerning strontium bromate, a change in the mechanism of decomposition seems likely at the discontinuity if no perbromate is formed, as is suggested by the infra red evidence. The electron microscope, differential thermal analysis and constant temperature experiments using different catalysts could clarify the mechanism of decomposition.

The Significance of the Kinetic Parameters

The advantages of evaluating reaction kinetics by a continuous increase in sample temperature are that consider-

ably less data are required than by the isothermal method and the kinetics can be probed over an entire temperature range in a continuous manner without any gaps. In addition, where a sample undergoes considerable reaction in being raised to the temperature of interest (as was the case with barium bromate decompositions at constant temperature), the kinetic parameters derived are often questionable. Jach²⁸ found that the main part of the decomposition of potassium bromate fitted an exponential law

$$P = P_{\infty} (1 - e^{-kt})$$

However P_{∞} was chosen by trial and error such that $\ln(P_{\infty} - P)$ gave a straight line. In effect, Jach arbitrarily chose $t = 0$ for the decomposition so that a straight line plot was obtained.

Jach states²⁸ that the rate constants for solid state decompositions can be represented by

$$k = Na e^{-\frac{E^*}{RT}}$$

where N is a number which varies with external features such as surface area and type of decomposition. Thus the A values given in Table 10 ($A = Na$) have no physical significance. The activation energy E^* also varies with conditions except in the simplest decompositions such as calcium oxalate monohydrate. From Table 10, the higher the heating rate, the

higher the apparent activation energy. Thus the calculated activation energy for the cesium bromate decomposition at a heating rate of 2.5° C/min is 33 kcal/mole whereas the calculated activation energy for the same compound at a heating rate of 1° C/min is 26 kcal/mole. A similar trend is also evident for rubidium bromate. Particle size is also important. Unground samples tended to explode in the heating chamber. Thus in general, the larger the particle size, the higher the apparent activation energy. All samples were ground vigorously in a mullite mortar for five minutes to ensure some kind of uniformity of particle size. Since each bromate was treated in the same way and since the calculated activation energy for the calcium oxalate monohydrate was in excellent agreement with that calculated by previous workers, then if a straight line kinetic plot was obtained, the calculated activation energies should be very close to the true values.

Except for the decompositions of calcium and lithium bromates a straight line was obtained over at least two-thirds of the decomposition, Fig. 32. For calcium and lithium a straight line was obtained for about half of the decomposition. The remaining portion of the decomposition could perhaps be fitted by another rate law. In the study of the decomposition of nickel oxalate monohydrate⁶⁹, the

decomposition curve was fitted by three different rate expressions so that a straight line Arrhenius plot could be obtained over the entire decomposition and so that different activation energies could be calculated for the three different steps of the decomposition. In a general study of this type, curve fitting does not seem to be feasible, when the activation energies are of somewhat doubtful meaning. The activation energies derived for the lithium and calcium bromates seem exorbitant. Perhaps the assumption that $n = 1$ breaks down for these bromates. Because of the complexity of the reaction, the significance of a first order reaction is not really known. It would be just as fruitful to fit the deviating portion of the Arrhenius plot with some other rate equation without worrying about what n has to be to fit the thermobarogram. The activation energies calculated for sodium and potassium bromates are almost double those calculated by Jach^{27,28} i.e. 84 and 118 kcal/mole as compared to 43-47 and 50-60 kcal/mole respectively. Excellent straight line kinetic plots were obtained for sodium and potassium bromates. The rate law used by Jach to determine the activation energy is, in the opinion of the author, no more fundamental to the theory of solid state decompositions than the one used in this study. However the advice of F. S. Stone⁷⁰ will be

heeded. He states, "Conclusions drawn from the fit of a particular rate expression at least provide the framework; physical methods such as optical or electron microscope examination, conductivity and absorption spectroscopy are needed to establish the details". Thus the activation energies will be used for comparative purposes only.

The results of these experiments shed little light on the nature of the fundamental steps which lead to the decompositions. Any discussion must be somewhat speculative. For the nickel, cadmium and zinc bromates, the activation energies calculated are fairly near the value quoted for the Br-O bond strength - 50.6 kcal⁷¹. Perhaps for these decompositions the rate controlling step is the stepwise breakage of the bromine-oxygen bonds. The resultant oxygen atoms would tend to collapse into the metal oxide structure when the bromine atoms become depleted in the neighbourhood. The result would be a gradual advance of the reaction zone into the crystal.

In the case of bromates that decomposed to the bromide, it is reasonable to assume that, except for calcium and strontium bromates, the bromide ions are instrumental in catalyzing the decomposition of the bromate ion. They may act as electron donors and attract oxygen atoms from neighbouring bromate ions. The resulting hypobromite ion would

decompose almost spontaneously. Another interpretation is analogous to that given by Glasner and Weidenfeld⁷². The bromate ion, when deprived of some of its oxygen atoms might attract oxygen atoms from its neighbours deeper in the crystals and atomic oxygen might diffuse through the partially decomposed solid. This oxygen atom diffusion mechanism was postulated because potassium iodide when heated with potassium perchlorate yielded potassium iodate. It is clear that more definite information regarding the chemical step leading to decomposition must rest on experiments more especially designed for its elucidation.

The Thermodynamics

The Free Energy Differences

The thermodynamic method of Markowitz, as described in the introduction, considers only the relative stabilities of the final products in predicting the decomposition products. No consideration was given to the kinetics or the kinetic steps involved in these decompositions. Thermodynamics can usually predict the equilibrium concentrations of a particular reaction. However the time taken to reach this equilibrium is dependent on the rate of the reaction which of course is determined by the kinetic parameters. In the experiments of this study, the gases (bromine and

oxygen) were evolved from the decomposing bromate into a very low pressure of about one micron as the reaction started to about five cms of Hg when decomposition finished. This is nearly the equivalent to pumping off the gases as they are being evolved (especially at the start of the decompositions). Thus the nature of these decompositions, as with most thermogravimetric decompositions seems to be irreversible and equilibrium does not seem likely to be reached either between the bromate and the decomposition products or the bromide and the oxide i.e.

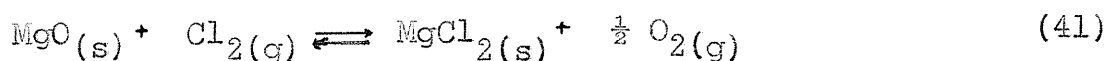


However at the end of the decomposition, the final gas pressures are probably not equilibrium values and if the bromide and oxide are present, the equilibrium represented by equation (40) may be approached at a measurable rate.

Because of the irreversible nature of the decompositions, it would seem reasonable that the kinetics should play an important role in determining the decomposition products. However, it should be noted that Markowitz was able to predict the decomposition products of all the perchlorates except magnesium just using $(\Delta F_f Cl^- - \Delta F_f O^-)_{equiv}$. For all the perchlorates except magnesium, $(\Delta F_f Cl^- - \Delta F_f O^-)_{equiv}$ is either more negative than -15kcal or more positive than

5 kcal whereas for magnesium it is almost zero. For the decompositions of the bromates of lithium, calcium, cadmium, cobalt, nickel and zinc, $(\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^-)_{\text{equiv}}$ is between -15 kcal and +5 kcal. Thus the bromates should test the thermodynamic method more severely than the perchlorates did.

Before discussing the results, it would be useful to review the method Markowitz⁵¹ used to interpret the decomposition products of magnesium perchlorate. Since $(\Delta F_f \text{ Cl}^- - \Delta F_f \text{ O}^-)_{\text{equiv}}$ is zero, about equal amounts of each of the chloride and oxide should be formed according to thermodynamics since the equilibrium constant is equal to 1. However depending on conditions, mostly chloride or oxide was formed. To explain this deviation on a thermodynamic basis, an equilibrium was postulated:



such that

$$\Delta F = RT \ln \frac{P_{\text{O}_2}^{\frac{1}{2}}}{P_{\text{Cl}_2}} \quad (42)$$

since $(\Delta F_f \text{ Cl}^- - \Delta F_f \text{ O}^-)_{\text{equiv}}$ is approximately zero.

Since $R = 1.98 \times 10^{-3} \text{ kcal mole}^{-1} \text{ }^\circ\text{K}^{-1}$

and $T = 600^\circ \text{ K}$

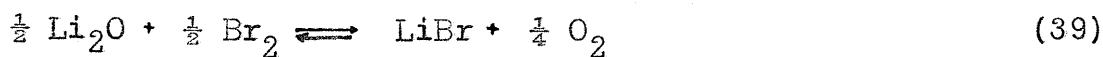
$$\text{then } \Delta F = 2.73 \log_{10} \frac{P_{\text{O}_2}^{\frac{1}{2}}}{P_{\text{Cl}_2}}$$

Thus the oxygen pressure would have to be 10,000 times that of the chlorine pressure for this term to be 5.46 kcal. Thus for magnesium perchlorate, large local concentrations in the body of the decomposing perchlorate might be a sufficient driving force to produce some oxide or chloride by reaction (41) and not by the straight decomposition of the perchlorate. Thus Markowitz says⁵¹, "if appropriate control of the gas ratio

$$\frac{P_{O_2}^{\frac{1}{2}}}{P_{Cl_2}}$$

could be maintained throughout a mass of decomposing magnesium perchlorate, the reaction products could be predetermined".

In the decomposition of lithium bromate perhaps some of the bromide or oxide could be formed from the oxide or bromide respectively via equation (39) i.e.



For this reaction

$$\begin{aligned} \Delta F_{39} &= \Delta F_f Br^- - \frac{1}{2} \Delta F_f O^{=} + RT \ln \frac{P_{O_2}^{\frac{1}{4}}}{P_{Br_2}^{\frac{1}{2}}} \\ &= -11.6 + RT \ln \frac{P_{O_2}^{\frac{1}{4}}}{P_{Br_2}^{\frac{1}{2}}} \end{aligned}$$

As seen for magnesium perchlorate the logarithm term will not appreciably effect ΔF unless one pressure is very much

larger than the other. Thus ΔF_{39} approximately equals -11.6 kcal. Thus some of the bromide could have been formed by a two step process:

1. decomposition of the bromate to the oxide which is not predicted thermodynamically

2. reaction of the oxide with bromine by equation (39) to form the bromide.

This might have been the cause of the slight decrease of lithium oxide in Fig. 34. However as noted earlier p. 94 lithium oxide, prepared by heating lithium carbonate to 800° C under vacuum, did not react with bromine at 250° C. This is not conclusive evidence that reaction (39) does not proceed because oxides formed at very high temperatures become extremely unreactive. However in the next section the formation of oxide or bromide by the two step process will not be considered, because there is no evidence as yet that a reaction such as (39) occurs in these experiments.

Even if it is assumed that reaction (39) does proceed from left to right an important conclusion can be stated concerning the decomposition of lithium bromate. Since reaction (39) should not proceed thermodynamically from right to left and since direct decomposition of the bromate to the oxide cannot be predicted thermodynamically, it is concluded that the presence of a large amount of oxide in the residue

cannot be explained solely by thermodynamics. Other discrepancies in the thermodynamic approach will be discussed in the next section.

The Role of Thermodynamics and Kinetics in Predicting the Decomposition of Metal Bromates

As stated on page 30 of the introduction, Nyholm has written that the formation of an organic compound is usually kinetically controlled, whereas the product formed in an inorganic reaction is usually decided by the laws of thermodynamics. For this statement to be true for the decomposition of bromates, the rate controlling step would have to have the same activation energies for the bromate decomposing to the oxide and bromide. However, it is obvious from Table 5 and 10 that the activation energy for the bromate to oxide decomposition is in general much lower than the activation energy for the bromate to bromide decompositions. Thus, it appears that kinetics does play an important role in these decompositions. It must be stressed again that the molecular mechanism and rate controlling process are not known for these decompositions. Thus it will be assumed that each reaction has a simple potential barrier (unknown) which must be reached by many bromate molecules if decomposition is going to take place at a

significant rate.

Thermodynamics cannot predict the decomposition products of lithium bromate, as seen in the last section. However when $(\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^{2-})_{\text{equiv}}$ is large and negative (greater than -15 kcal) then the decomposition product can be predicted. Table 7 shows that the bromates of sodium, potassium, rubidium, caesium, strontium, barium and silver fall into this category. However for cadmium, $(\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^{2-})_{\text{equiv}}$ is -13 kcal, and nearly all oxide is formed whereas for calcium, $(\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^{2-})_{\text{equiv}}$ is -9 kcal, and only bromide is formed. For cobalt, $(\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^{2-})_{\text{equiv}}$ is zero and 98% oxide is formed whereas $(\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^{2-})_{\text{equiv}}$ for the rare earths is more positive, yet less oxide is formed on decomposition. These results cannot be predicted using thermodynamic considerations. Undoubtedly the kinetics are responsible for the anomalies in the thermodynamic predictions.

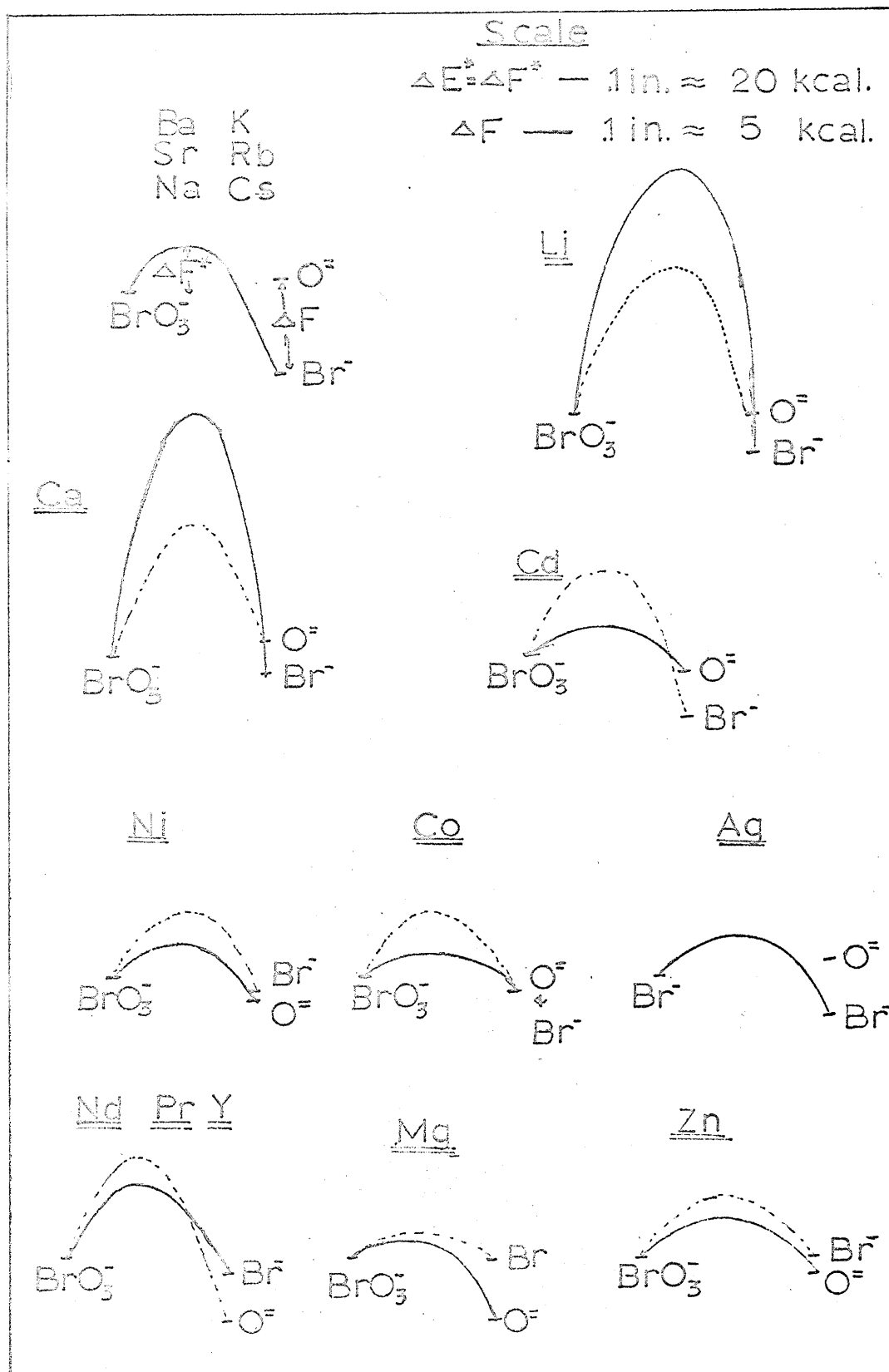
For the alkaline earths, the activation energy increases enormously from barium to calcium and then drops off sharply when magnesium oxide is formed from magnesium bromate. These results suggest that the activation energy for the bromate to bromide decomposition increases until the rate becomes so slow that the oxide begins to form because of its lower activation energy. However magnesium

oxide would also be predicted thermodynamically since $(\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^-)$ equiv is 19.8 kcal. The same general trend in activation energies is noticed for the alkali metals. The activation energies for sodium and potassium are slightly out of line, but the enormous activation energy for the lithium bromate decomposition indicates that although the bromide is favoured thermodynamically, some oxide is formed because of its smaller activation energy. This seems to be confirmed by Fig. 34. The oxide is initially formed because of its lower activation energy, but due to some process (perhaps melting) the thermodynamically favoured bromide then forms.

With the help of Fig. 37, the rest of the results will be discussed. Simple free energy values for bromates (inferred), oxides and bromides are shown along with traces that signify the activation energy of both decompositions. These are not drawn to scale because of the decision to treat the activation energies qualitatively. There is also no significance in the differences in activation energies shown for the two modes of decomposition. In most gas phase reactions, a difference in activation energy of 2 kcal makes one rate about fifty times as fast as the other. This assumes a constant frequency factor for the two

FIGURE 37

Free energy plots representing thermodynamic and kinetic
values for the thermal decompositions



reactions (i.e. $k = A e^{-\frac{E^*}{RT}}$). However in these processes the frequency factor depends on lattice type and type of surface and should not be constant for the two modes of decomposition.

Perhaps the biggest anomaly in the results can be simply explained using these free energy plots. Calcium decomposes to the bromide whereas cadmium decomposes to the oxide, yet the activation energy for the bromate-bromide mode of decomposition for calcium is enormous (280 kcal). However molecules tend to react spontaneously only if they approach a state of lower free energy. If the oxide of calcium has a higher free energy than the bromate then the oxide should not form. However for the cadmium bromate decomposition, the oxide probably has a slightly lower free energy than the bromate and because the bromate-oxide mode of decomposition has a lower activation energy than the bromate-bromide mode, then the oxide forms. For the bromates of silver, sodium, potassium, rubidium, caesium, barium and strontium, the free energy of formation of the oxide per equivalent is probably higher than that of the bromate, and thus the oxide will not form. For potassium this statement is verified since $\Delta F_f \text{ BrO}_3^-$ is -58.2 kcal/equiv. and $\Delta F_f \text{ O}^-$ is -38.5 kcal/equiv.⁵⁴. However free energy data for all the bromates would have to be determined

to prove this statement conclusively.

For nickel and cobalt, the bromate oxide mode of decomposition probably has a lower activation energy than the bromate-bromide mode since $(\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^-)_{\text{equiv}}$ for these elements is very small. The rare earth bromates thermodynamically should form the oxides i.e. $(\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^-)_{\text{equiv}}$ is positive. For these it appears that the bromate oxide mode of decomposition has a lower activation energy than the bromate-oxide mode.

From the results two general conclusions may be stated on the use of thermodynamics and kinetics in predicting the decomposition products of metal bromates:

1. If $(\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^-)_{\text{equiv}}$ is large (greater than ± 15 kcal) then thermodynamics can be used to predict the decomposition products.

2. If $(\Delta F_f \text{ Br}^- - \Delta F_f \text{ O}^-)_{\text{equiv}}$ is smaller than ± 15 kcal then the kinetics of the reaction become important.

A more detailed study of each bromate needs to be undertaken to determine the rate determining step of these decompositions. Since the curves are in general autocatalytic, perhaps the addition of cadmium bromide to cadmium bromate would lower the activation energy of the bromate-bromide mode of decomposition and more bromide would be produced on decomposition. If this did happen it would be good evidence for the

importance of kinetics in determining the reaction products. However cadmium bromide might also lower the activation energy for the bromate-oxide mode of decomposition. Some catalyst, however, should influence one step only.

SUMMARY

A thermobarogravimetric apparatus was built to study the decomposition of metal bromates. As the bromate was heated at a linear rate, temperature, pressure and weight were plotted automatically against time with a one pen recorder. The thermobarograms and decomposition data such as the decomposition products are presented. Although the chlorates and iodates form perchlorates and periodates when heated in a similar way, there was no evidence for perbromate formation. In the study of competitive decompositions and equilibria involving two solids and two gases, the apparatus has unique advantages.

To justify the results theoretically, free energies and activation energies were calculated for the decompositions. The role of kinetics and thermodynamics in predicting the decomposition of bromates and the significance of the kinetics and thermodynamics in solid state decomposition is discussed. The heat of formation of the bromate ion in the gaseous state $\Delta H_f \text{BrO}_3^-(g)$ was calculated using lyotropic numbers to be 26.3 kcal/mole.

BIBLIOGRAPHY

- 1a. H. Kammerer, Pogg. Ann. 138, 391 (1869)
- 1b. Gmelins Handbuch Der Anorganischen Chemie Brom.
Edited by R. S. Meyer, Berlin (1931)
2. E. MacIvor, Chem. News 33, 35 (1876) see lb.
3. M. M. Muir, J. Chem. Soc. 30, 469 (1876)
4. M. M. Muir, J. Chem. Soc. 27, 324 (1874)
5. A. Riche, Compt. Rendu 46, 351 (1858) see lb.
6. C. Rammelsburg, Pogg. Ann. 52, 83 (1841) see lb.
7. P. W. Robertson, Chem. News 108, 50 (1912)
8. J. Fritzsche, J. Pr. Ch. 24, 285 (1841) see lb.
9. A. Potylizyn, J. Russ. Ges. 27, 271 (1895) see lb.
10. E. H. Cook, J. Chem. Soc. 65, 813 (1894)
11. A. Potylizyn, J. Russ. Ges. 19, 351 (1887) see lb.
12. A. Michael and W. T. Conn, J. Am. Chem. Soc. 23, 89
(1901)
13. F. Allison, E. R. Bishop and A. L. Sommer, J. Am. Chem.
Soc. 54, 616 (1932)
14. F. Allison and E. S. Murphy, J. Am. Chem. Soc. 52, 3796
(1930)
15. H. Hughes, J. Am. Chem. Soc. 58, 1924 (1936)
16. D. D. Bond, J. Am. Chem. Soc. 59, 439 (1937)
17. Hackspill and Winterer, Compt. Rendu 191, 665 (1930)

18. W. F. Decoursey, Ph.D. Thesis, Iowa State College
(1953)
19. C. Rocchiccioli, *Ann. de Chemie* 5, 999 (1960)
20. Z. Z. Hugus, *J. Am. Chem. Soc.* 74, 1076 (1952)
21. L. Pauling, *Chem. Eng. News* 25, 2970 (1947)
22. R. S. Nyholm, *Proc. Chem. Soc.* 276 (1961)
23. W. E. Dasent, *J. Chem. Ed.* 40, 130 (1963)
24. D. S. Urch, *J. Inorg. Nucl. Chem.* 25, 771 (1963)
25. G. E. Kimball, *J. Chem. Phys.* 8, 188 (1940)
26. C. Rammelsburg, *Pogg. Ann.* 55, 63 (1842) see lb.
27. J. Jach, *J. of Phys. & Chem. of Solids* 24, 63 (1963)
28. J. Jach, Reactivity of Solids, Editor J. H. DeBoer
Elsevier Publishing Company, Amsterdam (1961) p.
334.
29. Lowig, Brom, see lb.
30. A. Potylizyn, *J. Russ. Ges.* 22, 454 (1890) see lb.
31. F. R. Duke and E. A. Shute, *J. Phys. Chem.* 66, 2114
(1962)
32. A. E. Newkirk, *Anal. Chem.* 32, 1558 (1960)
33. C. Duval, Inorganic Thermogravimetric Analysis,
Elsevier Publishing Company, 2nd Edition (1963)
34. K. Honda, *Sci. Repts. Tohoku Imp. Univ.* 4, 97 (1915)
see reference 33.
35. D. Chevenard, X. Wache, and R. de la Tullage, *Bull.*

- Soc. Chim. France 10, 41 (1944)
36. J. W. McBain and A. M. Baer, J. Am. Chem. Soc. 48,
600 (1926)
37. M. Heinrichs and W. J. Biermann, Can. J. Chem. 40,
1361 (1960)
38. J. Hooley, Can. J. Chem. 35, 374 (1957)
39. C. Campbell and S. Gordon, Anal. Chem. 28, 124 (1956)
40. S. Gordon and C. Campbell, Anal. Chem. 32, 271R (1960)
41. P. D. Garn, Anal. Chem. 29, 839 (1957)
42. M. V. Pirani, Verh. d. deutsch Physik Ges. 6, 686
(1906) see 42b.
- 42b. A. Farkas and H. W. Melville, Experimental Methods in
Gas Reactions, Macmillan & Company (1939)
43. E. Ladenburg and E. Lehman, Verh. d. deut. phys.
Gesell 8, 20 (1906) see 42b.
44. M. G. Johnson and D. McIntosh, J. Am. Chem. Soc. 31,
1138 (1909)
45. J. Hooley, Can. J. Chem. 35, 1414 (1957)
46. E. D. Buckley, Proc. Nat. Acad. Sci. 2, 683 (1916)
see 42b.
47. S. Dushman and C. G. Found, Phys. Rev. 17, 7 (1920)
see 42b.
48. K. J. Laidler and B. W. Wojciechowski, Proc. Roy. Soc.
(London) Ser. A 259, 257 (1960)

49. L. Cahn and H. Schultz, *Anal. Chem.* 35, 1729 (1963)
50. E. Eyraud and K. Goton, *Bull. Soc. Chim. France* 1009 (1953)
51. M. M. Markowitz, *J. Inorg. Nucl. Chem.* 25, 407 (1963)
52. C. J. Smithells, Metals Reference Book, Vol. 2 pp. 590-91 and 596-98, Interscience, N.Y. (1955)
53. J. P. Coughlin, *Contributions to the Data on Theoretical Metallurgy XII Heats and Free Energies of Formation of Inorganic Oxides.* Bureau of Mines Bulletin 542 U.S. Government Printing Office, Washington, D.C. (1954)
54. F. D. Rossini et al, *Circ. Natl. Bur. Stand.* #500 (1952)
55. F. R. Bichowsky and F. D. Rossini, The Thermochemistry of the Chemical Substances, Rheinhold Publishing Company (1936)
56. D. F. C. Morris, *J. Inorg. Nucl. Chem.* 62, 394 (1958)
57. A. Voet, *Chem. Reviews* 20, 169 (1937)
58. E. S. Freeman, B. Carroll, *J. Phys. Chem.* 62, 394 (1958)
59. P. Kofstad, *Nature* 179, 1362 (1957)
60. H. H. Horowitz and G. Metzger, *Anal. Chem.* 35, 1464 (1963)
61. A. W. Coats and J. P. Redfern, *Nature* 201, 68 (1964)

62. H. T. S. Britton and H. G. Britton, *J. Chem. Soc.* 3887 (1952)
63. J. Kashoulis, Master's Thesis, Israel Institute of Technology, October (1962)
64. R. Hammer, *Bulletin of the Israel Ceramics Research Association #12* (1961)
65. K. Nakamoto, Infra Red Spectra of Inorganic and Co-ordination Compounds, Wiley and Sons (1963)
66. P. W. M. Jacobs and F. C. Tompkins, Chemistry of the Solid State, Editor W. E. Garner, Butterworths, London (1955) p. 184
67. C. E. H. Bawn, Chemistry of the Solid State, Editor W. E. Garner, Butterworths, London (1955) p. 254
68. W. E. Garner, Chemistry of the Solid State, Editor W. E. Garner, Butterworths, London (1955) p. 232
69. P. W. M. Jacobs and A. R. T. Kureishy, Reactivity of Solids, Editor J. H. De Boer et al, Elsevier, Amsterdam (1961) p. 352
70. F. S. Stone, Reactivity of Solids, Editor J. H. De Boer et al, Elsevier, Amsterdam (1961) p. 19
71. G. Herzberg, Molecular Spectra and Molecular Structure I Spectra of Diatomic Molecules 2nd Edition, New York (1950)
72. A. Glasner and L. Weidenfeld, *J. Am. Chem. Soc.* 74, 2467 (1952)

APPENDIX

Thermodynamic Data

Supplementary data for Table 2b⁵²

Cation	$-\Delta F_{fCl^-}$ 27°	$-\Delta F_{fI^-}$ 27°	$-\Delta F_{fCl^-}$ 227°	$-\Delta F_{fI^-}$ 227°	$-\Delta F_{fCl^-}$ 727°	$-\Delta F_{fI^-}$ 727°
Nd	228.8	157.9	218	142	192	115
Y	219.0	147.3	208.5	135	186	109
Pr	241.0	166.3	230.3	155	204.8	128.5

Supplementary data for Table 7^{52,53}

Cation	$-\Delta F_{fBr^-}$ 27°	$-\Delta F_{fO^=}$ 27°	$-\Delta F_{fBr^-}$ 227°	$-\Delta F_{fO^=}$ 227°	$-\Delta F_{fBr^-}$ 727°	$-\Delta F_{fO^=}$ 727°
	kcal/mole	kcal/mole	kcal/mole	kcal/mole	kcal/mole	kcal/mole
Li	80.7	133.8	76.7	127.6	67.1	111.7
Na	82.8	93.3	78.4	86.5	67.2	68.8
K	90.3	77.0	85.7	71.0	74.4	55.0
Rb	92.3	73	88.4	67	78.0	--
Cs	94.1	66	88.8	--	78.5	--
Mg	119.6	136.5	112.9	131.3	96.5	119.1
Ca	156.8	144.2	149.4	139.5	132.6	127.7
Sr	167.6	133.4	159.1	128.4	142.2	116.0

Supplementary data for Table 7 cont'd

Cation	$-\Delta F_{fBr^-}$	$-\Delta F_{fO^=}$	$-\Delta F_{fBr^-}$	$-\Delta F_{fO^=}$	$-\Delta F_{fBr^-}$	$-\Delta F_{fO^=}$
	27°	27°	227°	227°	727°	727°
	kcal/mole	kcal/mole	kcal/mole	kcal/mole	kcal/mole	kcal/mole
Ba	175	126.0	167.7	124.3	148.5	109.7
Zn	73.3	76.2	66.6	71.8	55.2	60.1
Cd	72	55.1	65	50.9	47.5	39.0
Co	53	51.6	46	47.3	33	38.4
Ag	23.2	2.55	20.7	--	16.6	--
Ni	50.6	51.4	44.0	46.7	26.5	34.9
Nd	195.4*	408.8	182.0*	392.0	155.5*	347.0
Pr	205.6*	420.2	194.7*	407.6	168.6*	376.0
Y	185.1*	408.0	173.9*	383.4	149.5*	347.4

-- values not known