NRL REPORT 3508

RATE OF REACTION OF ALKALI METALS AND ALUMINUM BOROHYDRIDE WITH WATER

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ABSTRACT

Experimental methods and apparatus are described for the determination of rapid reaction rates, specifically those of sodium, potassium, sodium-potassium alloys, and aluminum borohydride with water. Under specific conditions, times for completion of the aluminum borohydride and alkali-metal reactions with water have been as short as one millisecond. It is believed that the measured rates for these reactions are governed by the extent of mixing of the reactants. If efficient mixing of the reactants is secured by some means such as spray contact, the reactions would be relatively instantaneous.

The mechanisms of reactions between alkali metals and water are discussed in the light of published literature. The reactions of alkali metals with water and ammonia are compared. All of the factors influencing the reaction of pure metals are not elucidated by studies on the reaction of alkali-metal amalgams.

Modifications made on a commercial pressure pickup are discussed along with phenomena which influence pickup of rapid pressure change. Calculations of the natural frequency of the diaphragm were not satisfactory since the standard equations were not adequate for diaphragms used at the boundaries between different fluids. The influence on pressure pickup by oscillating pressures of gas bubbles in water is considered.

PROBLEM STATUS

This is a final report on one phase of two authorized problems; work is continuing on the general problems.

AUTHORIZATION

NRL Problem C01-08R
NR 401-080, NO 216-144
NRL Problem C11-02R
NS 622-024

PART I

THE MEASUREMENT OF RATES OF REACTION OF WATER-REACTIVE CHEMICALS

INTRODUCTION

The specific problem was to determine the rate at which sodium, potassium, sodium-potassium alloy and aluminum borohydride react with water. The reactions are known to be vigorous and to produce a copious evolution of gas and heat. The rapidity of the reaction between water and these compounds results in sudden changes in measurable properties, e.g., pressure, temperature, ion concentration, etc., which may be used to follow the extent of reaction. From these measurements plotted against a time scale, rates of reaction can be determined; however, the accurate recording or following of the changes for the compounds studied becomes the difficult part of the research.

Inherent to a study of this kind is an attempt to discover the factors which govern the reaction and limit the rate. Correlation of the data with a possible mechanism may then enable one to postulate a stage of the reaction which is rate determining.

The products of the reaction are well-known but, contrary to the apparent simplicity of the reaction of a metal with water or with an aqueous solution of an acid, the exact mechanism involved is not known, and the rate-limiting step or stage in the over-all reaction (e.g., diffusion of reactants or products, discharge of ions, combination of atoms into molecules, adsorption of ions or atoms at a metal surface, etc.) has not been determined. All that is known with certainty is the stoichiometric equation for the reaction:

$$M + H_2O \longrightarrow (M^+) + (OH^-) + 1/2\ H_2$$

and the fact that the reaction goes to completion, sometimes with extreme violence.

The preceding equation is evidently not a true picture of how the reaction takes place. To outline the chemical course of the reaction, the following stages are suggested and are more fully discussed in Part II.

$$M \longrightarrow (M + e)$$

$$(M + e) \xrightarrow{H_2O} (M^+) + e$$

$$2\ H_2O \longrightarrow (H_3O^+) + (OH^-)$$

$$H_2O + e \longrightarrow (OH^-) + H$$

and/or

$$(H_3O^+) + e \longrightarrow H_2O + H$$

$$2\ H \longrightarrow H_2$$

In the case of aluminum borohydride, the reaction with water appears to be far more complex than that of alkali metals with water. The summarizing equation for the reaction is $Al(BH_4)3 + 12\ H_20 \longrightarrow Al(0H)_3 + 3\ H_3BO_3 + 12\ H_2$. Observations have shown that this reaction is not the only one since from 60 to 80 percent of the hydrogen obtainable is evolved. Another indication of the incompleteness of this reaction is the residual slow evolution of hydrogen and the yellowish gray color of the solution which persist after the fast portion of the reaction is concluded.

The mechanism involved in the reaction is unknown. The reaction certainly is not a collision of twelve molecules of water with one of aluminum borohydride as indicated above since such a collision, if it could take place, would produce an extremely slow rate of reaction inconsistent with the rates observed. Stepwise hydrolysis as shown below is the most probable mechanism, but the exact steps are questionable. Any attempt to postulate a rate-limiting step would be sheer mental calisthenics since the information with regard to this reaction is far more limited than that available with respect to the reaction of alkali metals with water.

$$Al(BH_4)3 + H_20 \longrightarrow Al(BH_4)_2(0H) + H_2 + BH_3$$

$$BH_3 + H_20 \longrightarrow B(0H)H_2 + H_2$$

$$B(0H)H_2 + H_20 \longrightarrow B(0H)_2H + H_2$$

$$B(0H)_2H + H_20 \longrightarrow B(0H)_3 + H_2$$

The $Al(BH_4)_2(0H)$ could proceed through dihydroxy to $Al(0H)_3$ or Al_20_3 in the dehydrated state or, if the hydroxyl group enters into the double salt, the compounds $Al[BH_3(0H)]_3$, $Al[BH_2(0H)_2]_3$ etc. may exist but probably could be easily dehydrated by high temperatures to leave complexes of aluminum, boron, and small amounts of hydrogen which would be hydrolyzed slowly if at all.

CHOICE OF A METHOD

The choice of a method and apparatus for following such reactions is limited to some scheme which can utilize the fast response of a cathode-ray oscilloscope for recording a change produced during the course of the reaction. When it is realized that the phenomenon to be measured might be only a few milliseconds in duration, the need for fast response of instrumentation becomes important. Methods which have been employed in determining the relatively slow rates of reaction of metals such as copper, iron, and cadmium with acids are inadequate.

Since gas is produced in the reaction, the simplest and most obvious property to use in measurement is the pressure rise in a closed system. This was done and the reaction was allowed to take place in a closed vessel (bomb reactor). The pressure rise resulting from the generated hydrogen was detected by a suitable "pickup" or transducer whose output was made visible on the screen of a cathode-ray oscilloscope where it was recorded on film with a high-speed camera.

A method used by a number of investigators to study rapid reactions was also considered. It consists of the forcing of reactants by means of pistons into a reaction chamber where the pressures rise is measured. M. L. Kilpatrick et al[1], using this

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[1] *Kilpartick, M. L. et al, "Research on Liquid Fuels", Annual Report, September 15, 1947 to September 14, 1948, Illinois Institute of Technology, on ONR Contract N7onr-329.*

method, have recently incorporated the refinements of several pieces of apparatus in their pneumatic injector and bomb reactor. From measurements made on the decomposition of hydrogen peroxide in the presence of calcium permanganate, they estimated that injection of the reactants is completed within five milliseconds.

This method appears to be excellent for use in studying rapid reaction rates, but the question remains whether it is suitable for reactions which are complete in approximately one millisecond or less. It is obvious that the injection period should be well under a millisecond since only data taken after completion of the injection are representative of the rate of reaction. If it can be assumed that data obtained for the last half of the total reaction time are adequate, we can take a half-millisecond for the injection time and calculate a terminal velocity for the pistons. Taking two inches as the piston travel distance in one apparatus used, the terminal velocity turns out to be approximately 667 feet per second, a velocity almost that of a bullet at the muzzle of a small-calibre rifle.

In practice, where the reaction approaches completion as an exponential, (e.g., a reaction of the first order), procurement of data over the last half of the reaction period may be quite inadequate and, consequently, shorter injection periods would be necessary. For an injection period of one-tenth of a millisecond a terminal velocity of 3,333 feet per second for a piston travel of two inches would be needed. It is evident that the problem of stopping a piston at such velocities is difficult, and the usefulness of the apparatus for fast reaction-rate evaluation would be problematical.

APPARATUS

Figures 1 and 2 are self-explanatory photographs of the apparatus. The transducer shown in Figure 3 is essentially an alternating-current bridge whose output varies with the capacity of a pair of condensers, each consisting of an electrode and a movable plate. The condenser on the outer end of the transducer can be adjusted to change the air gap and thus balance the bridge for zero-voltage output. The plate of the other condenser is open to pressure which deflects it and alters the capacity. Originally, this plate (or diaphragm as it is more frequently called) was a removable disk with a narrow duct connecting it with the pressure source. To avoid recording of spurious pressures this was modified by eliminating the duct and machining a diaphragm of the appropriate thickness (0.030") in the bottom of the fitting which screws into the opening of the bomb reactor so that the diaphragm which is the pressure-sensitive element is flush with the inside wall of the pressure vessel.

In Figure 3 is shown the bomb reactor which is composed of two main parts, the reaction chamber with a threaded opening in its side for the pressure transducer and the closure for the bomb. The closure has incorporated with it: (1) two needle valves which close off two side openings at points nearly flush with the underside surface of the bomb closure, (2) a spring-loaded piston for crushing glass capsules containing samples of the chemical to be tested, held in position below the piston by metal fingers, (3) a spring catch to prevent undue oscillation of the piston after its descent, and (4) a fine-mesh, nickel screen to prevent particles of alkali metal from rising to the water surface. When the closure is bolted into place atop the reaction chamber a copper gasket effectively seals the system for either high or low pressures. With the bomb so sealed, a chosen volume of liquid can be introduced to the chamber through one of the side openings, and any residual space may be flushed out with inert gas.

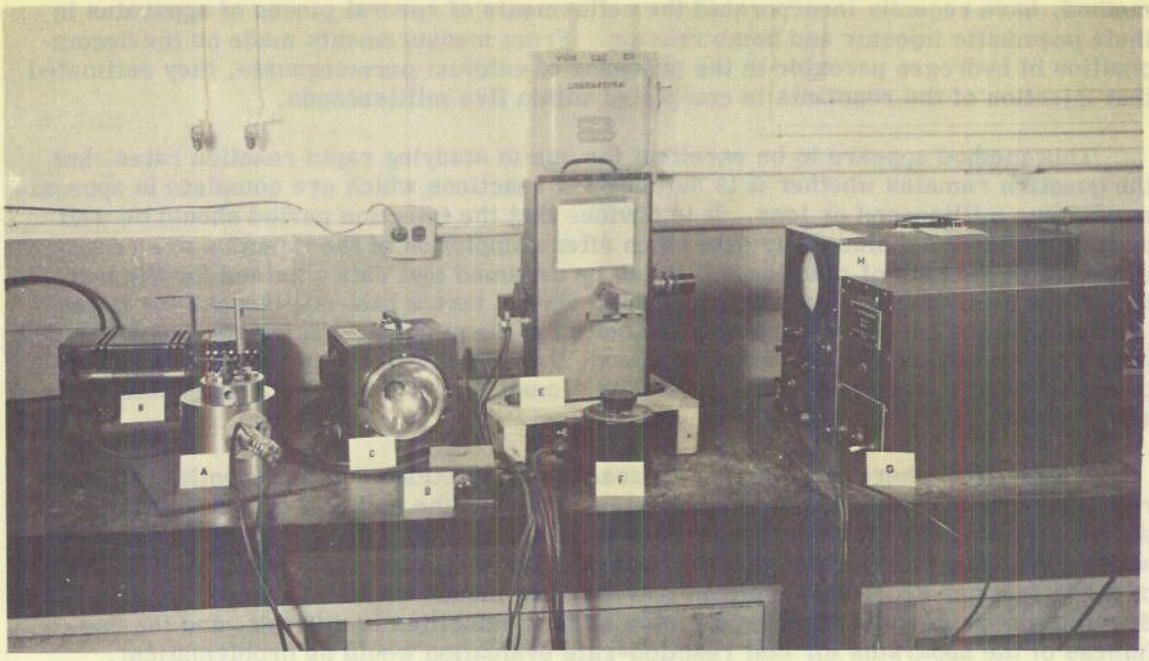

Figure 1.--Assembled Apparatus

A - Bomb reactor with the pressure transducer in place

B - Constant-voltage transformer

C - General Radio Strobotac, Type 631-B used for energizing the time-marker coil of the camera

D - Foot-switch for starting the time marker

E - General Radio High Speed Camera, Type 651-AG

F - General Radio Variac for changing speed of camera

G - Electro Products Laboratories' Electro Pressuregraph, consisting of a 100-kcs signal generator, amplifier for transducer output, negative modulation suppressor and a demodulator

H - DuMont Oscilloscope, Type 208B, with a screen intensified for photographic purposes. On occasion a DuMont dual oscilloscope, type 279, was used to permit use of a sine-wave generator for timing purposes.

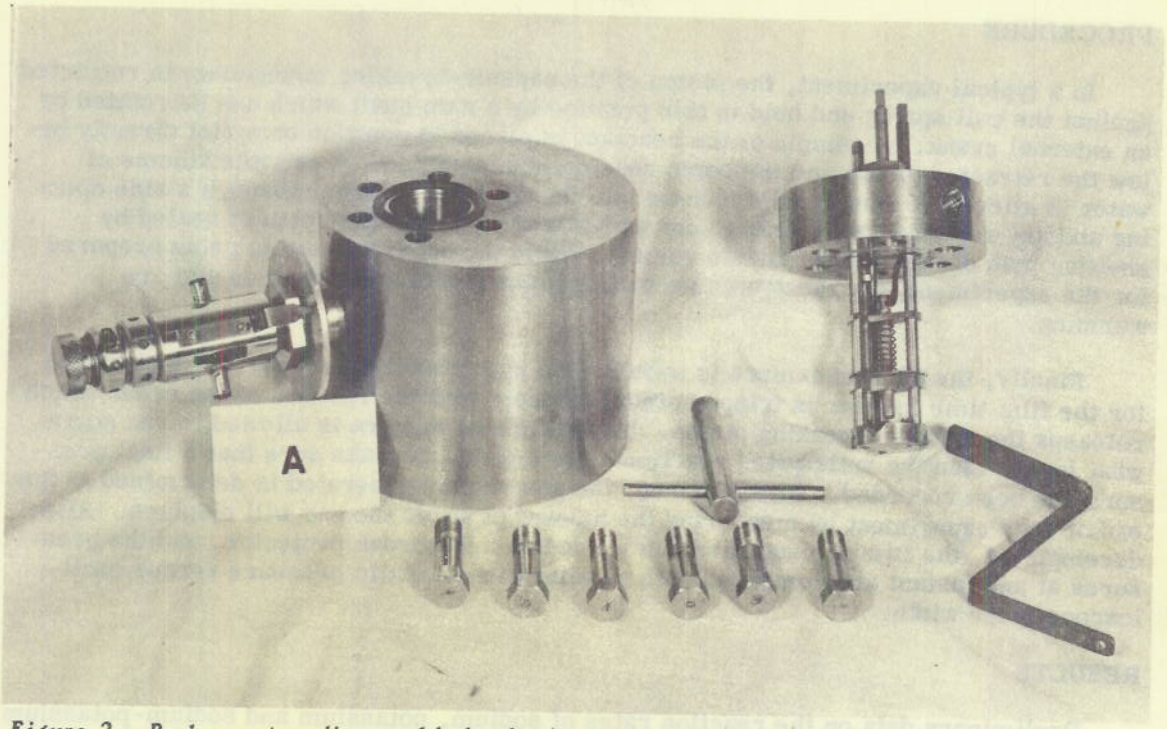

Figure 2.--Bomb reactor disassembled, showing reaction chamber and bomb closure with capsule-breaking mechanism

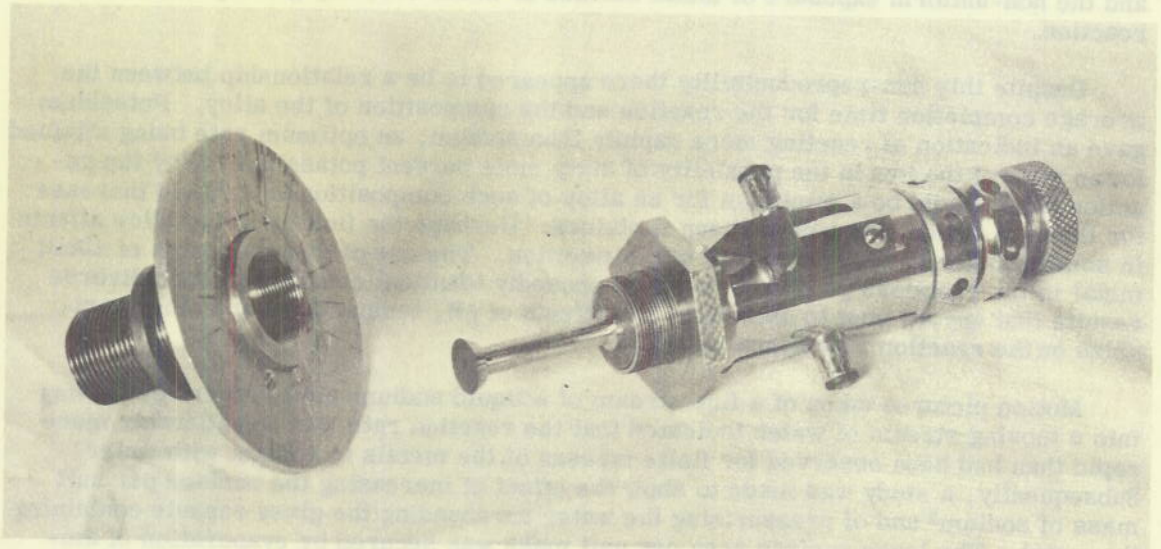

Figure 3.--Modified pressure transducer (Electro Products Laboratories), partially disassembled

PROCEDURE

In a typical experiment, the piston of the capsule-breaking mechanism is retracted against the coil spring and held in this position by a cam shaft which can be rotated by an external crank. A sample of the reactant is placed in position on a slot directly below the retracted piston and the bomb reactor is assembled. A suitable volume of water is allowed to flow from a burette into the reaction chamber through a side opening and any residual air is flushed out with nitrogen. Then the bomb is sealed by shutting both of the built-in needle valves. While the bomb reactor is being prepared for the experiment, the electronic recording instruments are turned on and are warming.

Finally, the 35-mm camera is switched on and, shortly thereafter, a foot switch for the film time marker is tripped simultaneously with the rotation of the crank which releases the capsule-breaking piston. The recording camera is allowed to run somewhat longer than the anticipated reaction-time interval to make sure that a final pressure has been recorded. When desired, the gas volume generated is determined at the end of each experiment by measuring the amount of water the gas will displace. After development, the film is magnified and viewed on a Recordak projector, and the pressures at any instant are compared with a calibration of static pressure versus oscilloscope trace width.

RESULTS

Preliminary data on the reaction rates of sodium, potassium and sodium-potassium alloys were presented in an earlier report.[2] The difficulty of obtaining reproducible data was emphasized. As was shown by photographing capsules being broken under water, two causes for the non-reproducibility are the variability in capsule breakage and the non-uniform exposure of metal surface to water over any given period of the reaction.

Despite this non-reproducibility there appeared to be a relationship between the average completion time for the reaction and the composition of the alloy. Potassium gave an indication of reacting more rapidly than sodium, an optimum rate being attained for an alloy of the two in the proximity of sixty mole percent potassium. Why the reaction time should be a minimum for an alloy of such composition and should increase for those to either side has not been explained. Perhaps the fluidity of the alloy affects in some manner the observed rate of the reaction. The use of large amounts of alkali metal in the reactions produced, under supposedly identical conditions, such diverse results that any attempt to determine the effects of pH, temperature and other variables on the reaction rate appeared futile.

Motion pictures taken of a fine stream of a liquid sodium-potassium alloy flowing into a moving stream of water indicated that the reaction rate was considerably more rapid than had been observed for finite masses of the metals in contact with water. Subsequently, a study was made to show the effect of increasing the surface per unit mass of sodium[3] and of pressurizing the water surrounding the glass capsule containing the metal. The large surface area per unit mass was secured by evaporation of ammonia from a solution of the metal in liquid ammonia.

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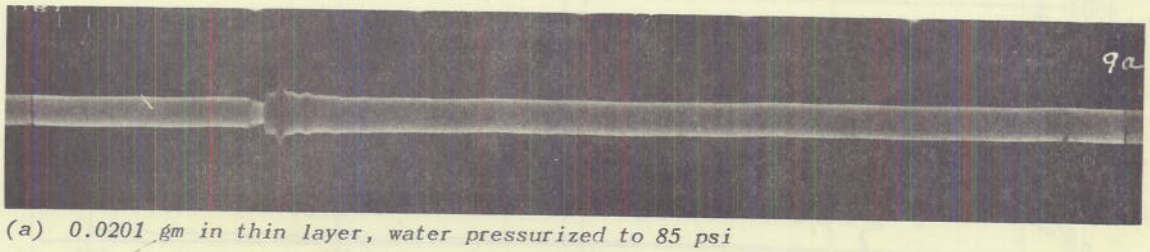
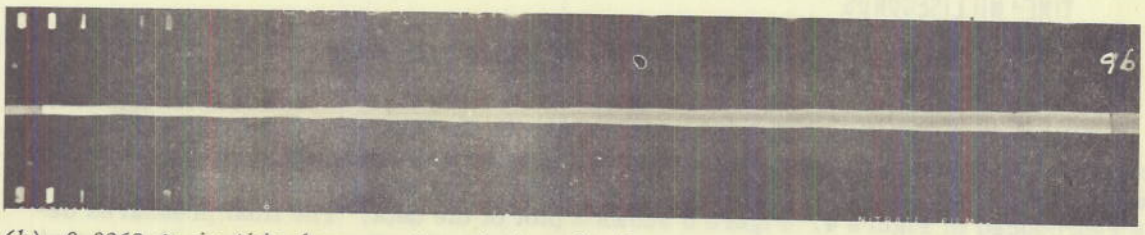
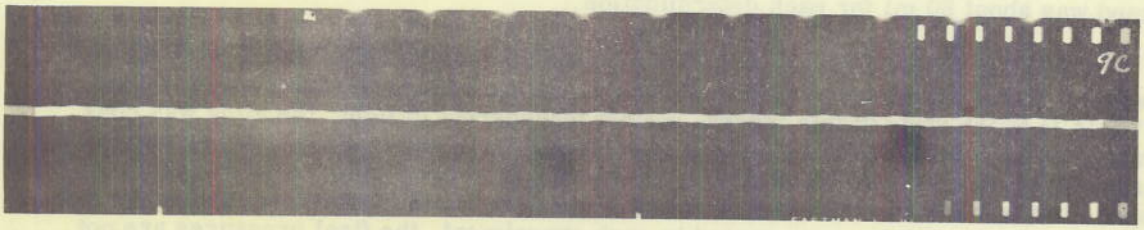
[2] *Ewing, Atkinson, Rice, NRL Report No. C-3287, dated May 24, 1948.*
[3] *Samples in glass capsules were prepared by D.D. Williams of the Analytical Section.*



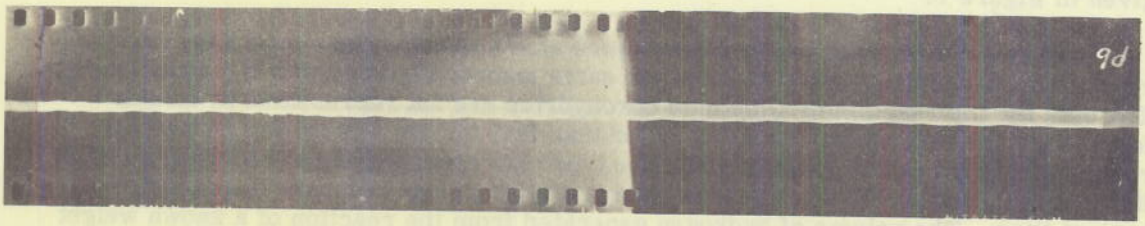
(a) 0.0201 gm in thin layer, water pressurized to 85 psi



(b) 0.0268 gm in thin layer, water at atmospheric pressure



(c) 0.0152 gm in spherical pellet, water at atmospheric pressure



(d) 0.0130 gm in thin layer, water at atmospheric pressure

Figure 4.--Reaction of sodium with water in bomb reactor. Marginal time marks are 0.01 second apart in (a), (b), and (d), and 1/60 second apart in (c).

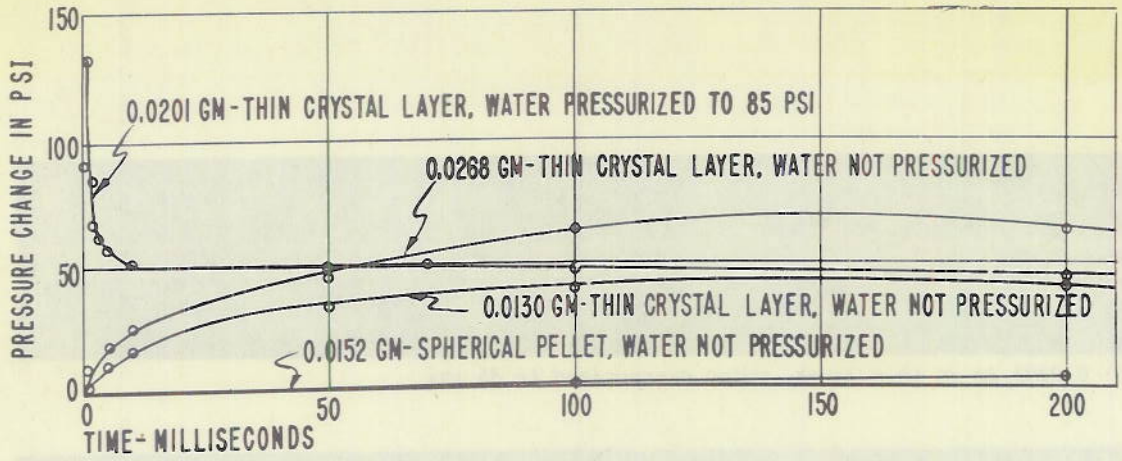


Figure 5.--Reaction of sodium with water

The sodium remaining after evaporation was in the form of a thin layer of fine crystals (maximum dimension approximately 10 microns) uniformly covering the inside walls of the glass capsule. The film of this study, from which Table 1 was prepared, is reproduced in Figure 4. Figure 5 shows a plot of the data. The final pressures developed are not comparable with respect to the weight of sodium used since the amount of free space in each evaluated capsule was slightly different. The volume of water used was about 80 ml for each determination.

Table 2 gives data for the reaction of a sodium-potassium alloy (12 wt % K) with water. These have been plotted in Figure 6. In contrast to the samples of sodium (Table 1) which were in thin layers, almost transparent to light, the alloy was contained as a thick layer on the bottom of each capsule. As the alloy samples were quite large, a certain amount (depending upon the weight of alloy taken) of nitrogen-filled space had to be left in the chamber of the reactor to avoid formation of excessive final pressures. Since this space varied in each experiment, the final pressures are not comparable in magnitude. The calibration curves for data of Tables 1 and 2 are given in Figure 7.

Samples of aluminum borohydride [4] were also sealed in glass capsules, and the reaction measurements were made in the same manner as those with the alkali-metals. The data for the reaction of aluminum borohydride are not represented in tabular form since the reproducibility is no better than that for the sodium and potassium reactions. Figures 8 through 10 show the type of pressure changes recorded on film. In Figures 11 through 13 the pressure changes for each reaction have been plotted against time. The volume of hydrogen generated from the reaction of a known weight of aluminum borohydride was considered a measure for the completeness of reaction. This showed a reaction completion varying from 60 to 80 percent, the smaller samples reacting more completely.

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4 Samples in glass capsules were prepared by Somers H. Smith, Jr. of the Physical & Inorganic Branch.

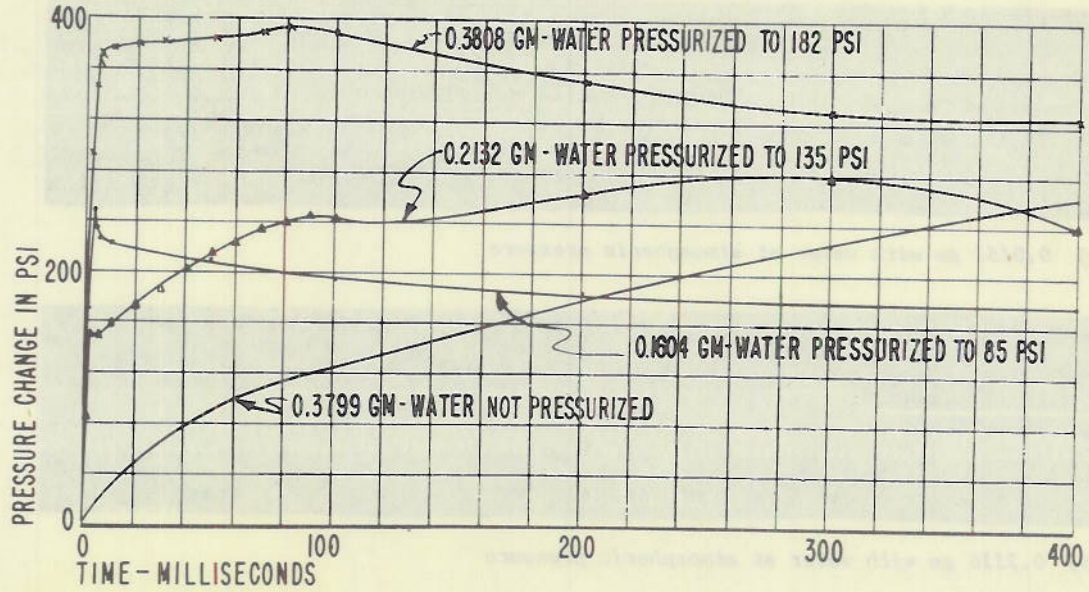


Figure 6.--Reaction of heavy layers of sodium-potassium alloy (12 wt % K) with water

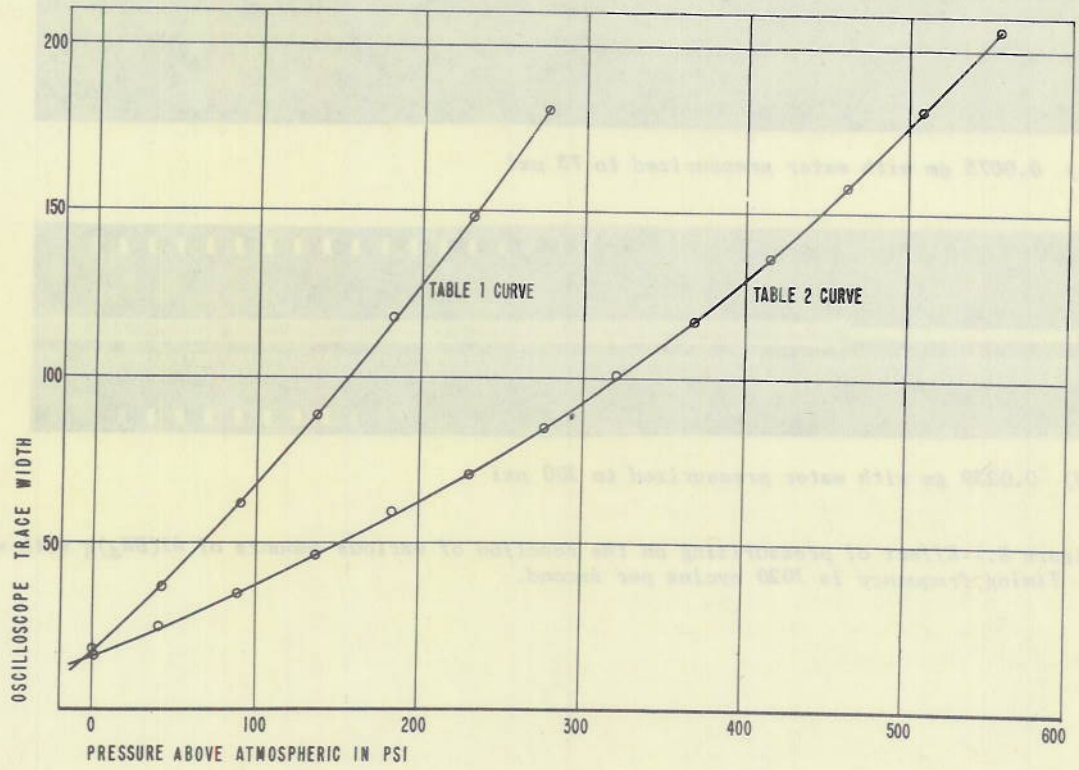
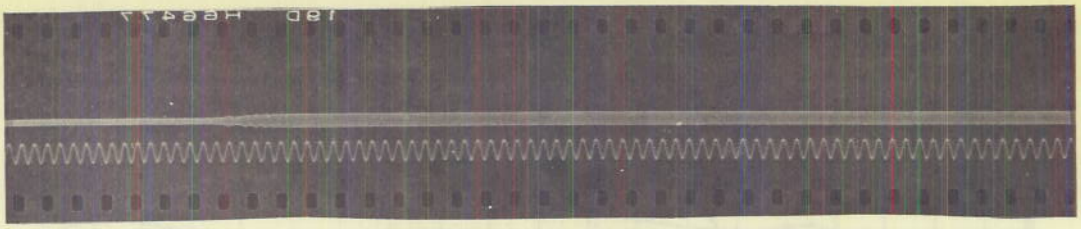
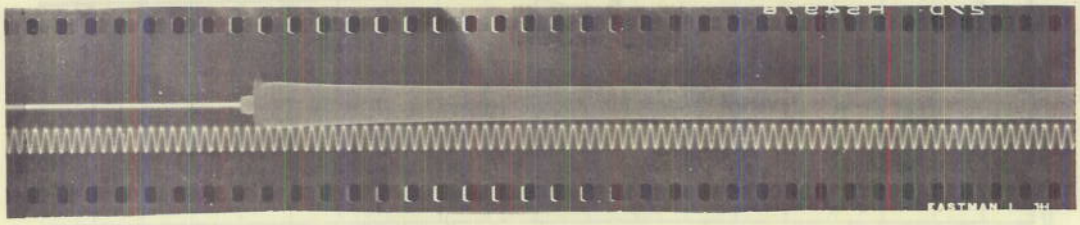


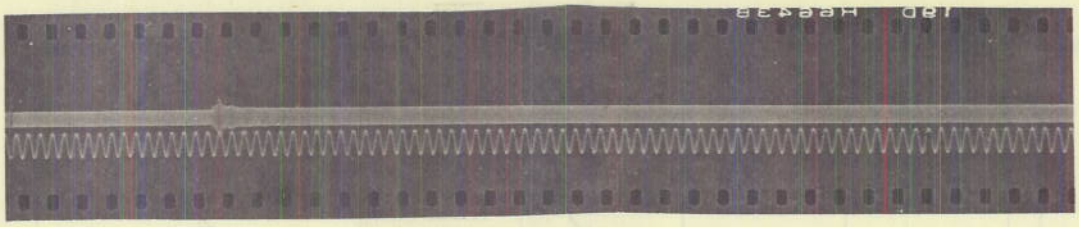
Figure 7.-- Calibration curves for pressure transducer, showing oscilloscope trace width at different static pressures



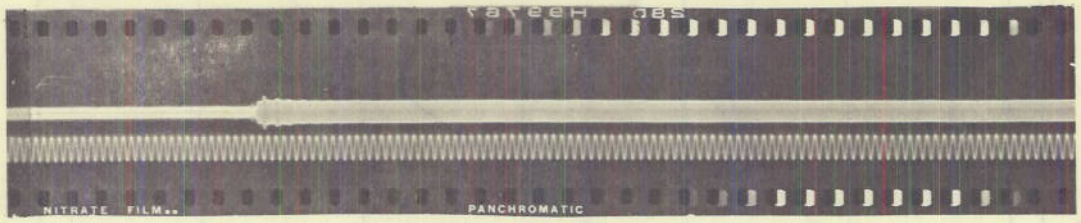
(a) 0.0151 gm with water at atmospheric pressure



(b) 0.2116 gm with water at atmospheric pressure

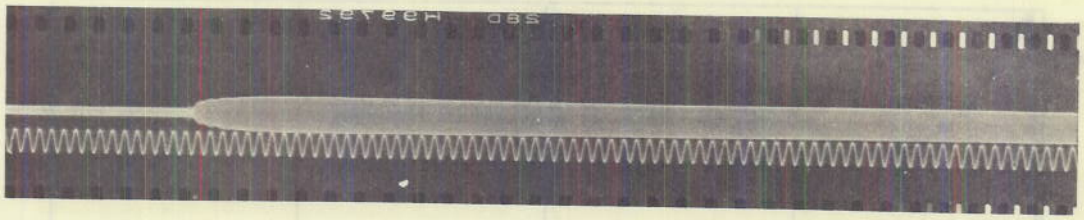


(c) 0.0075 gm with water pressurized to 73 psi

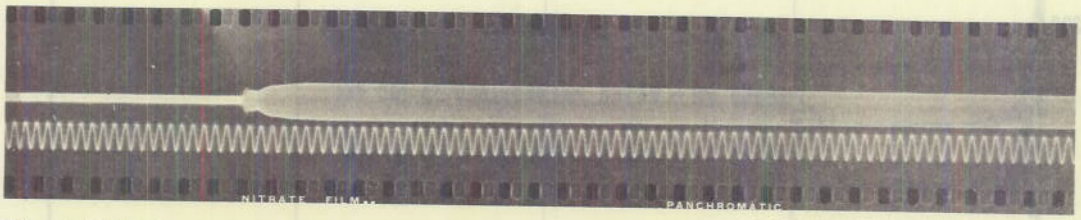


(d) 0.0239 gm with water pressurized to 100 psi

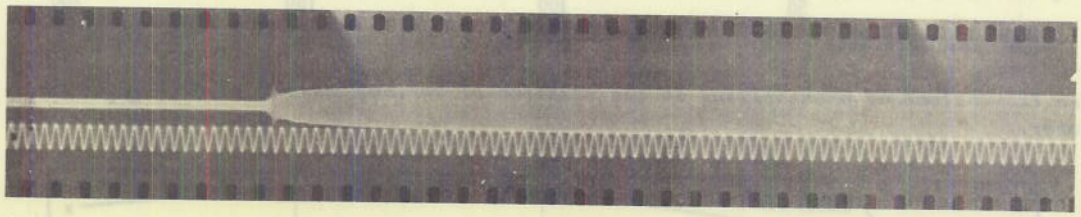
Figure 8.--Effect of pressurizing on the reaction of various amounts of $Al(BH_4)_3$ with water. Timing frequency is 1020 cycles per second.



(a) 0.0918 gm

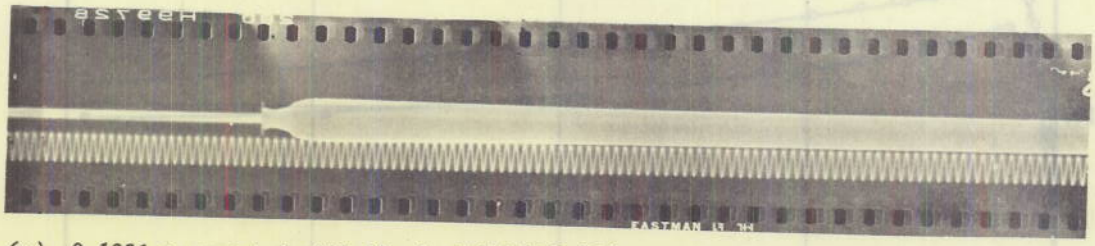


(b) 0.1282 gm

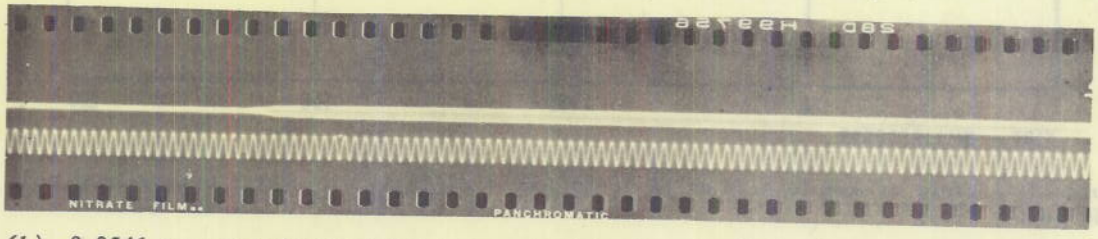


(c) 0.3328 gm

Figure 9.--Effect of sample size on the reaction of $Al(BH_4)_3$ with water pressurized to 60 psi. Timing frequency is 1020 cycles per second.



(a) 0.1356 gm reacted with 60 ml of 1.057 N HCl, pressurized to 60 psi.



(b) 0.0546 gm reacted with water pressurized to 20 psi. Only the neck of the capsule broke to permit inter-access of the reactants through a 2 mm hole.

Figure 10.--Effect of acid and small contact area between reactants on the reaction of $Al(BH_4)_3$ with water. Timing frequency is 1020 cycles per second.

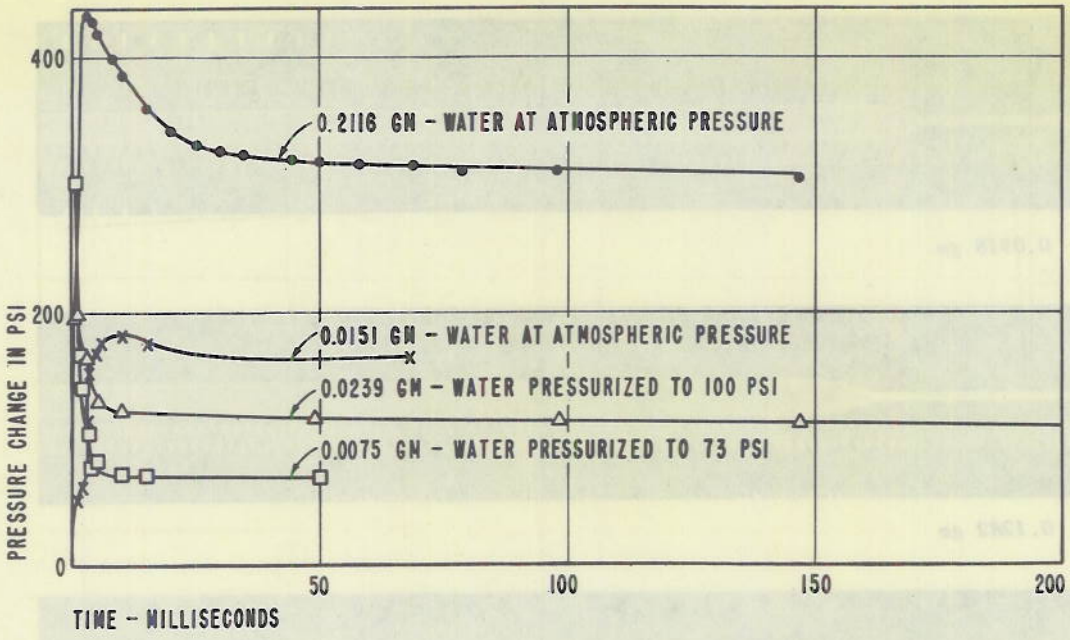


Figure 11.--Effect of pressurizing on the reaction of various amounts of $Al(BH_4)_3$ with water.

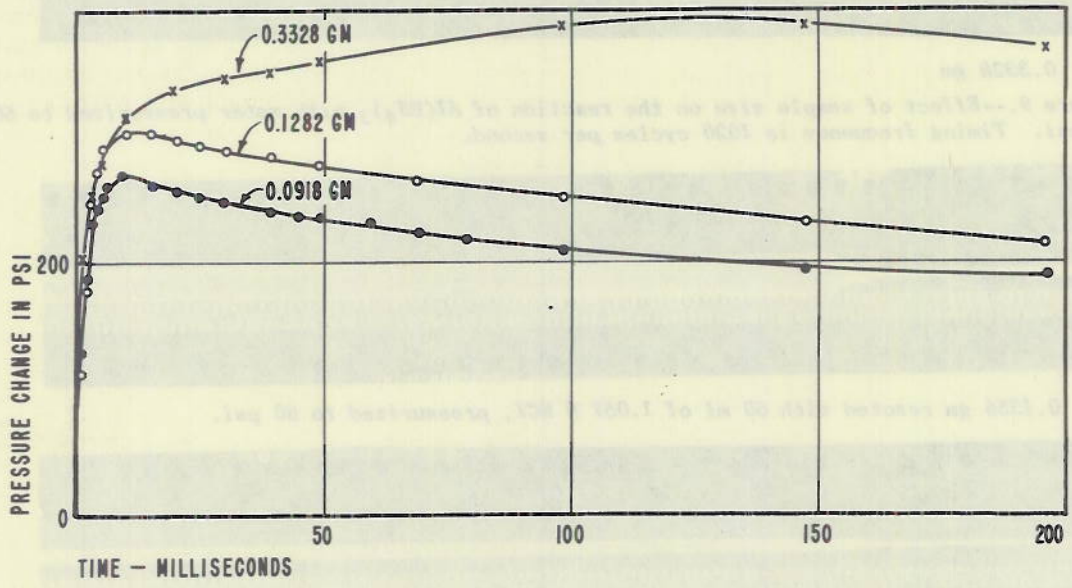


Figure 12.--Effect of sample size on the reaction of $Al(BH_4)_3$ with water pressurized to 60 psi.

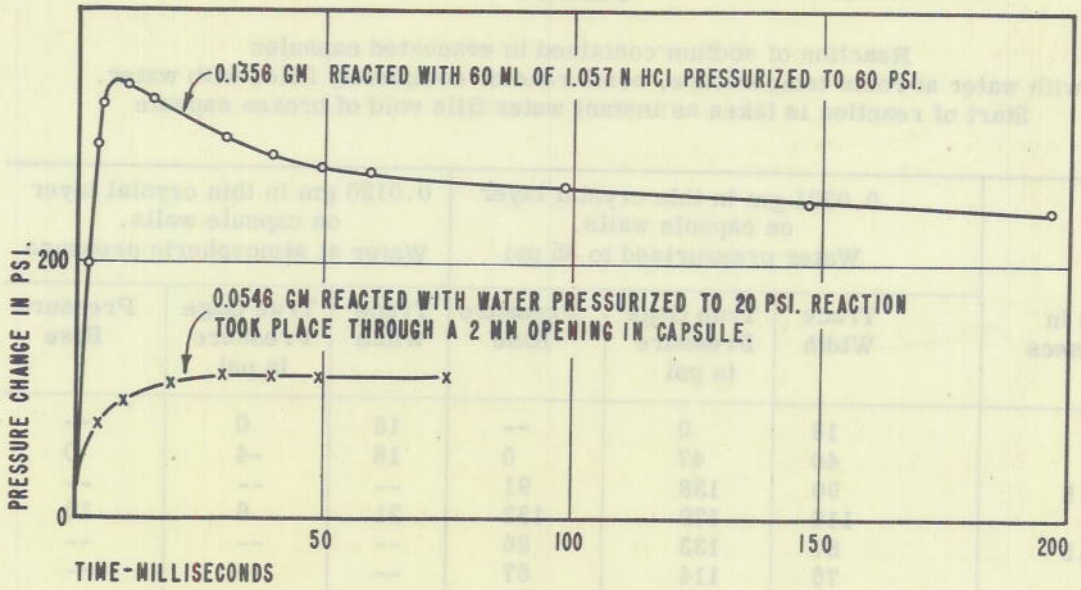


Figure 13.--Effects of acid and small contact area between reactants on the reaction of $Al(BH_4)_3$ with water.

Figure 13 illustrates the kind of reaction which results when only the sealing stem of the capsule broke to leave a small opening of 2 mm in diameter for the access of water to the aluminum borohydride. Surprisingly enough, the reaction was relatively rapid in contrast to the slowest reactions obtainable with alkali metal in contact with water.

TABLE 1

Reaction of sodium contained in evacuated capsules
with water at room temperature, bomb reactor completely filled with water.
Start of reaction is taken as instant water fills void of broken capsule

Time in Millisecs	0.0201 gm in thin crystal layer on capsule walls. Water pressurized to 85 psi			0.0130 gm in thin crystal layer on capsule walls. Water at atmospheric pressure		
	Trace Width	True Gage Pressure in psi	Pressure Rise	Trace Width	True Gage Pressure in psi	Pressure Rise
--	18	0	--	18	0	--
0	40	47	0	16	-4	0
0.5	90	138	91	--	--	--
1	116	179	132	21	6	10
1.5	87	133	86	--	--	--
2	76	114	67	--	--	--
3	73	109	62	--	--	--
5	70	104	57	25	15	19
10	67	98	51	28	21	25
50	66	96	49	33	32	36
100	65	94	47	35	36	40
200	63	91	44	35	36	40
300	63	91	44	34	34	38
400	--	--	--	37	40	44
500	--	--	--	36	38	42
600	--	--	--	35	36	40
700	--	--	--	--	--	--
1000	--	--	--	35	36	40
	0.0268 gm in thin crystal layer on capsule walls. Water at atmospheric pressure			0.0152 gm in single spherical bead. Water at atmospheric pressure.		
--	17	0	--	-17	0	--
0	15	-4	0	15	-4	0
0.5	--	--	--	--	--	--
1	16	-2	2	--	--	--
1.5	--	--	--	--	--	--
2	--	--	--	--	--	--
3	--	--	--	--	--	--
5	20	7	11	--	--	--
10	23	12	16	15	-4	0
50	39	39	43	--	--	--
100	45	59	63	16	-2	2
200	45	59	63	17	0	4
300	44	57	61	--	--	--
400	47	63	67	--	--	--
500	46	61	65	--	--	--
600	45	59	63	--	--	--

TABLE 1--Continued

Reaction of sodium contained in evacuated capsules with water at room temperature, bomb reactor completely filled with water. Start of reaction is taken as instant water fills void of broken capsule

Time in Millisecs	0.0268 gm in thin crystal layer on capsule walls. Water at atmospheric pressure			0.0152 gm in single spherical bead. Water at atmospheric pressure.		
	Trace Width	True Gage Pressure in psi	Pressure Rise	Trace Width	True Gage Pressure in psi	Pressure Rise
700	45	59	63	--	--	--
1000	45	59	63	20	6	10
1600	--	--	--	23	12	16
2100	--	--	--	25	17	21
	--	--	---	33	55	59

TABLE 2

Reaction of indicated amounts of sodium-potassium alloy of 12 Wt %K in thick layer in evacuated capsules with water at room temperature, bomb reactor not completely filled with water

Time in Millisecs	0.1604 gm; Water Pressurized to 85 psi			0.3799 gm; Water at Atmospheric Pressure		
	Trace Width	True Gage Pressure in psi	Pressure Rise	Trace Width	True Gage Pressure in psi	Pressure Rise
--	16	0	--	16	0	--
0	30	70	0	16	0	0
0.5	49	146	76	--	--	--
1	66	210	140	--	--	--
2	88	284	214	--	--	--
3	100	320	250	--	--	--
4	95	304	234	--	--	--
5	93	296	226	--	--	--
10	91	294	224	--	--	--
50	88	284	214	35	90	90
100	82	264	194	43	122	122
200	78	252	182	57	179	179
300	77	248	178	70	224	224
400	76	246	176	82	264	264
500	75	242	172	95	304	304
600	74	239	169	107	339	339
700	--	--	--	121	377	377
800	74	239	169	129	397	397
900	--	--	--	117	367	367
1000	--	--	--	109	344	344

TABLE 2--Continued

Reaction of indicated amounts of sodium-potassium alloy of 12 Wt %K in thick layer in evacuated capsules with water at room temperature, bomb reactor not completely filled with water

Time in Millisecs	0.1604 gm; Water Pressurized to 85 psi			0.3799 gm; Water at atmospheric Pressure		
	Trace Width	True Gage Pressure in psi	Pressure Rise	Trace Width	True Gage Pressure in psi	Pressure Rise
1100	--	--	--	106	336	336
1200	--	--	--	104	330	330
1500	--	--	--	103	328	328
2000	--	--	--	103	328	328
	0.3808 gm; Water Pressurized to 182 psi			0.2132 gm; Water Pressurized to 135 psi		
--	16	0	--	16	0	--
0	58	182	0	45	135	0
0.5	--	--	--	--	--	--
1	113	354	172	68	219	84
2	149	476	294	72	284	149
3	174	528	346	72	284	149
4	184	546	364	72	284	149
5	188	554	372	72	284	149
10	190	558	376	75	293	158
20	192	562	380	80	317	172
30	193	564	382	85	320	185
40	--	--	--	90	336	201
50	195	566	384	95	350	215
60	196	568	386	98	358	223
70	198	572	390	102	370	235
80	200	575	393	104	374	239
90	--	--	--	106	380	245
100	197	570	388	109	387	252
200	177	533	351	113	397	262
300	165	510	328	119	412	277
400	158	496	324	104	374	239
500	153	486	314	99	360	225
600	152	484	312	96	352	217
700	--	--	--	94	347	212
800	--	--	--	94	347	212
900	--	--	--	93	344	209
1000	150	480	308	93	344	209

DISCUSSION

Since the data obtained are not reproducible, only factors which have a strong influence on the reaction rate can be detected. As evidenced by the behavior of the reaction when water is forced under pressure against thin layers of sodium, the intimacy of contact between water and an atom of sodium (or the extent or degree of mixing) appears to be such a factor. By decreasing the thickness of the layer of sodium so that it approaches a film of monatomic thickness, the reaction rate should approach a limiting one which would be comparatively instantaneous. This same consideration should hold equally well when, instead of using thin layers, the metal or alloy is introduced to water in a very fine spray.

However, when such ideal conditions for the reaction exist, response of the instrumentation becomes a critical factor. The time interval over which the instrumentation will have a true response is limited by the lowest natural frequency of the apparatus. Inasmuch as the lowest frequency of vibration observed was approximately 1000 cps this time interval is then around one millisecond. Consequently, pressure changes occurring in less time would not be accurately determined.

With pressure-time relationships as a criterion, the reaction of aluminum borohydride is similar to that of the alkali metals with water. As is perceptible from a comparison of the pressure-versus-time curves, the reaction completion times are of about the same order of magnitude. Hydrogen-ion concentrations involved did not appear to have any noticeable effect on the rate.

All of the data were complicated by the presence of two different types of phenomena. The first of these is a natural frequency (See Part III) considered to be either a frequency produced by the vibration of the pressure transducer electrode and case, or the oscillation of gas bubbles in the liquid in the bomb reactor. The former appears to be the more plausible of the two. The second is a tendency for the recorded pressures to reach peaks far in excess of the final equilibrium pressure which prevails in the bomb after the reaction is over. The exact reason for the excess pressure peaks is not available. Simple cooling of the solution (at less than 20°C above room temperature), dissolution of evolved hydrogen, and formation and recombination of atomic hydrogen are believed to be insufficient to account for the total effect.

That this phenomenon cannot be attributed to the dynamic response of the apparatus to pressure changes is fairly well established by the facts, (1) that gaseous carbon dioxide under pressure suddenly released within the bomb reactor did not produce the pressure peak and (2) that in most of the experiments the duration of pressure peaks was manyfold the period of vibration of the lowest frequency component observed for the apparatus (See Part III).

The peaks which in some instances have been nearly 100% greater than the final equilibrium values are undoubtedly related to the distribution of the heat of reaction in the reaction system. If the reaction is sufficiently rapid the heat transfer through the liquid surrounding the reaction zone may be insufficient to dissipate the heat as fast as it is produced. Consequently, a higher temperature will persist in the locale of the reaction and result in a greater vapor pressure of the water as well as an expansion of the gaseous product. A pressure peak would then be formed when the gas cooled and the water vapor recondensed. Motion pictures taken of an alkali-metal reaction with water have shown formation of opaque gas bubbles. This opaqueness has been considered to be due to water vapor.

CONCLUSIONS

1. The instrumentation used for following the course of reaction in a closed vessel is considered adequate in response if the period of pressure transients is greater than one millisecond. Response to periods less than one millisecond is questionable.

2. The observed reaction rates have been complicated by the presence of two phenomena. One is an anomalous vibration believed to be related to a vibration of an electrode in the transducer, although some possibility exists that this vibration may be related to the oscillation of gas bubbles in water. The second is the existence of definite peak pressures considered to be due to heating and cooling of the reaction zone in the aqueous solution within the bomb reactor.

3. Under conditions which promote mixing of the reactants sodium has been observed to react completely with water in one millisecond. It is believed that, if an alkali-metal can be sufficiently dispersed at its contact boundary with water, either by having the metal in thin layers or by spraying it through an appropriate nozzle, reaction rates of magnitudes beyond resolution with the available instrumentation can be attained.

4. The mechanism governing the reaction of alkali-metals with water is open to speculation. The extent of the surface of contact between the reactants appears to be a critical parameter.

5. The rate of reaction of aluminum borohydride appears to be of the same magnitude as the optimum rate for sodium. It could be that the rates are considerably different, but that this difference is not visible because of the pressure indicator's probable inability to follow pressure transients which last less than one millisecond.

PART II

REVIFW AND DISCUSSION OF THE ALKALI-METAL REACTIONS WITH WATER

REACTION OF PURE METALS

The question as to how a metal reacts with water or with aqueous solutions has not received an adequate answer. Various theories with respect to the mechanism of the dissolution process have stemmed from work on reaction rates, corrosion phenomena, and over voltage, but none of these has met with complete acceptance. Before considering the possibilities of the reaction mechanism, a survey will be given of some of the properties of the metals in the alkali group.

In the order of increasing atomic weights the alkali metals are lithium, sodium, potassium, rubidium and caesium. It is generally accepted that their lattices, like those of all true metals, are held together by a bond which has to some extent the character of both covalent and electrovalent linkages. This unique type of linkage is commonly termed a metallic bond. Glasstone [5] generalizes by saying that in this type of bonding a relatively small number of electrons are able, in some manner, to bind together a large number of atoms, or more correctly, ions. According to Frenkel [6] these electrons, since they are mobile and capable of moving throughout the volume

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[5] *Glasstone, Samuel, Text-Book of Physical Chemistry, Second Edition, D. Van Nostrand Co., Inc., pp. 377-379 (1946).*

[6] *Frenkel, J., Kinetic Theory of Liquids, Oxford University Press, p. 427, (1946).*

of the metal, have been called "free electrons" by many writers, but they are not free in the same sense as electrons released from the atoms in a gas phase by the action of some ionizing agents.

Yet, despite their power to bind the metal lattice, these electrons in the alkali metals are more readily removed than those of the other elements in the Periodic Table. This is illustrated by their low ionization potentials which decrease from lithium to caesium. Consequently, in any reaction which involves a loss of an electron from the metal, it would be reasonable to expect that alkali metals would be highly reactive, with such reactivity increasing from lithium to caesium.

The study of solutions of alkali metals in liquid ammonia has contributed materially toward the understanding of conduction in metals and in electrolytes, of the effect of solvents on acids and bases, and of ionization in solution. Such solutions are extremely stable inasmuch as only slight reaction and evolution of hydrogen occur at room temperature. Dilute solutions appear blue in transmitted light while the concentrated ones are bronze-red. Although the basis for its formation still lacks a complete explanation, this color has been attributed to the presence of free electrons in the solution.[7] Birch and MacDonald[8] claim the color to be due to the existence of definite ammoniates of the alkali and alkaline-earth metals except those of sodium and potassium. They stated that in heavy layers the ammoniates are bronze-like in color while in thin ones they are blue. Because these authors did not obtain a characteristic color or breaks in a cooling curve with sodium and potassium in ammonia they concluded that their ammoniates do not exist.

However, this color has been observed at this Laboratory as well as by Kraus,[9] and it may well be that the ammoniates of sodium and potassium do exist but are too loose and unstable to permit their isolation. Svedberg[10] prepared colloidal solutions of the alkali metals in ethyl ether and showed colors of coarse and fine ethyl-ethersols which were predominantly blue. Perhaps the color observed in liquid ammonia is produced in like manner by a suspension of minute, charged particles or sols dispersed in this solvent.

The most important fact in the color phenomena is that all metals, when in solution in solvents with which they do not react to any appreciable extent, yield a blue color if the solution is dilute and a bronze-like color if concentrated. Undoubtedly, the similar color behavior is due to a common property, such as free electrons in solution. That electrons, dissociated from the parent metal atoms, do exist in such solutions has been well established although uncertainty exists as to the atmosphere surrounding them[11]; this atmosphere could be solvent molecules closely associated with the electron to form a solvated electron.

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7 *Gibson, G.E. and Argo, W.L., The absorption spectra of the blue solutions of certain alkali and alkaline earth metals in liquid ammonia and in methylamine. J. Am. Chem. Soc. 40, p. 1327-1361, (1918).*

8 *Birch, A.J. and MacDonald, K.C., The nature of metal-ammonia solutions, Part II. Trans. Far. Soc., 44, pp. 735-742, (1948).*

9 *Kraus, C.A., Solutions of metals in non-metallic solvents, I. J.Am. Chem. Soc., 29, p. 1557-1571. (1907).*

10 *Mellor, J.W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. II., Longmans, Green & Co., p. 462, (1922).*

11 *Kraus, C.A., The Properties of Electrical Conducting Systems, Chemical Catalog Co., Chap. XIV, (1922).*

In water the alkali metals react vigorously and hydrogen is liberated. There is no indication of a blue color. If free electrons in solution are the cause of such color when an alkali metal is dissolved in liquid ammonia, its absence when water is the solvent indicates that no such electrons are present. Apparently these electrons do not exist in aqueous solution because of the reactions,

$$H_2O + e \longrightarrow OH^- + H \text{ and}$$

$$H_3O^+ + e \longrightarrow H_2O + H,$$

which remove any such electrons as rapidly as they become available from the metal. If such were not the situation, water in contact with these metals should soon acquire a blue color.

Undoubtedly the reactions in liquid ammonia and water are quite similar except that in ammonia the reaction is much slower and the metals, as such, go into solution. The voluminous work of Cady, Franklin and Kraus[12] is a testimonial to the parallelism in the chemistry between liquid ammonia and aqueous solutions. Kraus measured the very slow reaction rate of sodium in liquid ammonia which can be accelerated through use of a suitable catalyst such as iron-oxide or platinum black.[13] The slowness of this reaction in contrast to the reaction with water is probably due to the stability of the H-N bond over that of the H-O bond.[14]

In conformity with what has been said the following parallel mechanisms for reaction of an alkali metal with liquid ammonia and with water are proposed. It is realized that any attempt of this kind is bound to be rather controversial, since factual evidence in support of any hypothetical scheme in this instant, is virtually non-existent.

(1) $M \rightleftharpoons (M + e)$	$M \rightleftharpoons (M + e)$
(2) $(M + e) \underset{\rightleftharpoons}{H_2O} (M^+) + e$	$(M + e) \underset{\rightleftharpoons}{NH_3} (M^+) + e$
(3) $2H_2O \rightleftharpoons (H_3O^+) + (OH^-)$	$2NH_3 \rightleftharpoons (NH_4^+) + (NH_2^-)$
(4) $H_2O + e \longrightarrow (OH^-) + H$	$NH_3 + e \longrightarrow (NH_2^-) + H$
and/or	and/or
$(H_3O^+) + e \longrightarrow H_2O + H$	$(NH_4^+) + e \longrightarrow NH_3 + H$
(5) $2H \longrightarrow H_2$	$2H \longrightarrow H_2$
$M + 2H_2O \longrightarrow (M^+) + 2(OH^-) + 1/2H_2$	$M + NH_3 \longrightarrow (M^+) + (NH_2^-) + 1/2H_2$

The mechanism described above illustrates the transfer of an electron from its usual level in the metal and its subsequent capture by a solvent molecule or ion which then decomposes with a liberation of atomic hydrogen. Whether molecular hydrogen results from a combination of two atoms or directly from a decomposition of two

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12 *Kraus, C.A., ibid, p. 1571.*

13 *Franklin, E.C., The Nitrogen System of Compounds, Reinhold Publishing Corp., p. 53, (1935).*

14 *Kraus, C.A., Reactions and reagents in liquid ammonia, Chem. Rev., 26, p. 95-104, (1940).*

hydronium or water molecules, after an absorption of electrons has taken place, is not known. Elaborating in a little more detail, (1) represents the removal of an electron from its normal valence orbit or energy level, but not to the extent of causing the formation of a stable ion of the metal.[15] As the temperature of a metal is increased this equilibrium is thrown more and more to the right and electrons may exist a considerable distance from the initial quantum level as illustrated by their behavior in a radio vacuum tube.

Equation (2) shows the complete removal of this electron either by the action of the solvent as in liquid ammonia or by its interaction with an ion or molecule with a subsequent capture and breakdown as in the instance when the reaction in (4) takes place. Since there is no definite evidence for excluding interaction between an unionized water molecule and an electron, this reaction step has also been included with the one which shows interaction of an electron and an ion in the equations shown in (4). Equation (5) merely illustrates the combination of atomic hydrogen to form the molecular species.

It is quite obvious that a chemical reaction can progress no faster than the slowest step necessary in the over-all process. From the work which has been done on the rates of dissolution of metals in aqueous solution it is not clear what the limiting step is. A variety of theories have been offered,[16] but none of them have been accepted in entirety. Stages (1) and (2) in the reaction scheme proposed in this report have been suggested since the extent of exposed surface of a metal appears to be a critical factor in some manner related to the rate-limiting stage of the reaction. By increasing the surface to a point where the metal in contact with the aqueous medium would be in a layer one atom in thickness, it would seem that the hydrogen evolution in the reaction could be made a maximum. Under such a circumstance the only essential reaction might be the freeing of an electron from the metal and its subsequent capture by a hydrogen ion, the rate of which would then determine the observed rate of reaction.

REACTION OF ALKALI-METAL AMALGAMS.

A number of investigators have studied the reaction of alkali-metal amalgams with a variety of solvent media. How their findings could be made to apply to the alkali-metal alone when it is not amalgamated escapes understanding. There is no reason why the behavior of the metal and its mercury amalgam in the presence of a solvent should be identical. The rates of reaction of the amalgams are considerably less than those for the pure metals. Diffusion of the alkali metal within the mercury may be an important parameter which limits the reaction to a rate less than that possible with the pure metal.

Brönsted and Ross Kane[17] studied the reaction of sodium amalgam with various buffer solutions and contended that the slow stage of the reaction is that of an electron with an acid molecule, while in strong acids the rate is determined entirely by a diffusion of the reacting substances into the surface of interaction. They showed that: (1) In a solution with a constant $_{p}H$ the rate of reaction is a function of the square root of the

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[15] *Frenkel, J., op. cit.*

[16] *Tafel, J., Z. physik. chem., 50, 641, (1905); Erdey-Gruz, F. and Volmer, M., Ibid, A150, 203, (1930); Gurney, R.W., Proc. Roy. Soc., A134, 137, (1931-2); Eyring, H., Glasstone, S., and Laidler, K.J., J. Chem. Phys., 7, 1053, (130); Kimball, George E., Ibid, 8, 820 (1940); Glasstone, Samuel, op. cit.; Glasstone, Laidler and Eyring, The Theory of Rate Processes, McGraw Hill Book Co. Inc., (1941).*

[17] *Brönsted, J.N., and Ross Kane, N.L., On the dissolution of metals in acids. J. Am. Chem. Soc., 53 pp. 3624-3644, (1931).*

concentration of sodium in the amalgam; $-dx/dt = K\sqrt{x}$ and $Kt = 2(\sqrt{a} - \sqrt{x})$ where a is the initial concentration at any time, t, and K the rate constants. (2) The reaction rate constant K is a linear function of the buffer concentration C_A, (i.e., $K = K_1C_A + K_0$, where K_1 is the slope of the line from the plot of K versus C_A, and K_0 is the intercept on one of the axes corresponding to the value of K at zero concentration of buffer). (3) The rate constant at zero buffer concentration increases with the hydronium ion concentration for the buffer used. (4) No reaction occurs with aprotic media such as benzene. (5) The reaction with the weak acid phenol in benzene obeys the "square root law", the plot of K versus C_A passing through the origin when water was not present in the benzene, whereas for the reaction with phenol in water solution this same type of plot did not pass through the origin but had an axis intercept and the rate constants were considerably smaller than those for the former. No visible attempt was made by these authors to account for the reaction rates being a function of the square of the sodium concentration in the amalgam, nor does a perusal of their data suggest an explanation for this strange relation.

Fletcher and Kilpatrick[18] paralled the work of Brönsted and Ross Kane by studying the kinetics of the reaction between lithium amalgam and various solvents. Their work with buffer solutions confirmed that of Brönsted and Kane, but in strong acids they indicated that the reaction is of the first order: $K = V/St \ln a/a-x$ where K is the rate constant; V, the volume of acide solution in cm^3; S, the area of mercury surface in cm^2; t, the time in minutes; a, the initial concentration of the acid; and a-x, the acid concentration after time t. In very weak acids the reaction obeyed the "square root law": $SKt = 2(\sqrt{C_0} - \sqrt{C_t})$, where C_0 and C_t represent the molar concentrations of alkali metal present initially and after time t in the amalgam, respectively, and the other symbols have the same meaning as before.

Fletcher and Kilpatrick explained their findings by postulating that the metal undergoes a simultaneous reaction with the molecules of water, with the various types of acids, and with the hydronium ions present, (i.e., $v = k_1C_{H_2O} + k_2C_{H_3O} + k_3C_{HA} + k_4C_{HB}$, etc., where HA represents a fairly weak acid, HB a very weak acid, H_3O^+ a strong acid and v the rate of reaction). From this assumption and the behavior of the amalgam in various solutions they derived the empirical equation to describe the reaction in any aqueous media.

$$-\frac{dx}{dt} = \frac{d(x_0 + x_1 + x_2 + x_3)}{dt} = \frac{VS}{1000}(K_w + K_{HB}C_{HB}\sqrt{C_m}) + S(K_{H_3O} + C_{H_3O} + K_{HA}C_{HA})$$

where dx_0/dt, dx_1/dt, etc., represent the rates of reaction of the amalgam with H_2O, HA, H_3O^+, etc; C_m, the concentration of alkali in the amalgam; V, the volume of acid solution; S, the area of the mercury, and the remaining symbols the same parameters as previously. For a metal to react with acid molecules as well as hydronium ions is not unreasonable and is in accord with the extended theory of acids and bases.

Sklyarenko and Sakharov[19] extended the work with respect to the amalgams by including in their investigations all of the alkali metals. Their empirical equation,

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[18] *Fletcher, F.A., and Kilpatrick, Martin, The rate of reaction of amalgams with acid I. J. Phys. Chem., 42, pp. 113-124 (1938).*

[19] *Sklyarenko, C.I. and Sakharov, B.A., J.Phys.Chem.,USSR, (In Russia) 42, pp. 113-124 (1938)*

$t = t_1 + 1/k_2 \ln C_o/C$, (where $t = 2(\sqrt{C_o} - \sqrt{C})/k_1 S$; C_o and C are respectively the concentrations of alkali metals in the amalgam present initially and at time t; t_1, the time for the concentrations to change from C_o to C if the reaction had taken place at constant pH; and S, the contact area of the amalgam with the solution), proposed to describe the reaction when the pH is permitted to vary at will, is similar to one which may be obtained by integrating the previously mentioned equation of Kilpatrick and Fletcher by not considering acids other than a strong acid present in the aqueous solution.

It should be noted that in the first order reaction the concentration values may be expressed as a concentration of the metal in the amalgam, or as the concentration of the hydronium ions in a solution of the strong acid, provided these are expressed in appropriate units. The interesting point of the Russians' work is that the reaction rates of the amalgams were observed to decrease as they went from lithium to caesium, which fact is in contradiction to the expected behavior of the pure metals in an aqueous medium. Assuming credibility of their investigation, this contradictory behavior perhaps has some explanation in the bonding of the alkali metal with mercury in the amalgam or the diffusion of the alkali within the mercury media.

DISCUSSION

The question with respect to the mechanism involved in the reaction of an alkali metal with water has not been resolved by the information available from studies with the pure metals or their amalgams with mercury. With both, the extent of exposed metal surface is a critical factor in determining the rate of the reaction. Undoubtedly, the rate-controlling step is some process affected by the extent of available surface.

PART III

A DISCUSSION OF APPARATUS AND PHENOMENA AFFECTING THE RECORDING OF RAPID PRESSURE CHANGES

MODIFICATIONS IN THE APPARATUS

Following an earlier report[20] a number of modifications have been incorporated in the apparatus for the purpose of obtaining greater reproducibility of data and of eliminating transient pressure oscillations. These modifications are listed below.

(1) Elimination of restricting passageway on the pressure side of the indicating diaphragm by redesigning the transducer head and machining it from a solid piece of 18-8 stainless steel so that the pressure-sensitive element would be flush with the inside walls of the bomb reactor. Caldwell and Fiock[21] have shown that erroneous pressure readings for burning or exploding gases are recorded when ducts are interposed between the diaphragm and the pressure source. McConnaughey in his work at this laboratory has observed a similar behavior for various passageways toward pressure changes under water.[22]

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[20] *Ewing, Atkinson, Rice, op. cit.*

[21] *Caldwell, F.R., and Fiock, E.F., J. Res. of Nat. Bureau of Stds., 26, pp. 175-196, (1941)*

[22] *McConnaughey, W.E., Naval Research Laboratory, Washington, D.C., Unpublished data.*

(2) Modification of the bomb closure by eliminating external valves. It was thought that oscillation of gas pressure might be due to vibration of a column of gas in the narrow pipes which connected the valves with the bomb reactor. Later data showed this supposition to be erroneous.

(3) Placement of a fine-mesh nickel screen in the reactor chamber to prevent particles of alkali metal from rising to the water surface and reacting there, partially submerged.

(4) Construction of a more massive reactor chamber with a cylindrical chamber cavity machined off-center. Earlier work had indicated the possibility that the pressure oscillations observed were caused by a lateral vibration of the chamber since its natural frequency was nearly identical with that of the phenomena observed.

(5) The amplifier of the original Pressuregraph tended to overload on use at high gains and resulted in a distortion of the transducer output as viewed on the screen of an oscilloscope. To overcome this difficulty the following changes were made in the original circuit?[23] The 6SF5 tubes were replaced by 6J5 tubes and appropriate changes in plate and cathode resistors were made to conform with the requirements of the new tubes. The operating voltage was raised by substitution of a small choke for the 15,000-ohm amplifier filter resistor and connecting it ahead of the VR-150 regulator tube. To maintain the high-frequency response of the amplifier the gain control value was reduced from 500K to 100K ohms. By replacing the 100 micromicrofarad coupling condensers with ones having a capacitance of 5000 micromicrofarads the amplifier gain was materially increased. An additional set of contacts was incorporated in the output switch to disconnect the second amplifier tube grid from the arm of the gain control on output switch position #1, thus making available the full gain of the first amplification stage without distortion. To maintain bias on output position #1 a megohm resistor was inserted at the grid of the second 6J5 tube.

(6) Utilization of evacuated glass capsules containing the alkali metal and pressurizing the water in the bomb reactor. This was done to assure a more rapid and homogeneous contact between the reactants when the capsule is broken. High-speed motion picture photography of the capsule being broken in an open vessel had revealed that quite often the fragmentation of the glass envelope is a progressive occurrence with only a small break taking place initially.

(7) Deposition of the alkali metal in a thin layer of crystals, approximately ten microns along an edge, on the inside walls of the glass capsule by evaporation of the solution of the metal in liquid ammonia at the temperature of a dry-ice in acetone bath.

THE CAUSE OF OSCILLATING PRESSURES

The presence of an anomalous pressure oscillation with a frequency varying between 500 and 1500 cycles per second around a mean frequency of 1000 cycles per second in the apparatus has already been mentioned. In order to determine whether the phenomenon was attributed to the chemistry of the reactions, glass capsules were loaded with gaseous carbon dioxide under pressure and these were broken under water in the bomb reactor in an identical manner as when they contained an alkali metal to be reacted with water.

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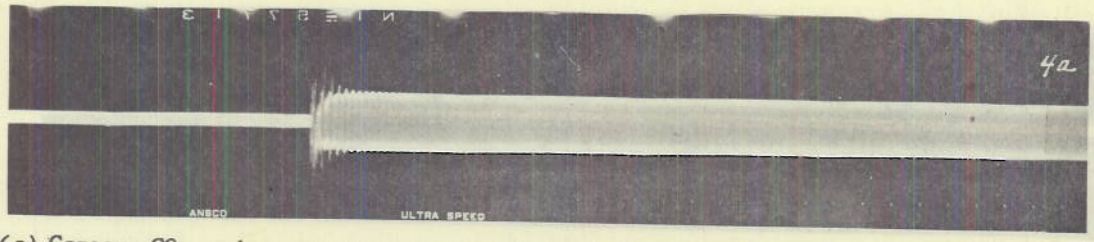
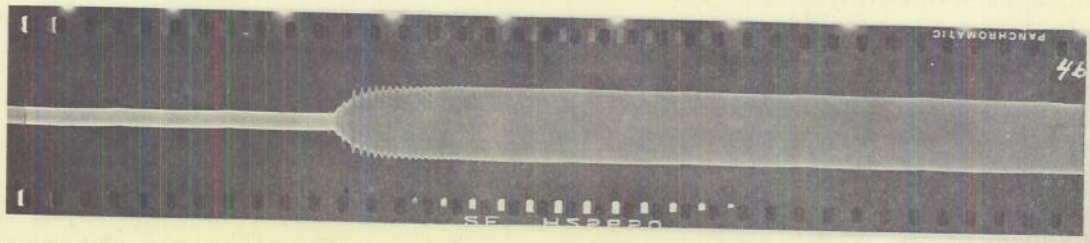
[23] *The modification and rebuilding of these instruments was done by C. H. Presbrey of the Instrumentation Section of the Chemistry Division.*



(a) Gaseous CO_2 under pressure released under water in bomb reactor when glass capsule is broken.



(b) Reaction of alkali metal with water in bomb reactor when glass capsule is broken.

Figure 14.--Comparison of frequencies of pressure oscillation resulting from release of CO_2 and reaction of alkali metal in the bomb reactor. Marginal time marks are 0.01 second apart.

The existence of the same oscillation (Figure 14) in these experiments and in those in which evacuated capsules were broken under water (Figure 15) is strong evidence that the cyclic pressures are not chemical in origin. Lewis and von Elbe[24] have reported finding an analogous vibration in explosions of gases containing an excess of oxygen and nitrogen, but they theorized that it is chemical in nature.

Since the pressure phenomenon was definitely non-chemical, steps were taken to determine its cause by a process of elimination. Calculations showed that the frequency of echo and re-echo of a pressure pulse in water contained in the reactor chamber would produce a frequency higher by a factor of ten than that observed. Elimination of ducts between valves and the chamber proper and those between the pressure-sensitive diaphragm had no effect on the frequency. Such considerations left only three probably sources for the disturbance: vibration of the transducer diaphragm, oscillation of a gas bubble under water, or vibration of several components of the apparatus to create a beat frequency.

The natural frequency of the pressure diaphragm, 0.030" thick, which was machined into the base of the threaded transducer head, is 24,000 cycles per second in air, but decreases in water to about 17,500 cycles per second. These frequencies were obtained by deflecting the diaphragm with a dropped ball-bearing and photographing the resulting vibration as seen on the screen of an oscilloscope. These observed values for the frequency in air and in water are approximately 80 percent of the calculated values obtained from the equation to be presented later. The poor agreement of observation with calculation may be due to not knowing what constitutes the effective vibration radius of

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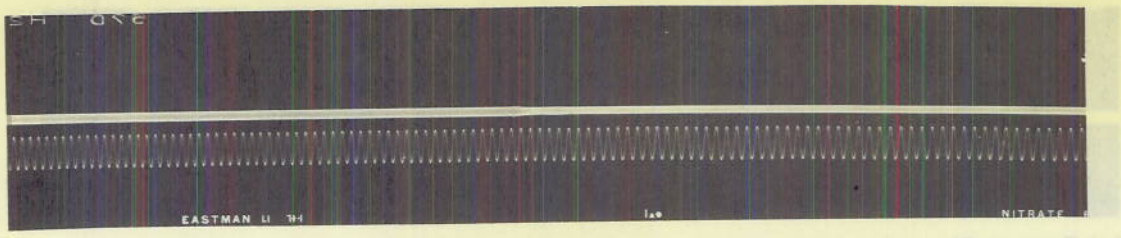
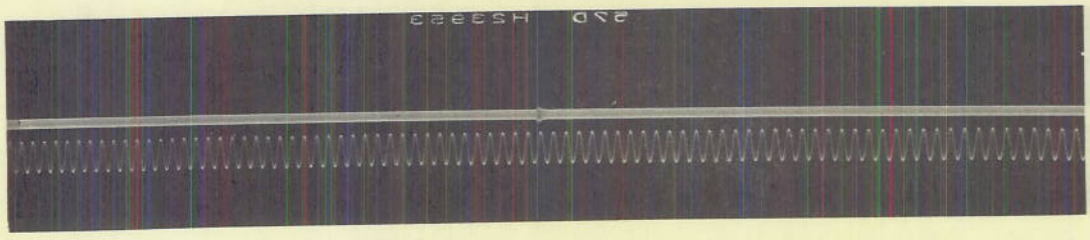
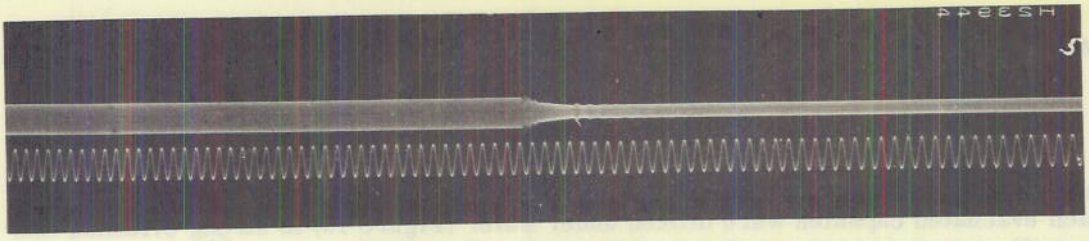
[24] *Lewis, Richard and von Elbe, Guenther, J. Chem. Phys., 3, pp. 63-71 (1935).*



(a) Evacuated capsule broken under water at atmospheric pressure.



(b) Unevacuated capsule under water at atmospheric pressure. Capsule did not break.



(c) Evacuated capsule broken under water pressurized to 85 psi with nitrogen.

Figure 15.--Frequency effects in bomb reactor filled with water, as shown by pressure trace on oscilloscope screen. Timing frequency is 900 cycles per second.

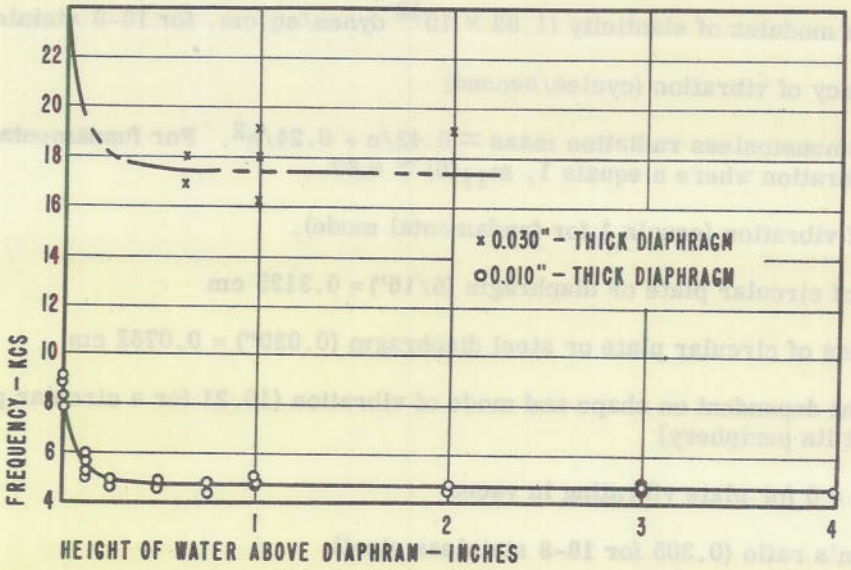


Figure 16.--Natural frequency of pressure transducer diaphragm.

the plate or diaphragm. In finite media a portion of the gas or liquid contributes its mass to that of the vibrating diaphragm to lower the natural frequency; however, in most instances, since the medium adjacent to the diaphragm is a gas, this contribution is very slight and the vibration, therefore, may be considered to take place in vacuo.

On the other hand, the influence of liquids on the frequency is pronounced and must be taken into consideration in the calculations. Figure 16 shows the effect of various amounts of water on the frequency of two diaphragms of different thickness. It is to be noted that the water is on one side of the diaphragm only. The equation reproduced below and used in calculating the frequency of the fundamental mode of vibration of the circular plate or diaphragm fixed rigidly at the periphery is equivalent to that given by Timoshenko.[25] By relatively simple mathematical manipulation it can be obtained from the equations used by Strasberg[26], Lax[27] and Lamb[28]. The symbol β in the equations of Lax and Strasberg should not be confused with its use by Timoshenko and Lamb.

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[25] *Timoshenko, S.P., Vibration Problems in Engineering, D. Van Nostrand Co., Inc., pp. 315-316; (1928).*

[26] *Strasberg, Murray, Radiation from a diaphragm struck periodically by a light mass, J.Acous. Soc. Am., 20, pp. 683-696, (1948).*

[27] *Lax, Melvin, Ibid., 16; p. 11, (1944).*

[28] *Lamb, Horace, Proc. Roy. Soc. London, 98, p. 208, (1920-21).*

$$f = \frac{\propto t}{4\pi r^2 \sqrt{1 - m_{11}(0)\beta}} \sqrt{\frac{E}{3\rho(1 - \mu^2)}}$$

E = Young's modulus of elasticity (1.93×10^{12} dynes/sq.cm. for 18-8 stainless steel).

f = Frequency of vibration (cycles/second)

$m_{11}(0)$ = Dimensionless radiation mass $\simeq 0.43/n + 0.24/n^2$. For fundamental mode of vibration where n equals 1, $m_{11}(0) \simeq 0.67$

n = Mode of vibration (equals 1 for fundamental mode).

r = radius of circular plate or diaphragm (5/16") = 0.3125 cm

t = Thickness of circular plate or steel diaphragm (0.030") = 0.0762 cm

$\propto$ = Constant dependent on shape and mode of vibration (10.21 for a circular plate held fixed at its periphery)

$\beta = \rho' r/\rho t = 0$ for plate vibrating in vacuo

μ = Poisson's ratio (0.305 for 18-8 stainless steel)

$\pi = 3.1416$

ρ = Density of 18-8 stainless steel = 8.03 gm/cu cm

ρ' = Density of medium adjacent to plate or steel diaphragm

This equation is applicable only in instances where the medium adjacent to the plate is infinite. It cannot be used for calculating the frequency where only small amounts of the liquid are next to the plate. When β equals zero the equation becomes the classical one used for calculating vibration frequencies of thin circular plates in vacuo.

The diaphragm frequency in water has been shown to be too high to account for the so-called anomalous vibration, but whether it is adequately high to reproduce faithfully short-duration pressure transients has not been mentioned. A kind of rule-of-thumb criterion often used in the selection of a transient pressure indicator is to have its fundamental frequency at least ten times that of the phenomenon to be measured; in other words the period or duration of the disturbance should be at least tenfold the natural frequency period of the indicator to be used.

A more precise relationship between duration of disturbance and period of vibration of an elastic mass has been given by Frankland[29]. He has shown mathematically that for most disturbances having a simple pressure-time configuration an elastic mass with a period of vibration less than one-fourth the period or duration of the disturbance will have adequate response. In compliance with this generalization an indicator designed to

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29 *Frankland, J.M., Effect of impact on simple elastic structures, D.T.M.B. Report #481, April 42.*

measure a pressure change of one millisecond's duration or longer should have a natural period of one-fourth a millisecond or less, i.e., a natural frequency of 4000 cycles per second or more.

During the evaluation of diaphragm frequencies the possibility of other components, such as the long electrode which forms the other plate of the pressure-sensitive condenser of the transducer vibrating during an experiment, was overlooked. Its frequency is just as critical as that of the diaphragm with respect to the instrument's response to rapid pressure changes. Quite by accident, it was discovered that this electrode had a relatively low frequency and could be set into oscillation by the mere tap of a finger. Subsequently records were taken of this vibration with the transducer suspended in air by a cord and with it screwed into place in the bomb reactor. Figure 17 is a photographic record of such vibrations. The frequency of the suspended transducer and the beat frequencies present when the transducer is attached to the bomb are in good agreement with the mean frequency of the pressure oscillation observed during reactions.

F. D. Smith[30] investigated the vibration of gas bubbles in water and proposed an equation for its frequency, the accuracy of which was later verified by careful measurements made by Meyer and Tamm[31] with respect to bubble diameter and frequency of oscillation. In Figure 18 are given curves at various pressures whose points have been secured through calculations using the Smith equation given below; for purpose of comparison the data of Meyer and Tamm have been plotted.

$$\omega = 2\pi f = 1/r \sqrt{\frac{3K(P_o + 2T/r)}{\rho}}$$

r = Radius of bubble (cm)

P_o = Hydrostatic pressure on bubble (dynes/cm^2)

ρ = Density of liquid (one for water)

T = Surface tension (dynes/cm)

K = Ratio of specific heats (1.47 for air)

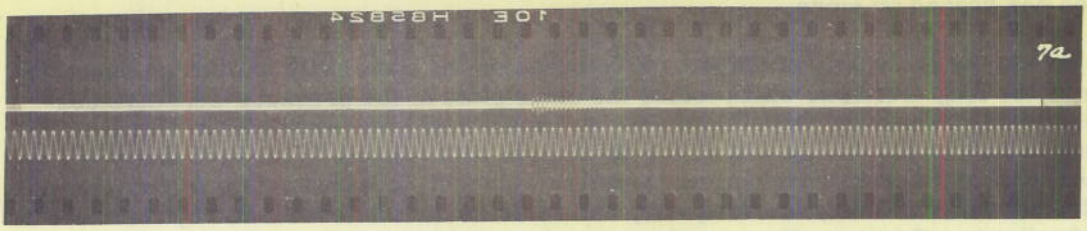
$\omega = 2\pi f$ = Circular frequency (radians/sec)

f = Fundamental frequency (cycles/sec)

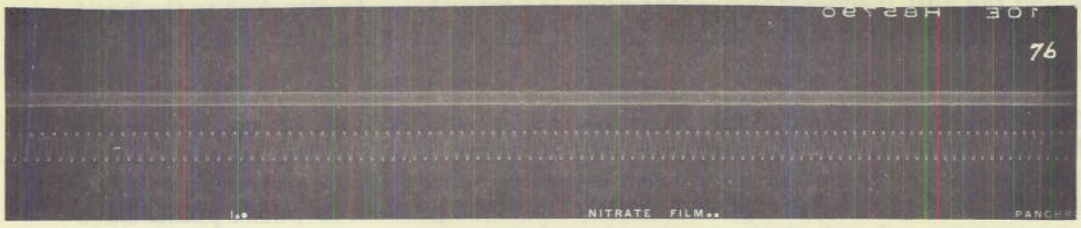
Since 2T/r is negligible for bubbles of finite size the above equation reduces to $f = 1/2\ \pi\ r \sqrt{\frac{3KP_o}{\rho}}$.

It can be seen from the curves that bubbles at pressures near atmospheric will have natural frequencies in the same range as those of the pressure oscillations present during reaction in the bomb reactor if their diameters are larger than 0.4 centimeters. Although it is absurd to expect any uniform size in the bubbles formed during reaction, it is quite plausible that during the short duration of the vibration phenomenon the mean diameter of the bubbles floating free in the water is greater than 0.4 centimeters.

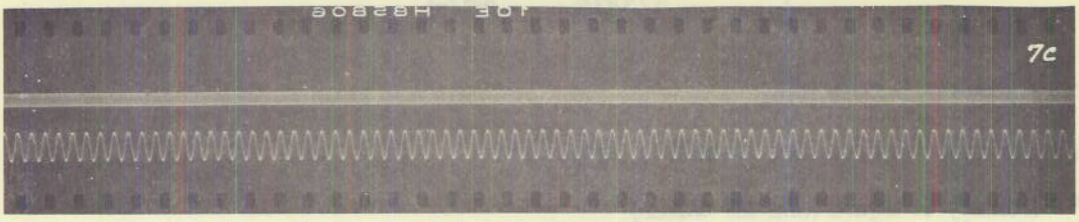
[30] *Smith, F.D., Phil. Mag., 19, pp. 1147-51, (1935).*
[31] *Meyer, Erwin and Tamm, Konrad, Akutische Zeitschrift, 4. No. 3 May 1939.*



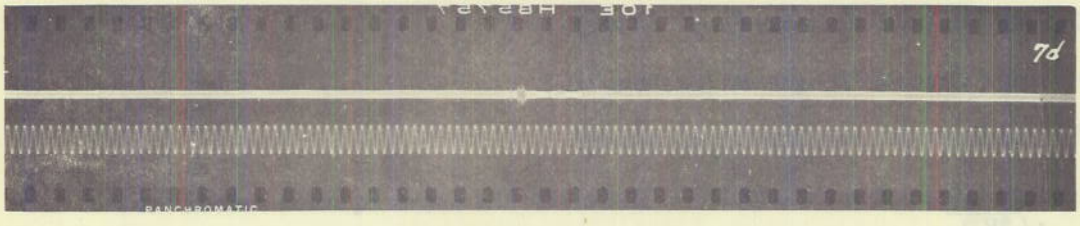
(a) Transducer suspended by a cord is struck.



(b) Transducer attached to bomb reactor, containing air at atmospheric pressure, is struck.



(c) Same as (b) except that bomb reactor is struck.



(d) Same as (b) except that bomb contains water at atmospheric pressure.

Figure 17.--Frequency in apparatus struck with a wooden mallet handle. Timing frequency is 1020 cycles per second.

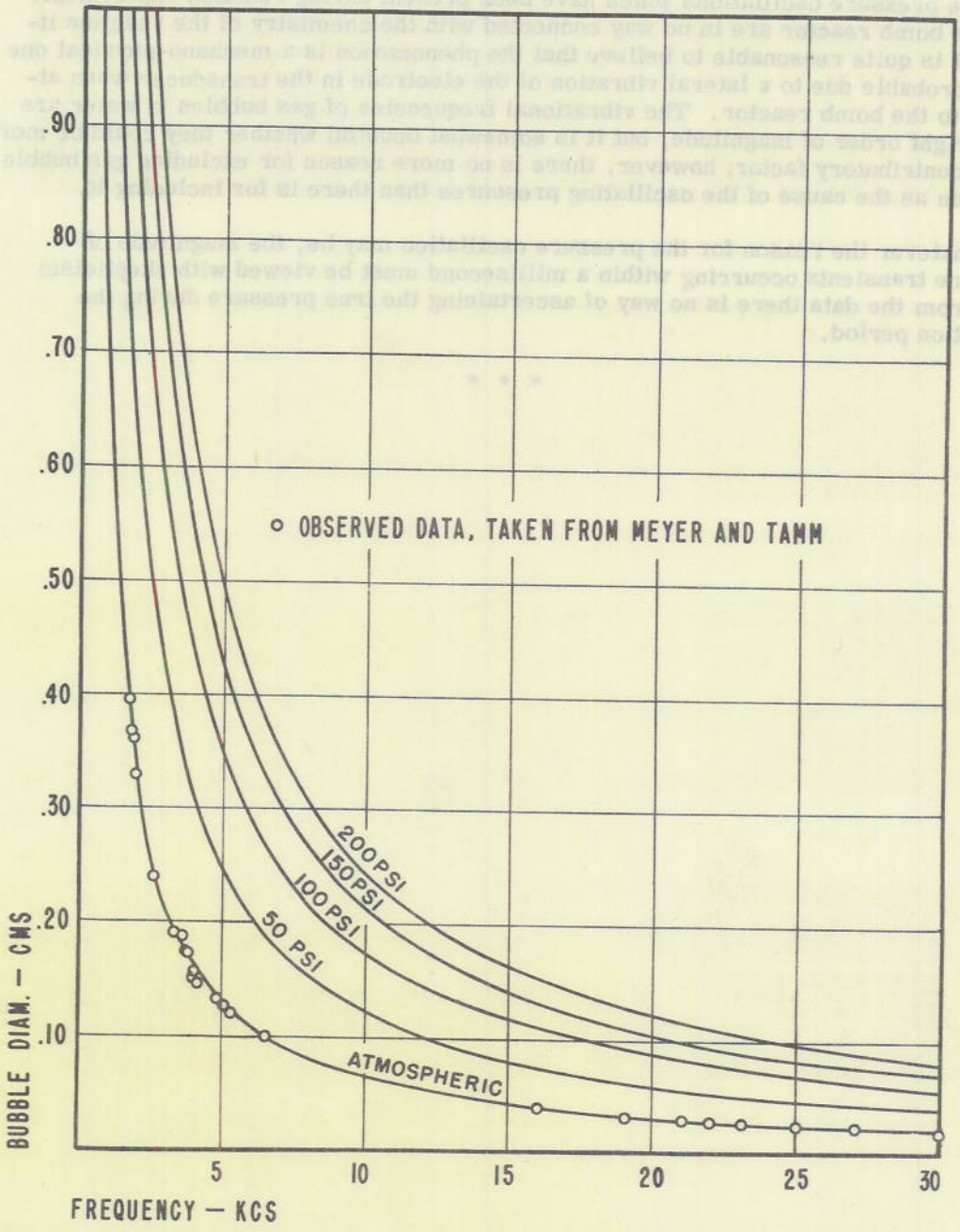


Figure 18.--Calculated frequencies of air bubbles, oscillating in water, at various pressures.

CONCLUSIONS

The pressure oscillations which have been present during reaction experiments with the bomb reactor are in no way connected with the chemistry of the reaction itself. It is quite reasonable to believe that the phenomenon is a mechano-physical one and is probable due to a lateral vibration of the electrode in the transducer when attached to the bomb reactor. The vibrational frequencies of gas bubbles in water are of the right order of magnitude, but it is somewhat doubtful whether they could be more than a contributory factor; however, there is no more reason for excluding gas bubble vibration as the cause of the oscillating pressures than there is for including it.

Whatever the reason for the pressure oscillation may be, the magnitude of pressure transients occurring within a millisecond must be viewed with skepticism since from the data there is no way of ascertaining the true pressure during the oscillation period.

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