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THEORETICAL SPECIFIC IMPULSES OF LITHIUM-BASED PROPELLANT SYSTEMS IN NUCLEAR AND CHEMICAL ROCKETS

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THEORETICAL SPECIFIC IMPULSES OF LITHIUM-BASED PROPELLANT SYSTEMS IN NUCLEAR AND CHEMICAL ROCKETS

(Title Unclassified)

by

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ABSTRACT

The theoretical specific impulses obtainable with shifting equilibrium for various lithium-based propellant systems have been calculated on an IBM 704 computer. The following systems have been investigated:

1. Nuclearly heated lithium, with and without condensation of lithium.
2. Nuclearly heated lithium hydride, with and without condensation of lithium.
3. Nuclearly heated lithium with oxygen and water "chemical afterburning", with condensation of lithium oxide but no condensation of lithium.
4. Chemical rocket using lithium as the fuel and oxygen or water as the oxidizer.

The largest specific impulse at sea level (469 sec) was obtained in the nuclearly heated lithium hydride system with condensation of lithium.

Afterburning of lithium by oxygen raises the specific impulse above the specific impulse obtainable for lithium with no condensation at the same initial conditions. These specific impulses are in the range 370 to 427 sec.

The specific impulse of a chemical rocket using lithium as the fuel and oxygen as an oxidizer was lower than the values in the open literature. This lower specific impulse is due to the inclusion of new thermodynamic data for the lithium-oxygen system in the present calculations. Previous calculations considered gaseous lithium oxide to be stable at elevated temperatures, whereas the new data show that lithium oxide is almost completely dissociated into the elements at these temperatures.

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ACKNOWLEDGEMENTS

The code for solving chemical equilibrium problems by Brinkley's method was supplied by Wildon Fickett of LASL Group GMX-10. Its existence has permitted these calculations to be performed at an earlier date than otherwise would have been possible.

Discussions with T. P. Cotter of LASL Group N-5 were of assistance in formulating the thermodynamic development presented in the appendices.

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INTRODUCTION

At the beginning of 1958 LASL received a copy of a proposal[1] from the Lockheed Missile Systems Division to Wright Air Development Center. This proposal dealt with the substantial gains in the specific impulses of nuclear propellants which would be obtainable if advantage could be taken of some of the real gas characteristics of certain propellants, such as lithium hydride, beryllium hydride, or boron hydride. For example, if lithium hydride were used, the condensation of liquid lithium within the rocket nozzle would be capable of liberating several times the energy that would be available from the expansion of hydrogen from the same initial reactor temperature.

This proposal stated that a specific impulse of 720 sec could be obtained from lithium hydride if the initial temperature and pressure were 3500°R and 150 psi and if the final temperature were 520°R. Hand calculations, based on the enthalpy change of pure lithium for a similar expansion process, indicated that lithium should have a specific impulse of about 700 sec. Since lithium melts at an appreciably lower temperature than lithium hydride, it was decided that lithium should be of more practical interest than lithium hydride and that detailed specific impulse calculations should be carried out for lithium as a potential nuclear propellant.

Propellant calculations based upon shifting equilibrium with and without condensation of lithium were made for both lithium and lithium hydride gases. The expected specific impulses (700 and 720 sec) were not obtained because the exhaust gas temperatures were never lowered by the nozzle to 520°R.

The specific impulses obtainable by "afterburning" preheated lithium with liquid oxygen or water were calculated for varying ratios of lithium to oxidizer and at several combustion chamber pressures. This study of "afterburning" was undertaken with the belief that the specific impulse of this type of system would be increased over that of the pure lithium system because of the additional enthalpy of combustion. This additional enthalpy was *not* obtained from the fuel because, in the expansion of the combustion chamber gases to *reasonable* exhaust pressures, the exhaust gas temperatures were not low enough to make this additional enthalpy available within the nozzle.

Calculations of specific impulses for chemical rockets with lithium as a fuel and oxygen or water as the oxidizer were made because it was thought that the values in the open literature were incorrect. Recent thermodynamic data have shown that Li_2O dissociates into the elements at high temperatures. The results given here are based upon this fact, whereas previous values for the specific impulses of these systems were obtained on the basis of Li_2O being stable at high temperatures.

Details of the calculations and thermodynamic data used are given in the following sections.

THERMODYNAMIC DATA

The thermodynamic data used for the calculations presented here were obtained from the sources listed below.

Selected Values of Chemical Thermodynamic Properties, Series III (National Bureau of Standards)	Li(gas) O_2(gas) O (gas) H (gas)
Argonne National Laboratory Report ANL-5750	Li_2O(liquid)
T. B. Douglas, L. F. Epstein, J. L. Dever, and W. H. Howland; National Bureau of Standards Report 2879	Li(liquid)
L. Haar and A. S. Friedman, J. Chem. Phys. 23, 869 (1955)	H_2O(gas) OH (gas)
Personal communication from A. S. Friedman of National Bureau of Standards	H_2(gas)

Computed at LASL; spectroscopic constants from G. Herzberg, Molecular Spectra and Molecular Structure, Vol. I., D. Van Nostrand Co., Inc., N. Y., 1950	Li_2(gas) LiH(gas)

Li_2O was assumed to decompose into the elements at elevated temperatures as shown by L. Brewer and J. Margrave[2] and G. D. Blue and J. L. Margrave,[3] hence no lithium oxide gaseous species were considered in these calculations.

The thermodynamic data for each of the above listed species were handled in the following manner.

The enthalpy function, $(H - H_0^\circ)/RT$, and the heat capacity, C_p, each were fitted over the temperature range of interest by a least-squares quartic fit of the form

$$Y = a + bT + cT^2 + dT^3 + eT^4, \qquad (1)$$

where Y represents either the heat capacity or enthalpy and T represents the temperature in degrees Kelvin.

If the constants obtained from equation (1) for the heat capacity fit of any one species are used, the heat content, H_T, is then given by the expression

$$H_T = aT + \frac{bT^2}{2} + \frac{cT^3}{3} + \frac{dT^4}{4} + \frac{eT^5}{5} + H_0^\circ, \qquad (2)$$

where H_0° is the standard enthalpy of formation at 0°K.

The free energy functions, $-(F - H_0^\circ)/RT$, which were actually used in the equilibrium calculations were obtained for each of the molecules by the method of Fickett and Cowan.[4] In this method the coefficients from the least-squares fit of the enthalpy by equation (1) are substituted into the equation

[redacted]

$$-(F - H_0^\circ)/RT = a \ln T + bT + \frac{cT^2}{2} + \frac{dT^3}{3} + \frac{eT^4}{4} + k \qquad (3)$$

and the value of k is determined so that the free energy function evaluated from equation (3) agrees with the value of the free energy function obtained by statistical thermodynamic methods. The evaluation of k is carried out at even 100° temperature increments within the temperature interval of interest and the average value of the k's so determined is used for the free energy expression over the entire temperature interval. The value of k so determined is generally fairly constant.

The expression finally used for the evaluation of the free energy for the Brinkley method[5] of computing equilibrium compositions of a chemical system is

$$\frac{-F}{RT} = a \ln T + bT + \frac{cT^2}{2} + \frac{dT^3}{3} + \frac{eT^4}{4} + k - \frac{H_0^\circ}{RT} - \ln p, \qquad (4)$$

where H_0° is the standard heat of formation of the species at 0°K and p is the pressure of the system in atmospheres.

CALCULATION OF SPECIFIC IMPULSES

For calculation of specific impulses a general program, "Nozzle", has been coded for the IBM 704 computer. It has three parts, identified as "Nozzle 4", "Nozzle 5", and "Nozzle 6".

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The "4" code is used to generate input data for the "5" and "6" codes when they are used to study chemical rocket propellants or nuclearly heated propellants with chemical afterburning. "Nozzle 4" permits variations of the input weight ratio of fuel to oxidizer, choice of the fuel and oxidizer input temperatures, and choice of the chamber pressures; it will then compute the resulting chamber temperature for any given set of conditions.

"Nozzle 5" computes the specific impulse for a chemical system undergoing an isentropic expansion with the conditions of shifting equilibrium, whereas "Nozzle 6" does the same for the case of frozen equilibrium. The input data for both "5" and "6" are the chamber pressure, chamber temperature, the chemical species present, and the molecular weights of the elements present.

For a pure nuclear rocket (no combustion) direct use of "5" or "6" is possible as here the chamber temperature and pressure are chosen.

The limiting feature of the present program is the section which computes equilibrium composition at given conditions. This section is the same in all three codes, "4", "5", and "6". Systems of either one or two phases with as many as fourteen chemical species can be calculated now. The capacity can be extended to twenty species by increasing

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certain regions of the codes. An improved version for solving equilibrium compositions will be available soon and it will permit computations for systems of five distinct chemical phases and twenty-five chemical species.

This method of calculation of specific impulses will be described in a stepwise fashion following the logic of the IBM 704 programs. Only "Nozzles 4" and "5" will be explained here as none of the results presented later were for frozen equilibrium.

"Nozzle 4"

1. Calculates the equilibrium composition of the oxidizer at its input temperature and pressure, and the equilibrium composition of the fuel at its input temperature and pressure by the Brinkley[5] method.

2. Calculates the total initial enthalpy, H_i, for a given weight of oxidizer and fuel at their input thermodynamic states prior to reaction.

3. Computes the total enthalpy, H_1, of an equilibrium mixture of the chemical species resulting from the oxidizer-fuel reaction at a given chamber pressure and at a guessed chamber temperature, T_1.

4. Compares the initial enthalpy, H_i, with the first guessed enthalpy, H_1.

5. Repeats steps 3 and 4 for a second guessed temper-

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ature, T_2.

6. Uses a linear iterative procedure based upon the values of $H_i - H_1$, $H_i - H_2$, and T_1 and T_2 to converge upon a final chamber temperature, T_c, such that $H_{initial} - H_{final}$ equals zero.

7. Prints out the results of step 6 and then reads in new data for another problem.

"Nozzle 5"

1. Calculates the equilibrium composition of a given system at a given chamber pressure, P_c, and chamber temperature, T_c, by Brinkley's method.

2. Evaluates the total enthalpy, H_i, and the total entropy, S_i, at the conditions given in step 1.

3. Computes the equilibrium composition of the given chemical system at a given exhaust pressure, P_1, and a guessed temperature, T_1.

4. Computes the total entropy, S_1, at the conditions given in step 3 and compares this with the initial entropy, S_i.

5. Repeats step 3 at the same pressure, P_1, but with a second guessed temperature, T_2, and repeats step 4, using the new entropy value, S_2, for the comparison with S_i.

6. Uses a linear iterative procedure based upon the values of $S_i - S_1$, $S_i - S_2$, and T_1 and T_2 to converge upon a

[redacted]

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final temperature, T_e, such that $S_{initial} - S_{final}$ equals zero for the given pressure, P_1.

7. Uses the composition found in step 6 at T_e to evaluate the total enthalpy, H_e, at this exhaust temperature.

8. Calculates the total enthalpy change associated with the process of expansion from P_c to P_1 by subtraction, $H_{initial} - H_e = \Delta H$.

9. Multiplies the ΔH of step 8 by two, multiplies this by 4.184×10^{-7} to convert ΔH from calories to ergs, divides by the mass of the system, and takes the square root of this result to get the velocity in centimeters per second. Converts this velocity to feet per second and divides by the acceleration of gravity, which gives specific impulse, I_{sp}, in seconds as defined by

$$I_{sp} = v/g,$$

where

$v = \sqrt{2\ \Delta H/m}$,

ΔH = enthalpy change,

m = mass,

v = velocity,

g = acceleration of gravity.

10. Prints out results.

11. Changes the exhaust pressure, P_1, to a new value, P_2, and repeats steps 3 through 9. Continues this cycle for

[redacted]

a given number of exhaust pressures.

12. Reads in new input data for another system.

All the specific impulse calculations done with these codes were carried out at the following exhaust pressures:

$P_1 = 1.0$ atm,
$P_2 = 0.1$ atm,
$P_3 = 0.01$ atm,
$P_4 = 0.001$ atm.

At the time the lithium system study was started none of the above programs was available to make the calculations on the computer, so the lithium system with and without lithium condensation was formulated analytically and evaluated by numerical integration. When the codes became available, the lithium system without lithium condensation was recomputed. The results obtained from the computer with the "Nozzle 5" code compared favorably with the values obtained by numerical integration. The results obtained from the computer are reported here because they are more accurate.

Details of the analytical formulation of these two systems are given in Appendices A and B.

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RESULTS

Tables 1 through 8 give the specific impulses and initial conditions for the systems studied.

It will be noted that the temperatures reported in the tables have digits to the fourth decimal place. This feature is of significance in the computer calculations since the enthalpy and entropy, which are used for convergence criteria, are very steep functions of temperature in the region where the condensed phase is in equilibrium with the gas phase.

Some of the symbols used in the tables and their meanings are:

I_{sp} = specific impulse (sec),
P_e = exhaust pressure (atm),
T_e = exhaust temperature (°K),
P_c = chamber pressure (atm),
T_c = chamber temperature (°K).

Figures 1 through 5 graphically represent the data contained in these tables. The broken lines in the graphs

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indicate extrapolations of the calculated data, which are represented by solid lines. For some of the graphs the calculated data are rather meager and the extrapolations rather large; however, generally in these cases the systems gave results such that extensive calculations seemed unnecessary. The extrapolations were made by drawing analogies from the more complete systems. Primarily, they are useful to indicate what may be expected in the regions beyond those calculated.

Also one or two of the systems have only two or three points. These enable one to determine the magnitude of the changes to be expected in the specific impulse for given changes in chamber pressure, in input fuel temperatures, or in the oxidizer-to-fuel ratio.

DISCUSSION

Tables 1 and 2 and Figure 1 indicate the results obtained for the lithium system, with and without condensation of lithium.

The species considered in the two systems are lithium monomer and dimer in the case of no condensation, and lithium monomer and dimer and liquid lithium in the case of condensation.

With nuclear heating to 2773°K at a pressure of 75 atm

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and then expansion to 1 atm, the specific impulse of the lithium system with condensation is 433 sec. Decreases in the pressure result in a lowering of the specific impulse, e.g., 433 sec for 75 atm, 419 sec for 50 atm, and 390 sec for 25 atm.

The effect of a decrease in the initial temperature upon the lithium system without condensation gives a decrease in the specific impulse of about 3.6% for a decrease of 173°. One might expect an effect of about the same magnitude as a first approximation for the system with condensation.

The specific impulses for the lithium system without condensation for initial pressures of 25, 50, and 75 atm and the initial temperature of 2773°K are, respectively, 366, 381, and 387 sec.

Tables 3 and 4 and Figure 2 show the results obtained for the lithium hydride system, with and without condensation of lithium.

The species considered in the equilibrium are Li(gas), Li_2(gas), H(gas), H_2(gas), LiH(gas), and for the case of condensation, liquid lithium.

Specific impulses from 428 to 469 sec are attained in this system for a chamber temperature of 2773°K and chamber pressures from 25 to 75 atm.

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Figure 2 shows clearly that if condensation of lithium occurs upon expansion of the lithium hydride system, an increase in specific impulse over that given for the case of no condensation of lithium is obtained. This increase in specific impulse is negligible for the expansion from 25 atm to 1 atm, but becomes larger as the chamber pressure increases from 25 to 75 atm.

A comparison of the specific impulses for the lithium system without condensation and the lithium hydride system without condensation shows that the lithium hydride system has larger values than the lithium system, i.e., 428 sec compared with 366 sec at a pressure of 25 atm, 450 with 381 sec at 50 atm, and 460 with 387 sec at 75 atm. Similarly, a comparison of the specific impulses for the lithium system with condensation of liquid lithium and the lithium hydride system with condensation of liquid lithium shows that the lithium hydride system has larger values than the lithium system, i.e., 429 sec compared with 390 sec at a pressure of 25 atm, 455 sec with 419 sec at 50 atm, and 469 sec with 433 sec at 75 atm.

Therefore, the lithium hydride system can be expected to yield larger specific impulses than the lithium system regardless of whether or not liquid lithium condenses. The assumption of condensation of lithium seems to be very

[redacted]

reasonable for reasons which will be discussed later.

Even though the lithium hydride system gives larger specific impulses than the lithium system, because lithium melts at a much lower temperature than lithium hydride and therefore is easier to handle, the lithium system appears to be the more attractive of the two systems.

Table 5 and Figure 3 show the results obtained for the specific impulses for a system of lithium heated nuclearly and then reacted with oxygen.

In the computations of this system the species considered are Li(gas), Li_2(gas), O(gas), O_2(gas), and Li_2O(liquid).

The highest specific impulse computed (427 sec) was for the conditions of lithium at 2600°K and 50 atm reacted with oxygen at 50 atm and 300°K with the ratio of the number of moles of oxygen atoms to the number of moles of the lithium atoms as 0.1. The gain obtained in the specific impulse over the specific impulse for lithium at the same initial conditions and <u>no</u> condensation is about 16%, from 367 sec to 427 sec.

This gain in specific impulse by afterburning with oxygen appears to decrease as the initial conditions (both temperature and pressure) of the lithium are increased, e.g., at 2000°K and 25 atm the gain is 29%, from 294 to 371 sec; at 2300°K and 50 atm the gain is 21%, from 337 sec to about

[redacted]

410 sec. The numerical values used for these comparisons are taken from Table 1 for the lithium system and from Figure 3 for the lithium-oxygen system. There is a maximum in the curve of specific impulse versus oxidizer-to-fuel ratio. This maximum occurs near the ratio of 0.1.

By rough extrapolations and interpolation from the points available on Figure 3, one can say the following as first approximations. There is about 0.8% increase in specific impulse for each 100° rise in initial temperature of the lithium. The specific impulse increases by about 8.5% for each doubling of the initial pressure of the lithium.

Table 6 and Figure 4 give the results obtained for the specific impulses for a system of lithium heated nuclearly and then reacted with water.

The species considered in the equilibrium for this system are Li(gas), Li_2(gas), H(gas), H_2(gas), O(gas), O_2(gas), H_2O(gas), OH(gas), and Li_2O(liquid).

The highest specific impulse computed (386 sec) was for the conditions of lithium at 2600°K and 50 atm pressure reacted with water at 350°K and 50 atm and with the ratio of oxygen atoms to lithium atoms of about 0.12. The gain obtained in the specific impulse over the specific impulse for lithium at the same initial conditions and <u>no</u> condensation is about 5%, from 367 to 386 sec.

[redacted]

As in the case with oxygen afterburning, the gain in specific impulse due to afterburning with water decreases as the initial temperature and pressure of the lithium are increased, e.g., at 2000°K and 25 atm the gain is 13.5%, from 294 to 334 sec; at 2600°K and 50 atm the gain is 5%, from 367 to 386 sec. The numerical values used in these comparisons are taken from Table 1 for the lithium system and from Figure 4 for the lithium-water system. The maximum in the curve of specific impulse versus oxidizer-to-fuel ratio occurs at about 0.12. This maximum tends to shift with changes in initial conditions.

Extrapolation of the data in Figure 4 allows the estimation of the position of the specific impulse plot for the system with the lithium at 2600°K and 75 atm. This gives a maximum specific impulse of about 400 sec. Other extrapolations and interpolations of the data available will permit the following statements to be made as first approximations. The gain in specific impulse obtained for an initial temperature increase of 100° will be about 0.9%. The gain in specific impulse obtained by doubling the initial pressure will be about 8%.

The results of the calculations for chemical rockets (no preheating of the fuel) using lithium as the fuel and oxygen or water as the oxidizer are presented in Tables 7 and

8 and Figure 5.

The species considered in the lithium-oxygen system are Li(gas), Li_2(gas), O(gas), O_2(gas), and Li_2O(liquid).

The species considered for the lithium-water system are Li(gas), Li_2(gas), H(gas), H_2(gas), O(gas), O_2(gas), H_2O(gas), OH(gas), and Li_2O(liquid).

Figure 5 shows plainly the maximum in the curve of specific impulse versus oxidizer-to-fuel ratio for the water-lithium system. The maximum specific impulses attained here were 205, 223, and 233 sec, for initial pressures of 25, 50, and 75 atm, respectively, and the initial temperatures for the lithium of 453°K and for the water of 350°K. The optimum oxidizer-to-fuel ratio is about 0.475.

Figure 5 also shows specific impulses for the oxygen-lithium system. Maximum values that are computed here are approximately 233, 255, and 265 sec for the corresponding initial pressures of 25, 50, and 75 atm and initial temperature of 453°K for the lithium and 90°K for the oxygen. These are assumed to be the values at an oxidizer-to-fuel ratio of about 0.3. The data obtained are extrapolated to this composition. Only for one curve was this point (at the ratio of 0.3) actually computed, and it seems to indicate that the curve is beginning to peak at this ratio. Therefore, these reported values may be a little low.

[redacted]

The specific impulse listed in the open literature for a lithium-oxygen chemical rocket is about 315 sec.[6,7] It is thought that this value is overly optimistic in the light of recently reported thermodynamic data for the lithium oxides. As stated previously, the calculations presented in this study are all based upon the fact that lithium oxide species in the vapor above lithium oxide solid have been found to be present in very minor concentrations at temperatures of 1400°K, the principal species in the vapor being the monomers and dimers of the elements. All previous computations on these systems that are known to the authors considered the oxides stable at the prevailing high temperatures. These assumptions probably account for the discrepancy in specific impulses.

The values for specific impulse discussed here are based upon expansion from the chamber pressures cited to 1 atm. If the expansion process could be carried out to lower exhaust pressures, e.g., the ambient pressures encountered by a vehicle in flight, significant gains in specific impulse could be obtained.

In all the calculations except those for lithium without condensation and lithium hydride without condensation, some condensation is considered. The specific impulses are increased due to this condensation. It is not possible to

[redacted]

state whether or not in practice the condensation occurs and particularly whether or not the extent of condensation that may occur corresponds to the assumed equilibrium values of condensate necessary for the calculations. Hence, if any of these systems are to be considered for use, experiments involving actual thrust measurements should be made.

Since the rate of condensation from a vapor is dependent upon the rate of nucleation, the exposure of the propellants to radiation should be of considerable assistance in establishing rapid equilibrium between the vapor and condensate.

In the studies of "afterburning" lithium with oxygen or water, only one condensed phase (liquid lithium oxide) was considered because the available equilibrium code can handle only a two-phase system (gas and one condensed phase). Theoretically one would expect some condensation of liquid lithium as well as the lithium oxide; consequently, the specific impulses presented for both the oxygen and water afterburning cases would be low. The magnitude of these differences cannot be estimated without solutions of the chemical equilibria existing in these systems.

The lithium hydride system with condensation of liquid lithium offers the highest specific impulse of all the systems presented here. The problems of handling lithium

[redacted]

hydride as a fuel are quite formidable. It has a high melting point, 680°C, and would probably have to be handled as a solid in powder form.

The lithium system with condensation of liquid lithium offers the second highest set of specific impulses. The melting point of lithium is 186°C so it could probably be handled as a liquid. The problems of storing and pumping liquid lithium have already received considerable attention.[8] Although the specific impulse of this system is not competitive with those of other fuels which present many handling problems, for some missions this loss in specific impulse conceivably could be out-weighed by the advantages of "readiness" and easier engineering.

[redacted]

TABLE 1

LITHIUM WITH NO CONDENSATION

		P_e = 1 atm		P_e = 0.1 atm		P_e = 0.01 atm		P_e = 0.001 atm	
T_c (°K)	P_c (atm)	I_{sp} (sec)	T_e (°K)	I_{sp} (sec)	T_e (°K)	I_{sp} (sec)	T_e (°K)	I_{sp} (sec)	T_e (°K)
2773	25	366	1405.3	430	1050.6	469	837.1	497	688
2773	50	381	1303.9	435	990.2	469	788.8	493	637.9
2773	75	387	1245.6	435	950.4	467	753.0	489	593
2000	25	294	1197.8	351	915.0	387	717.8	411	539
2000	50	303	1086.3	350	820.2	380	600.7		
2300	50	337	1191.8	387	910.3	420	712.9	442	531
2600	50	367	1268.6	419	966.6	453	768.1	476	613

TABLE 2

LITHIUM WITH CONDENSATION

		P_e = 1 atm		P_e = 0.1 atm		P_e = 0.01 atm		P_e = 0.001 atm	
T_c (°K)	P_c (atm)	I_{sp} (sec)	T_e (°K)	I_{sp} (sec)	T_e (°K)	I_{sp} (sec)	T_e (°K)	I_{sp} (sec)	T_e (°K)
2773	25	390	1599.8	474	1332	530	1141	572	1037
2773	50	419	1599.8	489	1332	537	1141	574	1037
2773	75	433	1599.8	495	1332	539	1141	573	1037

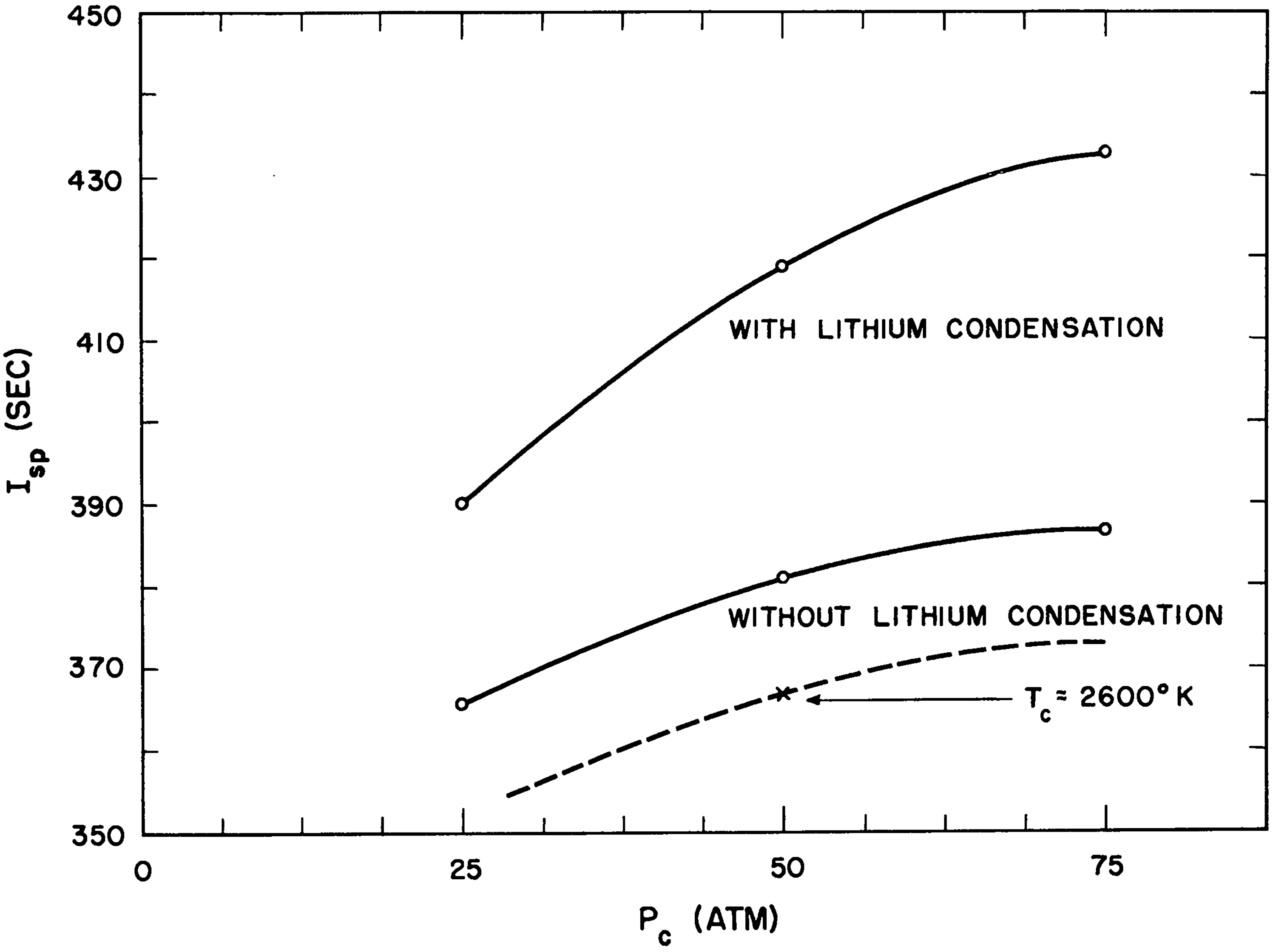

Fig. 1 Specific impulse versus chamber pressure for lithium with nuclear heating to 2773°K. P_e = 1 atm.

TABLE 3

LITHIUM HYDRIDE WITH NO CONDENSATION OF LITHIUM

		P_e = 1 atm		P_e = 0.1 atm		P_e = 0.01 atm	
T_c (°K)	P_c (atm)	I_{sp} (sec)	T_e (°K)	I_{sp} (sec)	T_e (°K)	I_{sp} (sec)	T_e (°K)
2773	25	428	1361.0	504	982.6	550	752.2
2773	50	450	1242.7	514	909.6		
2773	75	460	1178.5	518	862.2		

TABLE 4

LITHIUM HYDRIDE WITH CONDENSATION OF LITHIUM

		P_e = 1 atm		P_e = 0.1 atm		P_e = 0.01 atm		P_e = 0.001 atm	
T_c (°K)	P_c (atm)	I_{sp} (sec)	T_e (°K)	I_{sp} (sec)	T_e (°K)	I_{sp} (sec)	T_e (°K)	I_{sp} (sec)	T_e (°K)
2773	25	429	1453.0	513	1216.9	570	1046.4	611	917.5
2773	50	455	1445.9	530	1211.4	581	1041.9	619	913.5
2773	75	469	1441.0	538	1207.6	587	1038.8		

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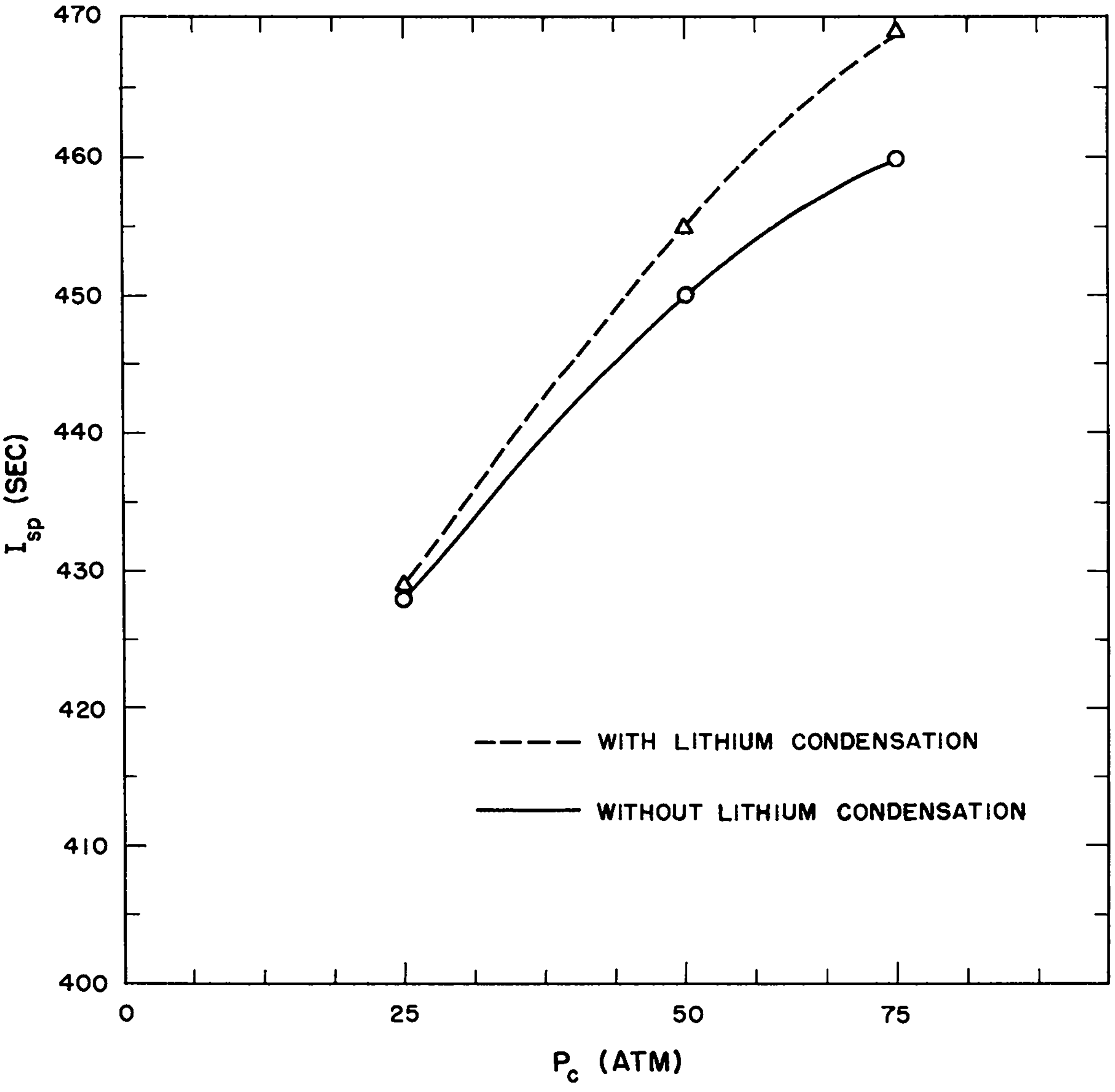

Fig. 2 Specific impulse versus chamber pressure for lithium hydride with nuclear heating to 2773°K. P_e = 1 atm.

TABLE 5

LITHIUM AFTERBURNED WITH OXYGEN*

Moles of O	Input T of Lithium (°K)	P_c (atm)	T_c (°K)	Specific Impulse (sec)			
				P_e= 1 atm	P_e= 0.1 atm	P_e= 0.01 atm	P_e= 0.001 atm
0.095	2000	25	3192.3753	314	388	439	477
0.090	2000	25	3192.0978	317	392	443	482
0.085	2000	25	3191.6029	320	396	448	486
0.080	2000	25	3190.8572	323	400	452	491
0.075	2000	25	3189.8200	327	404	457	496
0.070	2000	25	3188.4402	330	409	462	502
0.060	2000	25	3184.3753	338	418	473	514
0.050	2000	25	3177.8594	347	429	485	526
0.040	2000	25	3167.3488	356	440	498	540
0.030	2000	25	3149.2388	366	452	502	532
0.020	2000	25	3110.9364	370	438		
0.090	2000	50	3380.9215	344	410	456	491
0.070	2000	50	3376.4022	358	427	475	512
0.070	2300	50	3376.9463	367	437	486	523
0.070	2600	50	3377.3637	375	446	496	534
0.060	2600	50	3373.4087	384	457	508	547
0.040	2600	50	3357.6031	405	482	536	576
0.030	2600	50	3342.0952	417	496	545	574
0.020	2600	50	3314.1551	427	491	527	552
0.010	2600	50	3241.6704	407	462	497	521

*Input temperature of O_2 = 300°K; moles of lithium = 0.2.

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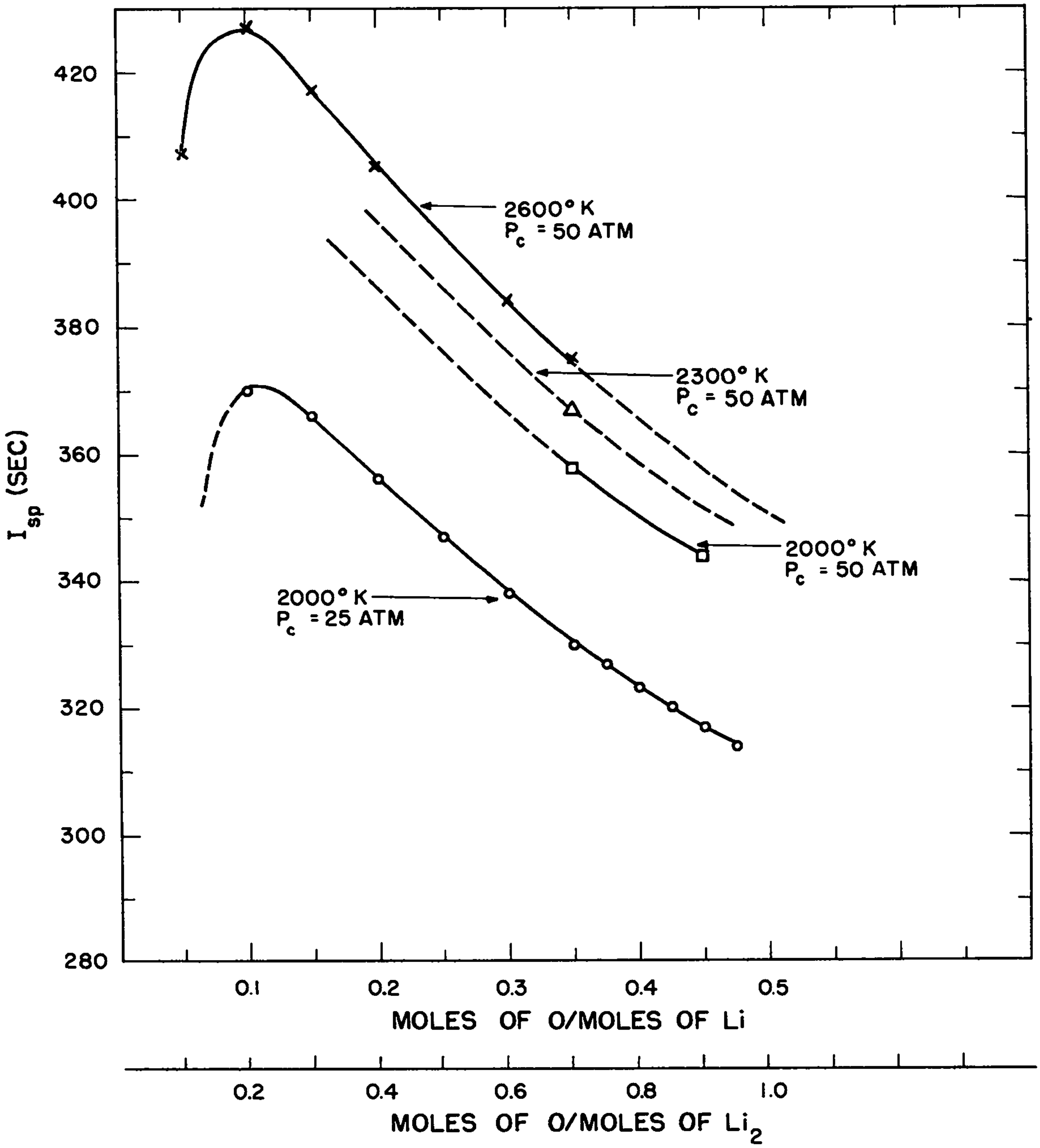

Fig. 3 Specific impulse versus oxidizer-to-fuel ratio for preheated lithium and oxygen at 300°K. P_e = 1 atm.

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TABLE 6

LITHIUM AFTERBURNED WITH WATER*

Moles of H_2O	Input T of Lithium (°K)	P_c (atm)	T_c (°K)	Specific Impulse (sec)			
				P_e = 1 atm	P_e = 0.1 atm	P_e = 0.01 atm	P_e = 0.001 atm
0.10	2000	25	2700.0414	289	359	408	444
0.09	2000	25	2707.0401	294	366	415	452
0.08	2000	25	2712.4279	300	372	422	460
0.10	2000	50	2818.4314	313	374	418	452
0.09	2000	50	2825.9358	318	381	425	459
0.08	2000	50	2831.2800	324	388	433	467
0.10	2000	75	2891.7121	325	383	424	456
0.09	2000	75	2899.6332	330	389	431	464
0.08	2000	75	2905.0105	336	396	439	472
0.10	2300	50	2852.8800	321	384	429	463
0.09	2300	50	2862.0205	327	391	436	471
0.08	2300	50	2869.6800	333	398	444	479
0.10	2600	50	2884.0800	328	392	438	472
0.09	2600	50	2894.8436	334	399	446	481
0.08	2600	50	2904.7200	341	407	454	490
0.06	2000	25	2715.6851	313	388	439	477
0.04	2000	25	2697.8483	327	403	447	477
0.02	2000	25	2595.1750	327	389	427	454
0.01	2000	25	2358.8437	248	313	352	379
0.08	2600	50	2904.2685	341	407	454	490
0.04	2600	50	2924.9232	375	445	488	517
0.02	2600	50	2897.8150	386	443	479	504

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*Input temperature of H_2O = 350°K; moles of lithium = 0.2.

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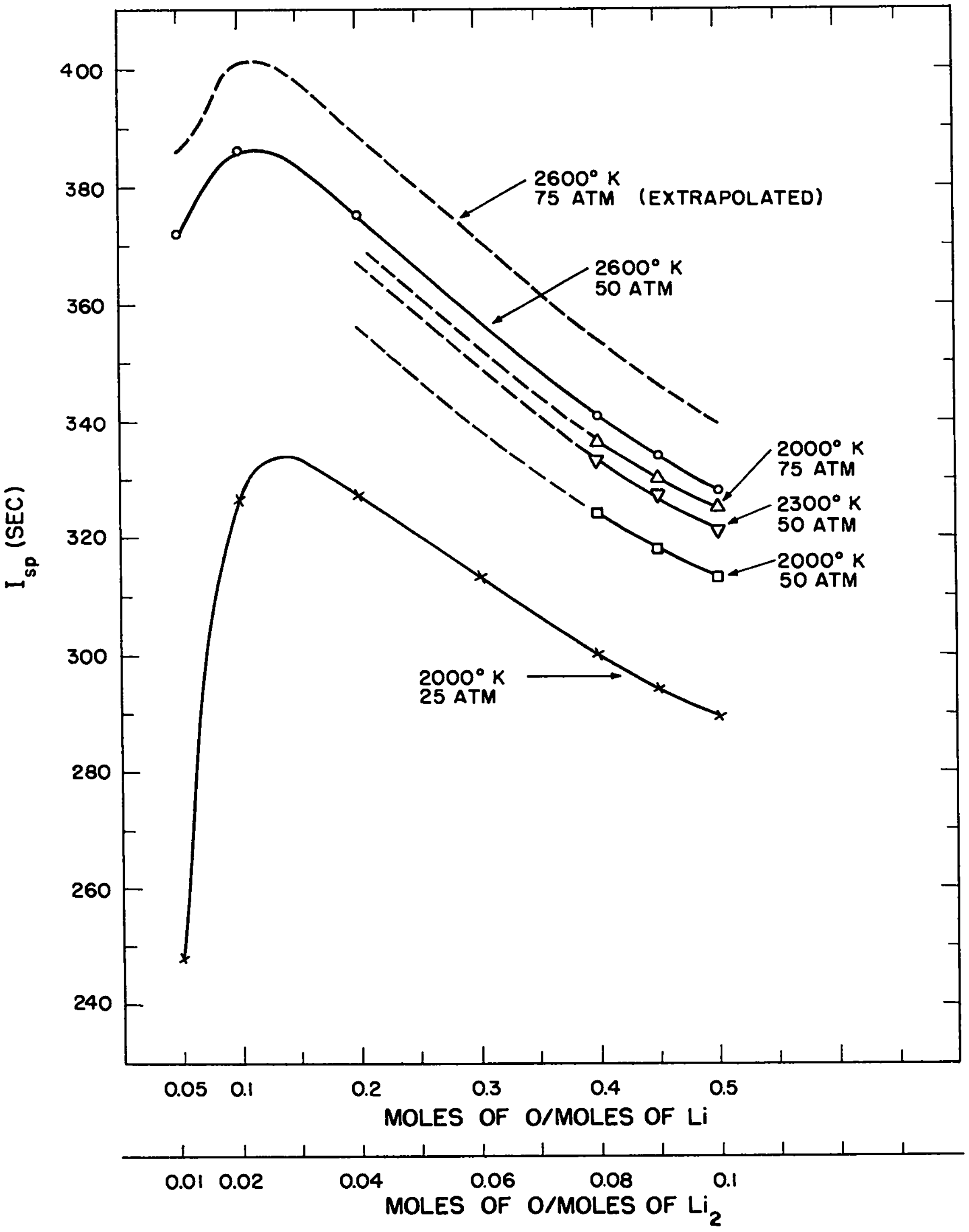

Fig. 4 Specific impulse versus oxidizer-to-fuel ratio for preheated lithium and water at 350°K. P_e = 1 atm.

TABLE 7

LITHIUM-OXYGEN CHEMICAL ROCKET*

Moles of O	P_c (atm)	T_c (°K)	Specific Impulse (sec) P_e = 1 atm	P_e = 0.1 atm	P_e = 0.01 atm	P_e = 0.001 atm
0.095	25	3192.0822	225	281	321	352
0.090	25	3190.7888	225	282	322	353
0.085	25	3188.2707	227	284	324	355
0.080	25	3184.0404	228	286	326	357
0.075	25	3177.2713	230	287	328	359
0.070	25	3166.3942	231	289		
0.095	50	3380.8968	244	295	332	360
0.090	50	3379.2849	246	297	333	362
0.085	50	3376.1281	247	298	335	364
0.080	50	3370.7819	249	300	338	366
0.075	50	3362.1276	250	302	340	369
0.070	50	3347.9603	252	304	342	371
0.060	50	3267.5999	254	306	342	369
0.095	75	3501.5426	255	303	338	365
0.090	75	3499.6880	257	304	340	367
0.085	75	3496.0416	258	306	342	369
0.080	75	3489.8320	259	308	344	372
0.075	75	3479.6981	261	310	346	374
0.070	75	3462.8921	263	312	348	376

*Input temperature of O_2 = 90°K, of lithium = 453°K; moles of lithium = 0.2.

TABLE 8

LITHIUM-WATER CHEMICAL ROCKET*

Moles of H_2O	P_c (atm)	T_c (°K)	Specific Impulse (sec) P_e = 1 atm	P_e = 0.1 atm	P_e = 0.01 atm	P_e = 0.001 atm
0.10	25	2256.1406	204	256	294	323
0.09	25	2213.2427	204	256	293	320
0.08	25	1990.3200	198	247	280	304
0.10	50	2323.1199	222	270	304	332
0.09	50	2266.5234	222	269	302	327
0.08	50	2014.2400	214	258	288	310
0.10	75	2361.0530	232	277	310	336
0.09	75	2294.0917	232	276	307	331
0.08	75	2028.3188	223	264	292	314

*Input temperature of H_2O = 350°K, of lithium = 453°K; moles of lithium = 0.2.

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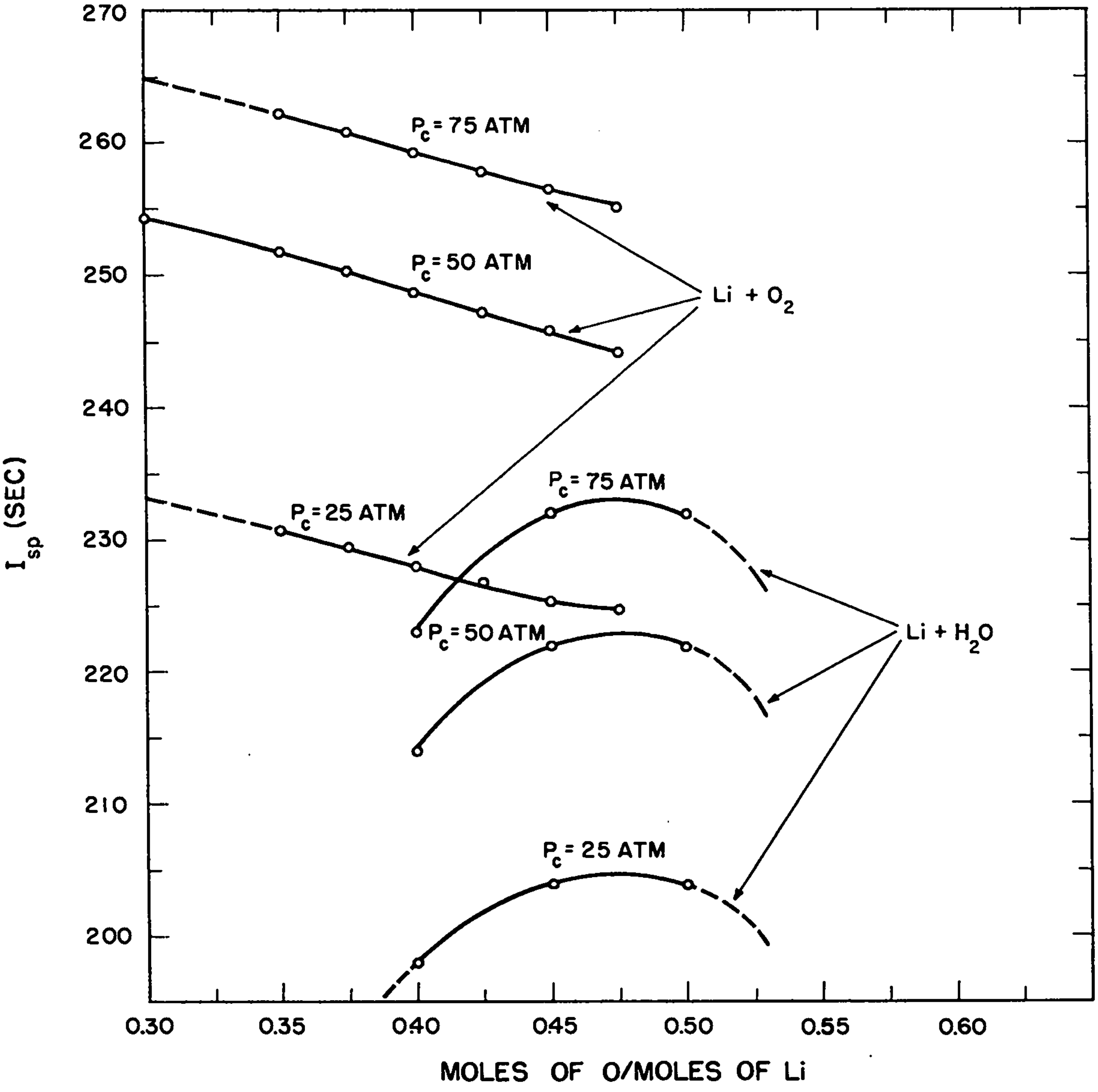

Fig. 5 Specific impulse versus oxidizer-to-fuel ratio for chemical rockets of the lithium-oxygen and lithium-water types. P_e = 1 atm. Input temperatures were: Li, 453°K; O_2, 90°K; H_2O, 350°K.

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Appendix A

EXPANSION OF A DISSOCIATING GAS

For an adiabatic expansion of an ideal gas mixture,

$$dE = -P\ dV, \tag{A.1}$$

and by substitution into equation (A.2),

$$dH = dE + P\ dV + V\ dP, \tag{A.2}$$

there results

$$\frac{dH}{dP} = V = \frac{1}{\rho}\ , \tag{A.3}$$

where ρ = density of the gas mixture. Also,

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT\ . \tag{A.4}$$

From equations (A.3) and (A.4),

$$\frac{dT}{dP} = \frac{(1/\rho) - (\partial H/\partial P)_T}{(\partial H/\partial T)_P}\ . \tag{A.5}$$

For a gas which consists of monomer and dimer the equilibrium concentrations can be expressed as follows:

$$\underset{(1 - \alpha)}{A_2} \rightleftharpoons \underset{(2\alpha)}{2A}, \tag{A.6}$$

where α is the fraction of originally undissociated A_2 which dissociates to form A.

Therefore if one mole of A_2 were present originally, upon attainment of equilibrium, the following expression holds:

$$H = 2\alpha\, H_1 + (1 - \alpha)\, H_2 \,, \tag{A.7}$$

where

H_1 = enthalpy of monomer,

H_2 = enthalpy of dimer.

Therefore

$$\left(\frac{\partial H}{\partial P}\right)_T = 2\alpha\left(\frac{\partial H_1}{\partial P}\right)_T + 2H_1\left(\frac{\partial \alpha}{\partial P}\right)_T + (1 - \alpha)\left(\frac{\partial H_2}{\partial P}\right)_T - H_2\left(\frac{\partial \alpha}{\partial P}\right)_T \,, \tag{A.8}$$

and if the gases are assumed to be ideal,

$$\left(\frac{\partial H_i}{\partial P}\right)_T = 0.$$

Therefore

$$\left(\frac{\partial H}{\partial P}\right)_T = (2H_1 - H_2)\left(\frac{\partial \alpha}{\partial P}\right)_T \,. \tag{A.9}$$

Also from equation (A.7),

$$\left(\frac{\partial H}{\partial T}\right)_P = 2\alpha\left(\frac{\partial H_1}{\partial T}\right)_P + 2H_1\left(\frac{\partial \alpha}{\partial T}\right)_P + (1 - \alpha)\left(\frac{\partial H_2}{\partial T}\right)_P - H_2\left(\frac{\partial \alpha}{\partial T}\right)_P \tag{A.10}$$

or

$$\left(\frac{\partial H}{\partial T}\right)_P = 2\alpha\, C_{P_1} + (1 - \alpha)\, C_{P_2} + (2H_1 - H_2)\left(\frac{\partial \alpha}{\partial T}\right)_P \,. \tag{A.11}$$

From equation (A.6) we can write

$$\alpha = \left(\frac{K_p}{4P + K_p}\right)^{1/2} , \qquad \text{(A.12)}$$

where K_p is the equilibrium constant in terms of partial pressures and P is the total pressure. Therefore

$$\left(\frac{\partial\alpha}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(\frac{K_p}{4P + K_p}\right)^{1/2} = \frac{-2\alpha}{K_p + 4P} \qquad \text{(A.13)}$$

and

$$\left(\frac{\partial\alpha}{\partial T}\right)_p = \frac{\partial}{\partial T}\left(\frac{K_p}{4P + K_p}\right)^{1/2} = \left(\frac{2\alpha P}{K_p + 4P}\right)\frac{\Delta H_d^\circ}{RT^2} . \qquad \text{(A.14)}$$

So equations (A.9) and (A.11) become

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{-(2H_1 - H_2)2\alpha}{(K_p + 4P)} , \qquad \text{(A.15)}$$

and

$$\left(\frac{\partial H}{\partial T}\right)_p = 2\alpha\, C_{p_1} + (1 - \alpha)C_{p_2} + \frac{(2H_1 - H_2)2\alpha P\, \Delta H_d^\circ}{(K_p + 4P)RT^2} . \qquad \text{(A.16)}$$

Also from the ideal gas law

$$V = \frac{1}{\rho} = \frac{nRT}{P} = \frac{(1 + \alpha)RT}{P} . \qquad \text{(A.17)}$$

Therefore substitution of equations (A.17), (A.16), and (A.15) into (A.5) yields

$$\frac{dT}{dP} = \frac{\dfrac{(1 + \alpha)RT}{P} + \dfrac{2\alpha(2H_1 - H_2)}{(K_p + 4P)}}{2\alpha\, C_{p_1} + (1 - \alpha)C_{p_2} + \dfrac{2(2H_1 - H_2)P\alpha\, \Delta H_d^\circ}{(K_p + 4P)RT^2}} . \qquad \text{(A.18)}$$

Rearrangement gives

$$\frac{dT}{dP} = \frac{\left\{(K_p + 4P) + \sqrt{K_p(K_p + 4P)}\right\}\frac{RT}{P} + 2\alpha(2H_1 - H_2)}{(K_p + 4P)\left[2\alpha\ C_{p_1} + (1 - \alpha)C_{p_2}\right] + \dfrac{2\alpha P(2H_1 - H_2)\Delta H^\circ_d}{RT^2}} \tag{A.19}$$

For calculations of specific impulses of lithium gas without condensation, equation (A.19) was used. With starting conditions of temperature equal to 2773°K and pressure equal to 25 atm equation (A.19) was numerically integrated stepwise using the Runge-Kutta method down to pressures of 1, 0.1, and 0.01 atm. The enthalpy changes from the initial conditions to the various chosen exhaust pressure conditions were then used to calculate the specific impulses.

In order to evaluate the integration of equation (A.19), the equilibrium constant, K_p, and degree of dissociation, α, must be known at the chosen steps of P and T. These were obtained by using an IBM 704 program which solved the equilibrium of $Li_2 \rightleftharpoons 2Li$ for α over a chosen range of temperature and pressure, and then using the relation given below to evaluate K_p from α.

$$K_p = \frac{4\alpha^2 P}{(1 - \alpha^2)} \ . \tag{A.20}$$

Although the above method was used to get some specific impulses for the lithium system without condensation of

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lithium, the values reported here were obtained from the "Nozzle 5" program, as these are assumed to be more accurate. The results from both methods were about the same; those obtained by the Runge-Kutta integration were about 1.5% higher.

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Appendix B

LITHIUM GAS WITH CONDENSATION OF LITHIUM

In order to calculate the specific impulse resulting from the expansion of lithium gas with condensation of lithium present, it is necessary to have some way of evaluating the amount of lithium which has condensed in order to compute the total enthalpy change involved in the process.

Consider a system composed of a single chemical element which can exist in the gas phase as a monomer, A_1, and as a dimer, A_2, and in the condensed phase as a monomer, A(c). The molecular weights of the monomer and dimer are M_1 and M_2, respectively.

Two simultaneous equilibria exist within the system, namely,

$$A(c) \rightleftharpoons A_2(g) + A_1(g) \qquad \text{(B.1)}$$

and

$$A_2(g) \rightleftharpoons 2A_1(g) \ . \qquad \text{(B.2)}$$

The first equilibrium must satisfy the vapor pressure curve of the system

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$$\frac{dP}{dT} = \frac{P\Delta H_v}{RT^2} , \tag{B.3}$$

where

P = total vapor pressure = $p_{A_2} + p_{A_1}$,

T = absolute temperature,

R = gas constant,

ΔH_v = heat of vaporization of the condensed phase.

The second equilibrium satisfies the following relation:

$$K_p = \frac{p_{A_1}^2}{p_{A_2}} . \tag{B.4}$$

If one designates by α the fraction of originally undissociated A_2 which has dissociated into A_1, then for 1 mole of A_2:

$$p_{A_2} = (1 - \alpha)P, \tag{B.5}$$

$$p_{A_1} = 2\alpha P, \tag{B.6}$$

where P equals the total pressure. Therefore

$$K_p = \frac{4\alpha^2}{(1 - \alpha^2)} P . \tag{B.7}$$

The amounts of A_1, A_2, and A(c) can be represented by weight fractions, f_i, with the results

$$f_1 + f_2 + f_3 = 1, \tag{B.8}$$

$$\frac{f_1}{f_2} = \frac{2\alpha M_1}{(1-\alpha)M_2} = \frac{2\alpha M_1}{(1-\alpha)2M_1} = \frac{\alpha}{1-\alpha} , \qquad \text{(B.9)}$$

$$f_1 = \alpha(1 - f_3) , \qquad \text{(B.10)}$$

$$f_2 = (1 - \alpha)(1 - f_3) . \qquad \text{(B.11)}$$

For a system with a total mass of 1 gm the enthalpy is the sum of the products of the weight fractions and the enthalpy per gram of the corresponding species is

$$H = f_1H_1 + f_2H_2 + f_3H_3 . \qquad \text{(B.12)}$$

The thermodynamic functions of the system of A(c), A_2, and A_1 are uniquely specified by two variables, f_3, and either the temperature, T, or the pressure, P, as long as there is some condensed phase present. Thus, one can write

$$H = H(f_3, T) . \qquad \text{(B.13)}$$

For any change in the system

$$dH = T\,dS + V\,dP . \qquad \text{(B.14)}$$

If the change is isentropic, equation (B.14) becomes

$$dH = V\,dP . \qquad \text{(B.15)}$$

Also, from equation (B.12)

$$dH = \left(\frac{\partial H}{\partial T}\right) dT + \left(\frac{\partial H}{\partial f_3}\right) df_3 . \qquad \text{(B.16)}$$

Combining equations (B.15) and (B.16), one gets

$$dH = V\ dP = \left(\frac{\partial H}{\partial T}\right) dT + \left(\frac{\partial H}{\partial f_3}\right) df_3\ , \qquad (B.17)$$

and

$$\frac{dH}{dP} = V = \left(\frac{\partial H}{\partial T}\right) dT + \left(\frac{\partial H}{\partial f_3}\right) df_3\ . \qquad (B.18)$$

For the isentropic expansion of this system, the change in weight fraction of the condensed phase with a change in pressure can be expressed as

$$\frac{df_3}{dP} = \frac{V - (\partial H/\partial T)(dT/dP)}{(\partial H/\partial f_3)}\ . \qquad (B.19)$$

The volume, V, of the system is equal to

$$V = \frac{f_1RT}{M_1p_1} + \frac{f_2RT}{M_2p_2} + \frac{f_3}{\rho_3}\ , \qquad (B.20)$$

where

p_1 = partial pressure of A_i in the gas phase,

ρ_3 = density of A(c).

If one neglects the volume contribution of A(c), lets $M_2 = 2M_1$, and uses equation (B.9), equation (B.20) becomes

$$V = \frac{(1 + \alpha)(1 - f_3)RT}{M_1P}\ , \qquad (B.21)$$

where

P = total pressure of the system.

Now equation (B.12) can be written as

$$H = \alpha(1 - f_3)H_1 + (1 - \alpha)(1 - f_3)H_2 + f_3H_3\ . \qquad (B.22)$$

Substitution of (B.22) and (B.21) into (B.19) gives

$$\frac{df_3}{dP} = \frac{\dfrac{(1 + \alpha)(1 - f_3)RT}{M_1P}}{\dfrac{\partial}{\partial f_3}\left[\alpha(1 - f_3)H_1 + (1 - \alpha)(1 - f_3)H_2 + f_3H_3\right]}$$

$$- \frac{\dfrac{\partial}{\partial T}\left[\alpha(1 - f_3)H_1 + (1 - \alpha)(1 - f_3)H_2 + f_3H_3\right]\dfrac{dT}{dP}}{\dfrac{\partial}{\partial f_3}\left[\alpha(1 - f_3)H_1 + (1 - \alpha)(1 - f_3)H_2 + f_3H_3\right]} . \qquad \text{(B.23)}$$

Now

$$\frac{\partial H}{\partial T} = \alpha(1 - f_3)\frac{\partial H_1}{\partial T} + (1 - \alpha)(1 - f_3)\frac{\partial H_2}{\partial T} + f_3\frac{\partial H_3}{\partial T}$$
$$+ (1 - f_3)(H_1 - H_2)\frac{\partial \alpha}{\partial T} , \qquad \text{(B.24)}$$

$$\frac{\partial H}{\partial f_3} = - \alpha H_1 - (1 - \alpha)H_2 + H_3 , \qquad \text{(B.25)}$$

and

$$\frac{\partial \alpha}{\partial T} = \frac{\partial}{\partial T}\left(\frac{K_p}{K_p + 4P}\right)^{1/2} = \frac{2\alpha P \, \Delta H_d^\circ}{(K_p + 4P)RT^2} , \qquad \text{(B.26)}$$

where

ΔH_d° = heat of dissociation of A_2 into $2A_1$,

K_p = equilibrium constant of the dissociation reaction.

Therefore, substitution of equations (B.26), (B.25), (B.24), and (B.3) into equation (B.23) yields

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$$\frac{df_3}{dP} = \frac{\dfrac{(1+\alpha)(1-f_3)RT}{M_1P}}{H_3 - H_2 - \alpha(H_1 - H_2)}$$

$$- \frac{\left[\alpha(1-f_3)C_{p_1} + (1-\alpha)(1-f_3)C_{p_2} + f_3C_{p_3}\right]\dfrac{RT^2}{P\Delta H_v}}{H_3 - H_2 - \alpha(H_1 - H_2)}$$

$$+ \frac{\left[(1-f_3)(H_1 - H_2)\,\dfrac{2\alpha P\ \Delta H^\circ_d}{(K_p + 4P)RT^2}\right]\dfrac{RT^2}{P\Delta H_v}}{H_3 - H_2 - \alpha(H_1 - H_2)} . \qquad (B.27)$$

To convert the H_i and C_{p_i} terms from enthalpy and heat capacity based upon 1 gm into the molar values, substitute the following:

$$H_1 \longrightarrow 2H_1/14\ ,$$

$$H_2 \longrightarrow H_2/14\ ,$$

$$H_3 \longrightarrow 2H_3/14\ ,$$

and substitute similarly for the C_{p_i} terms. After these substitutions and rearrangement the result is

$$\frac{df_3}{dP} = \frac{\dfrac{2(1 + \alpha)(1 - f_3)RT}{P}}{2H_3 - H_2 - \alpha(2H_1 - H_2)}$$

$$- \frac{\left[2\alpha(1 - f_3)C_{p_1} + (1 - \alpha)(1 - f_3)C_{p_2} + 2f_3C_{p_3}\right]\dfrac{RT^2}{P\Delta H_v}}{2H_3 - H_2 - \alpha(2H_1 - H_2)}$$

$$+ \frac{\dfrac{(1 - f_3)(2H_1 - H_2)2\alpha\ \Delta H_d^\circ}{(K_p + 4P)\ \Delta H_v}}{2H_3 - H_2 - \alpha(2H_1 - H_2)} . \qquad \text{(B.28)}$$

To calculate the specific impulse of the lithium system with condensation of liquid lithium, it is necessary to have enthalpy values of the system at the initial chamber conditions and at the chosen exhaust pressure. The initial enthalpy is obtained from the equilibrium composition of Li_2 (gas) and Li(gas) at the initial conditions. The enthalpy at a given exhaust pressure can be calculated if the amount of lithium which has condensed, and the temperature at the exhaust pressure, are known.

When lithium gas is expanded isentropically, the pressure-temperature curve will be crossed by the vapor pressure-temperature curve which presides when liquid lithium is present. The point at which the intersection occurs will be

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the pressure and temperature at which liquid lithium starts to form. Therefore, starting with lithium gas and allowing it to expand, the pressure-temperature relation for the system will follow the adiabat until it meets the point of intersection with the vapor pressure curve; from this point on it will follow the vapor pressure curve.

In the calculation of the specific impulse of the condensing system, one uses equation (B.28) and integrates it numerically by the method of Runge-Kutta to get the weight fraction, f_3, of the condensed phase. This integration is carried out in a stepwise fashion. The starting limit is the temperature and pressure where the adiabat and vapor pressure curves cross and it is assumed that initially f_3 is zero at this point. Integrating stepwise, f_3 is obtained for each chosen pressure step. When the integration steps have proceeded to the desired exhaust pressure, the corresponding enthalpies are calculated using the corresponding temperatures and equation (B.22). Subtraction of this exhaust enthalpy from the initial enthalpy then gives the change in enthalpy, which in turn allows calculation of the specific impulse.