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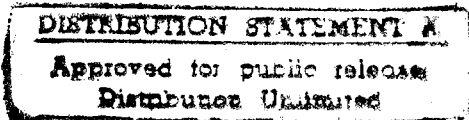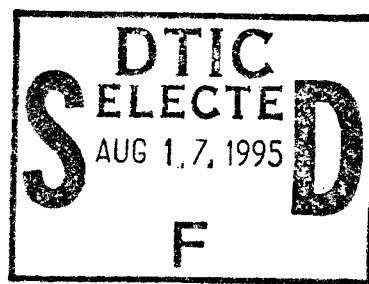
KAPL-722

UNITED STATES ATOMIC ENERGY COMMISSION

STATIC PRESSURE DUE TO SODIUM – WATER
REACTIONS IN CLOSED VESSELS

By
W. S. Horton

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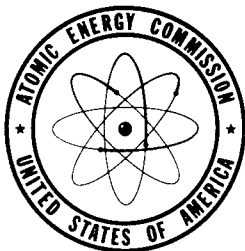
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KAPL-722

General Electric Company
KNOLLS ATOMIC POWER LABORATORY
Schenectady, New York

STATIC PRESSURE DUE TO SODIUM-WATER
REACTIONS IN CLOSED VESSELS

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ABSTRACT

The reaction between water and sodium, followed by reaction of the liberated hydrogen with air, in a closed vessel is treated as a thermodynamic problem at constant volume. The results for reaction of stoichiometrically equivalent amounts of sodium and water for varying size of vessel are found to follow the equation: $P = 3.44 + 45.64\,R - 7.97\,R^2$ where P is the final pressure in pounds per square inch gauge, and R is the ratio of sodium (in hundreds of cubic feet measured at 350°F) to dry air (in millions of cubic feet at 77°F). This equation is satisfactory when the final temperature is above the melting point of sodium hydroxide (591°K).

STATIC PRESSURE DUE TO SODIUM-WATER
REACTIONS IN CLOSED VESSELS

W. S. Horton

INTRODUCTION

In the development of the SIR, the bringing together within the same
general area of large quantities of molten sodium (as coolant) and water (as
shield) has necessitated an inquiry into the hazard associated with the acci-
dental mixing of these two substances. It has been stated that at reasonable
distances from the source of explosion any structure that will withstand the
static equilibrium pressure will also withstand the dynamic, transient ex-
plosion pressure which generally is of the order of twice as great as the
static equilibrium pressure. It appeared necessary therefore to compute the
static equilibrium pressure from reaction of sodium and water in a closed
vessel. For the calculations described herein, it was desired to compute the
pressure, the temperature of the gas phase, and the amount of energy released
or available to elevate the temperature of the materials above 25°C. Other
information, generally provided during the course of the calculations but not
described herein, includes the water content of the gas phase, the heat of
hydration of sodium hydroxide, and the minimum size of the vessel which would
ensure that the pressure would be no greater than a prescribed amount. This
report gives a detailed explanation of the similar calculations made by the
author for hazard evaluation of the SIR.

The numerical design data necessary for the calculation consisted of:

1. The weight of sodium involved.

2. The average temperature of the sodium.

3. The weight of water involved.

4. The average temperature of the water.

5. The volume of the containing vessel.

6. The composition of the original gas in the containing vessel.

7. The average temperature of the original gas in the containing vessel.

The assumptions made in the calculation include the following:

1. The evolved or available heat is partitioned among all products of
the reaction but not among any other materials.

2. Hydrogen, produced by the action of sodium on water, reacts with any
oxygen available in the containing vessel and liberates heat.

3. All gases behave like perfect gases under the conditions of the reaction.

4. The volume of substances destroyed in the reaction is insignificant compared to that available in the containing vessel.

Experiments have shown that the sodium-water reaction is not very fast as compared to a high explosive, and that a significant fraction of the liberated heat is given to neighboring materials. It was felt wise, in this calculation, however, to make Assumption 1 for a number of reasons. It is almost impossible to forecast accurately what fraction of the heat will be so distributed. The answer will depend upon where in the system the mixing occurs and upon the unknown time constant of the reaction as it may occur. By making the assumption a safety factor is provided, since accounting for the neglected heat loss would reduce the gas-phase temperature and consequently also reduce the pressure.

The general method of attack applies simple chemical thermodynamics to the two reactions, sodium plus water and hydrogen plus oxygen. The heat liberated at constant volume is partitioned among the products. The final temperature and the pressure of the gas is computed. The method is similar to that described by Glasstone.[1] The main difference between that description and the one in this report is that here constant volume, rather than constant pressure, is assumed. If the computed pressure is greater than the bursting pressure, the vessel will rupture. If the reverse is true, the computed pressure will be the true pressure at equilibrium under the assumptions given above.

It must be recognized that the details of calculation depend upon the physical states of the water and sodium hydroxide at equilibrium. Some combinations are listed.

1. Condensed water region

2. Vaporized water region

3. Molten sodium hydroxide region

4. Vaporized sodium hydroxide region

5. Hydrated sodium hydroxide region.

Within a region the pressure (or temperature) as a function of sodium weight per vessel volume ratio (or sodium per water ratio) is continuous. At the boundary between two regions, however, there is a point of discontinuity caused by differences in the heat capacity of the two phases of the changed substance (e.g., water vapor versus liquid water) and the heat of transition.

THERMODYNAMIC ANALYSIS

The process involved may be represented by the equation (the thermocynamic notation of Lewis and Randall[2] is used in this report):

$$Na(\ell, 644°K) + \frac{y}{x} H_2O(\ell, 339°K) + \frac{z}{x} O_2(g, 298°K) + \frac{4z}{x} N_2(g, 298°K) = NaOH(\ell, T_2)$$

$$+ \left(\frac{y}{x} - \frac{1}{2}\right) H_2O(g, T_2) + \left(\frac{z}{x} - \frac{1}{4}\right) O_2(g, T_2) + \frac{4z}{x} N_2(g, T_2).$$

$$(1)$$
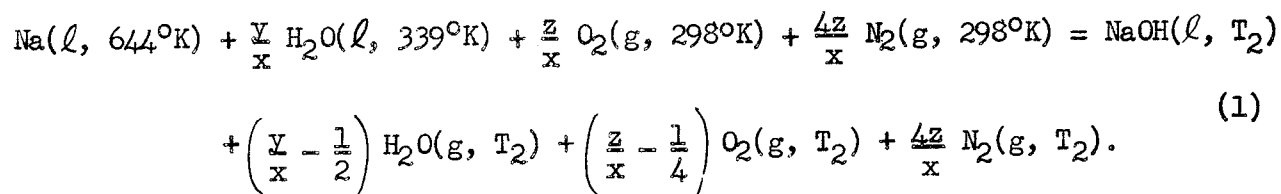
Here the sodium-water and hydrogen-oxygen reactions have been combined. The indicated temperatures of reacting substances apply to the SIR under operating conditions. Pure, dry air at room temperature has been used for the original gas in the containing vessel. The latter, of course, is a building. The reaction would involve x gram-moles of sodium with y gram-moles of water in the presence of 5z gram-moles of air. The equation has been divided by x since the resulting temperature and pressure depend upon the relative quantities and this division reduces the size of figures carried along in the calculations.

For most of the results used in the final phases of the SIR hazards evaluation, the molten sodium hydroxide region was involved. This made it convenient to adopt 591°K, the melting point, as a base temperature. The desired calculation goes through the following steps:

1. Determine $-\Delta E$ (the heat evolved at constant volume) for the reaction with 591°K for T_2.

2. From the combined heat capacities at constant volume of the products (including oxygen and nitrogen) and ΔE, determine ΔT, the actual amount by which T_2 is above 591°K.

3. Compute $T_2 = 591 + \Delta T$.

4. Compute the pressure from the perfect gas law.

Each of these steps will now be treated in detail. In order to fix the principles more firmly, a specific example will be carried through simultaneously.

The assumed example will concern the result of mixing 10760 pounds of sodium with a chemically equivalent amount ($\frac{y}{x} = 1$) of water in a 2×10^6 cubic foot vessel containing air. This leads to the following pertinent data.

$$Sodium = 2.12 \times 10^5 \text{ gram-atoms}$$

$$Original \text{ oxygen} = 0.464 \times 10^6 \text{ gram-moles}$$

$$Original \text{ nitrogen} = 1.86 \times 10^6 \text{ gram-moles}$$

$$\frac{Y}{X} = 1.00 \text{ (assumed)}$$

$$\frac{z}{x} = \frac{0.464 \times 10^6}{2.12 \times 10^5} = 2.19$$

$$4\frac{z}{x} = 4 \times 2.19 = 8.76$$

$$\left(\frac{Y}{x} - \frac{1}{2}\right) = 0.50$$

$$\left(\frac{z}{x} - \frac{1}{4}\right) = 1.94$$

To carry out Step 1, the standard values for ΔH of formation as obtained from reliable sources[3] are used to compute ΔH^0 for the reaction when all substances are in their standard states at one atmosphere pressure and 25°C. This yields $\Delta H^0 = -67.84$ kilocalories. To change this to constant volume conditions (ΔE) rather than constant pressure (ΔH) the equation

$$\Delta E = \Delta H - (\Delta N) \, RT \tag{2}$$

is used where ΔN is the change in the number of moles of gases for the reaction. When all the substances are in their respective standard states, only the oxygen and nitrogen are gaseous. Therefore
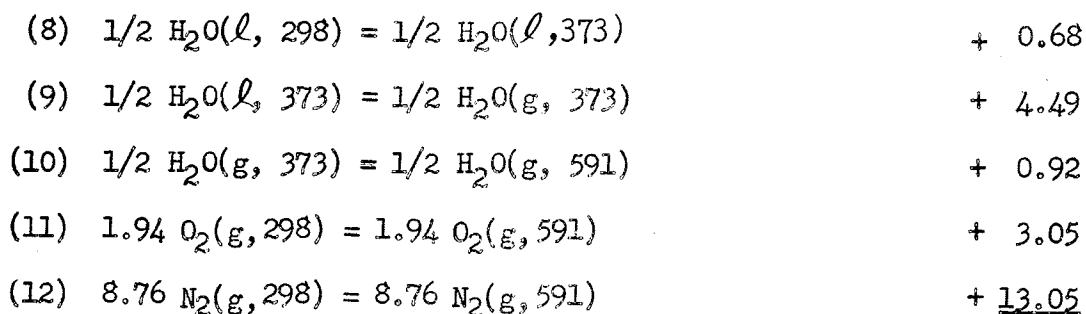
$$\Delta N = -\frac{1}{4},$$

$$-(\Delta N) \, RT = - \, (-0.25) \times 1.987 \times 298 = +15 \text{ cal} = 0.15 \text{ kcal},$$

$$\text{and } \Delta E = -67.84 + 0.15 = -67.69 \text{ kcal.}$$

To change the substances to their respective reaction temperatures and states, the following transformations are added.

(1)	Standard reaction	$\Delta E = -67.69$ kcal
(2)	$Na(\ell, 644) = Na(\ell, 371)$	-1.90
(3)	$Na(\ell, 371) = Na(s, 371)$	-0.63
(4)	$Na(s, 371) = Na(s, 298)$	-0.52
(5)	$H_2O(\ell, 339) = H_2O(\ell, 298)$	-0.72
(6)	$NaOH(s, 298) = NaOH(s, 591)$	$+7.47$
(7)	$NaOH(s, 591) = NaOH(\ell, 591)$	$+1.60$

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(8) $1/2\ H_2O(\ell,\ 298) = 1/2\ H_2O(\ell, 373)$ + 0.68

(9) $1/2\ H_2O(\ell,\ 373) = 1/2\ H_2O(g,\ 373)$ + 4.49

(10) $1/2\ H_2O(g,\ 373) = 1/2\ H_2O(g,\ 591)$ + 0.92

(11) $1.94\ O_2(g, 298) = 1.94\ O_2(g,\ 591)$ + 3.05

(12) $8.76\ N_2(g, 298) = 8.76\ N_2(g,\ 591)$ + 13.05

$$\Delta E = -40.22\ \text{kcal}$$

All energies in this set of 12 transformations are calculated from heat capacities at constant volume or heats of transition at constant volume. From this step - $\Delta E = 40,220$ calories per gram-atom of sodium is obtained—this is the heat available to heat the products above 591°.

In order to perform Step 2 conveniently, mean heat capacities are used (see Reference 1, pp. 52-4). Available equations (Reference 1, p. 503) for c_p were converted to the desired quantities. These are listed here.

Nitrogen (g): $\bar{c}_v = 4.906 + 0.625 \times 10^{-3}\ T_2$ cal/deg/g-mole   (3)

Oxygen (g): $\bar{c}_v = 4.957 + 1.369 \times 10^{-3}\ T_2 - 0.3077 \times 10^{-6}\ T_2^2$ (4)

H_2O (g): $\bar{c}_v = 5.981 + 1.205 \times 10^{-3}\ T_2 + 0.943 \times 10^{-6}\ T_2^2$ (5)

The heat capacities listed are mean values between 591°K and T_2. For liquid sodium hydroxide the equation

NaOH (ℓ): $\bar{c}_v = 18.22 - 3.836 \times 10^{-4}\ T_2 + \dfrac{4.77}{T_2}$ (6)

was derived from that given for NaOH (ℓ) by Epstein and Weber.[4] These four relations are plotted for various values of T_2. It is now possible to determine T_2 by successive approximations. The total heat capacity is given by

$$\bar{c} = \Sigma n_i\ \bar{c}_i \tag{7}$$

where $\bar{c}_i$ is the mean heat capacity of the ith product, n_i is the coefficient of that product in the balanced chemical equation (1). The difference between T_2 and 591°K is given by

$$\Delta T = \frac{-\Delta E}{\bar{c}}, \tag{8}$$

and T_2 then is:

$$T_2 = 591 + \Delta T. \tag{9}$$

Now if the $\bar{c}_i$'s are approximated, an initial approximation for T_2 can be calculated from the combination of Equations (7), (8), and (9) or

$$T_2 = 591 + \frac{-\Delta E}{\Sigma n_i \, \bar{c}_i} \tag{10}$$

This gives a new value for T_2. The process should then be repeated until no change occurs within the desired accuracy. For the numerical example included here the following table may be set up for the initial approximation of T_2.

Substance	n_i	$\bar{c}_i$	$n_i \, \bar{c}_i$
NaOH(ℓ)	1	18 cal/mole/deg	18 cal/deg
$H_2O(g)$	0.50	8	4
$O_2(g)$	1.94	6	12
$N_2(g)$	8.76	6	52
		$\bar{c} = \Sigma n_i \, \bar{c}_i =$	86

From this we obtain

$$\Delta T = \frac{40220}{86} = 468,$$

and $T_2 = 591 + 468 = 1059\,^{\circ}K$.

From the graphs of the $\bar{c}_i$ new estimates are obtained and the calculation is repeated as indicated below.

Trial	$\bar{c}$, cal/deg	ΔT, $^{\circ}K$	T_2, $^{\circ}K$
1	86	468	1059
2	82.58	487	1078
3	82.60	487	1078

The final step, computation of the pressure, requires the molar volume of the gases. The total number of moles of gas is given by

$$N = S \, \Sigma' n_i \tag{11}$$

where S is the number of gram-atoms of sodium and the "prime" indicates summation over gaseous products only. It should be noted that the air in the vessel is considered to be a product since it has been factored into the coefficients of Equation (1). Thus for the chosen example:

$$N = 2.12 \times 10^5 \, (0.50 + 1.94 + 8.76) = 2.374 \times 10^6 \text{ moles}$$

If the steps for the calculation of $-\Delta E$, hereafter to be called Q, are examined it is seen that this quantity can be expressed as

$$Q = E_s - 4 \frac{z}{x} E_n - \left(\frac{z}{x} - \frac{1}{4} \right) E_o \qquad (15)$$

This corresponds to dividing the energy into parts due to all other substances (Reactions 1 through 10) and those due to the air of the container (11 and 12). The ratio of water to sodium is considered constant and will be discussed later in the report. The equation can be rearranged as

$$Q = E_R - E' \left(\frac{5z}{x} \right) \qquad (16)$$

where

$$E_R = E_s + \frac{1}{4} E_o$$

and

$$E' = \frac{1}{5} \left(4E_n + E_o \right)$$

Since $\frac{5z}{x}$ is the ratio of air to sodium, it is replaced by R giving

$$Q = E_R - E'R. \qquad (17)$$

This shows that the energy is a linear function of the air-to-sodium ratio.

The combined mean heat capacity of the products may be written as

$$C = f_1 (T) + \frac{1}{2} f_2 (T) + \left(\frac{z}{x} - \frac{1}{4} \right) f_3 (T) + \frac{4z}{x} f_4 (T) \qquad (18)$$

where the functions of T are given for sodium hydroxide, water, oxygen, and nitrogen in Equations (3), (4), (5) and (6). They can be rewritten as

$$C = f(T) + \frac{5z}{x} g(T)$$

or

$$C = f(T) + g(T) \cdot R \qquad (19)$$

The expression for ΔT now becomes

$$\Delta T = T - T_R = \frac{E_R - E'R}{f(T) + g(T)R} \qquad (20)$$

Since the functions $f(T)$ and $g(T)$ are at least quadratics, Equation (20) becomes a cubic if a solution is sought for T in terms of R. It appears reasonable to assume that an explicit expression for T could be found by expanding in powers of R. Thus Equation (20) is replaced by

$$T = A_1 + B_1 R + C_1 R^2 + \ldots$$

To continue the development the molar volume is needed. The total moles of gas is given by $(0.5 + \frac{z}{x} - \frac{1}{4} + \frac{4z}{x})X$ or $(0.25 + R)X$. The total volume enclosing the gases is V or equal to $\overline{V}_a(5z)$ where $\overline{V}_a$ is the molar volume of air at normal conditions. The molar volume of the product gases then becomes

$$\overline{V} = \frac{5z\overline{V}_a}{(0.25 + R)X} = \frac{R\,\overline{V}_a}{(0.25 + R)} \tag{21}$$

The computed absolute pressure according to the perfect gas law is:

$$P = \frac{(0.082)T}{\overline{V}} = (0.082)\,\frac{A_1 + B_1R + C_1R^2 + \ldots}{R\,\overline{V}_a/(0.25 + R)}$$

$$= \frac{0.082}{\overline{V}_a}\left(\frac{0.25 + R}{R}\right)(A_1 + B_1R + C_1R^2 + \ldots)$$

Thus $P = f(R)$ (22)

Since it is now shown that the pressure is a function of R, the air-to-sodium ratio, it is evidently a ratio of $R' = R^{-1}$, also. The latter proves more convenient to use. It seems reasonable to take a number of values already computed by the long procedure and determine an equation of the form

$$P = a + bR' + cR'^2 + \ldots$$

to fit the data. The remaining problem now appeared to be the number of terms for a satisfactory fit. Actually, the initial attempt, which was for an approximate equation, proved to give the desired accuracy when checked against all previously calculated points. This was obtained merely by exactly fitting three constants to three points, one each at high, low, and intermediate values of R'. This equation is compared below with the results computed by the long method (see table on page 18).

For practical reasons it was convenient to use units other than moles and atmospheres. The sodium is given in hundreds of cubic feet measured at 350°F, the air in millions of cubic feet at 77°F, and the pressure in pounds per square inch gauge. The equation was used to draw generalized curves, presented in Figure MH-9A1804, which were sufficiently accurate to be used for the final phases of the Power Plant Building designing.

It can be shown by similar reasoning that if variable water-to-sodium ratio is to be considered, the equation for P becomes of third degree in R_A and R_W, with R_A = air/sodium and R_W = water/sodium. Since long-method computations had shown that the maximum pressure resulted for a y/x ratio of unity in the range of R_A shown in the table, the water ratio effect was not considered further.

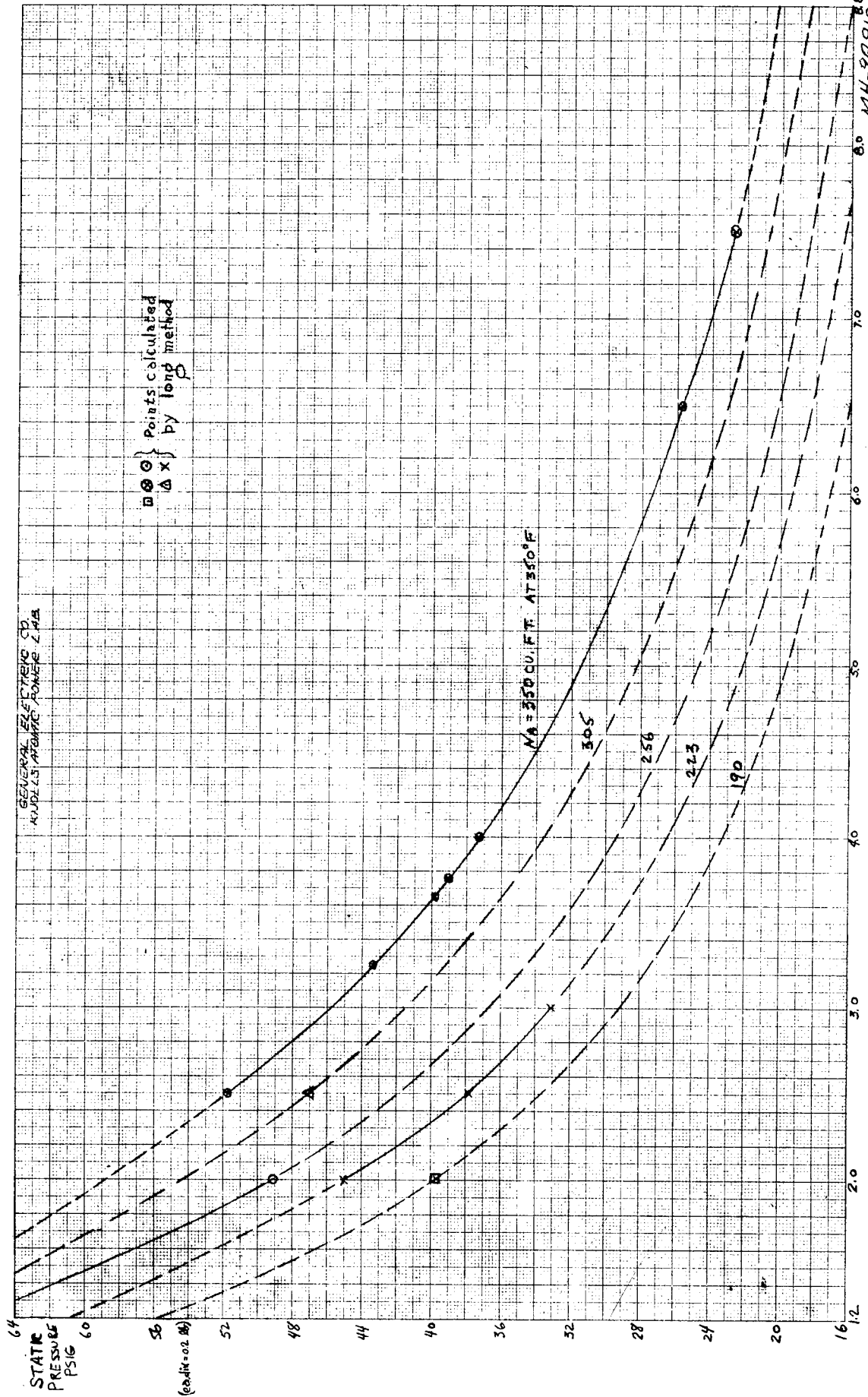Comparison of Equation ($P_e = 3.44 + 45.64R' - 7.97R'^2$)

with Values Computed by Long Method

	Sodium	Air	R'**	P	P$_e$	Δ
	1.90	2	0.950	39.7	39.6	+ 0.1
	2.23	2	1.115	44.4	44.4	0.0
(1)*	2.23	2.5	0.892	37.8	37.8	0.0
	2.23	3.0	0.743	33.1	33.0	+ 0.1
	2.56	2	1.28	49.1	48.8	+ 0.3
	2.90	2.7	1.074	43.3	43.3	0.0
	3.05	2.5	1.22	47.0	47.3	- 0.3
(2)*	3.50	2.5	1.400	51.7	51.7	0.0
	3.50	3.25	1.077	43.4	43.3	+ 0.1
	3.50	3.65	0.959	39.8	39.9	- 0.1
	3.50	3.76	0.931	39.1	39.0	+ 0.1
	3.50	4.00	0.875	37.3	37.3	0.0
(3)*	3.50	6.50	0.538	25.7	25.7	0.0
	3.50	7.00	0.467	22.7	23.0	- 0.3

*(1), (2), and (3) were the points used to determine the equation. P is computed by the long method, P$_e$ by the equation, Δ = P - P$_e$.
**R' is the ratio of sodium to air.

STATIC PRESSURE DUE TO $N_A - H_2O$
AND $H_2 - O_2$ REACTIONS

STATIC
PRESSURE
PSIG

64
60
56
(ea.div = 0.2 M)
52
48
44
40
36
32
28
24
20
16 1.2

GENERAL ELECTRIC CO.
KNOLLS ATOMIC POWER LAB.

$N_A = 350$ CU. FT. AT 350°F

305
256
223
190

□ ⊗ ⊙ } Points calculated
△ × } by long method

DOME VOLUME IN UNITS OF 10^6 CU. FT.
(ea. div = 0.02 × 10^6 Cu. Ft.)
NOVEMBER 2, 1957

2.0   3.0   4.0   5.0   6.0   7.0   8.0   8.8

MH-9A8104

19

20

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