AD-750 423

THE HETEROGENEOUS DECOMPOSITION OF HYDRAZINE: PART 5. THE KINETICS OF THE DECOMPOSITION OF LIQUID HYDRAZINE ON A SUPPORTED RUTHENIUM CATALYST

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January 1972

AD750423

UDC 546.171.5: 542.924.2

ROCKET PROPULSION ESTABLISHMENT
WESTCOTT

Technical Report No. 72/1
January 1972

THE HETEROGENEOUS DECOMPOSITION OF HYDRAZINE
PART 5. THE KINETICS OF THE DECOMPOSITION OF LIQUID HYDRAZINE ON A SUPPORTED RUTHENIUM CATALYST

by

C. F. Sayer

SUMMARY

The heterogeneous decomposition of liquid hydrazine on a supported ruthenium catalyst is a complex reaction. The kinetics have been analysed in terms of two simultaneous reactions:

$$(1) \quad 3N_2H_4 \rightarrow N_2 + 4NH_3$$

$$(2) \quad 2N_2H_4 \rightarrow N_2 + H_2 + 2NH_3 \quad .$$

Both reactions are first order with respect to hydrazine concentration (c). The rate equation of reaction (1) is

$$v_1 = 8.7 \times 10^3 \, e^{-54,400/8.314T} \times c \text{ mole } (N_2) \text{ gm}^{-1} \text{ sec}^{-1} \quad ,$$

and that of reaction (2) is

$$v_2 = 3.0 \, e^{-34,100/8.314T} \times c \text{ mole } (H_2 + N_2) \text{ gm}^{-1} \text{ sec}^{-1} \quad .$$

It is suggested that reaction (1) occurs when hydrazine is associatively adsorbed on the catalyst but that when it is dissociatively adsorbed reaction (2) occurs.

CONTENTS

1 INTRODUCTION

A study of the kinetics of liquid hydrazine decomposition on a supported iridium catalyst (the Shell 405 catalyst)[1] proved the reaction rate to be a linear function of the hydrazine concentration over the range 15% to 100% w/w hydrazine. The activation energy for the reaction was calculated to be 65,400 ± 90 J mole^{-1} (15,628 ± 22 cal mole^{-1}). Analysis of the products of this decomposition showed that it may be represented by the reaction:

$$3N_2H_4 \rightarrow N_2 + 4NH_3 .$$

The decomposition of liquid hydrazine on a supported rhodium catalyst was shown to follow a different reaction[2]:

$$2N_2H_4 \rightarrow N_2 + H_2 + 2NH_3$$

and the kinetics showed a variation from a half order reaction in low concentrations of hydrazine to a zero order reaction in high concentrations[3]. The activation energy of the reaction was calculated to be 41,300 ± 340 J mole^{-1} (9,876 ± 81 cal mole^{-1}) and the pre-exponential factor was 3.45×10^2 mole gm^{-1} sec^{-1} .

Workers who have studied the decomposition of hydrazine vapour on tungsten and molybdenum films have postulated two modes of adsorption and decomposition on these metals[4,5]. On some sites hydrazine is associatively adsorbed to form an activated complex which then breaks down to form nitrogen and ammonia in accordance with the reaction:

$$3N_2H_4 \rightarrow N_2 + 4NH_3 .$$

On other surface sites hydrazine is dissociatively adsorbed as NH_2 radicals. Further surface dissociation occurs to form adsorbed NH , N and H , the latter combining to form hydrogen molecules which are desorbed. Nitrogen is not among the products of the decomposition on these sites and it is suggested that it is chemisorbed on the metal by the formation of a strong triple bond.

It has been suggested that the dissociative adsorption of hydrazine is the initial step in its decomposition on a supported rhodium catalyst[3] and that further dissociation to NH radicals, which in turn react with other hydrazine molecules, leads to the formation of hydrogen, ammonia and nitrogen.

In addition to iridium and rhodium, other platinum group metals have been considered for use as supported metal hydrazine decomposition catalysts[6] and some practical tests have been carried out using a ruthenium catalyst[7]. However, laboratory testing of the initial rate of gas evolution showed[7] that the activity of the ruthenium catalyst (Esso 500) was only 1% of that of the iridium catalyst (Shell 405). The present report describes the investigation of the kinetics of hydrazine decomposition on a supported ruthenium catalyst, and discusses some aspects of possible reaction mechanisms.

2 EXPERIMENTAL

In all the experiments propellent grade[8] hydrazine of 97.7% w/w concentration (obtained from the Olin Mathieson Corporation, USA) was used, diluted with demineralised water. The concentrations of the resulting solutions were determined by measuring their refractive indices[9]. The catalyst sample was in the form of 1/8 inch alumina pellets (1/8 inch length by 1/8 inch diameter) impregnated with 20% ruthenium and obtained from Engelhard Industries, Ltd., UK.

The apparatus, shown in Fig. 1, was similar to that previously described[3]. 50 ml of hydrazine solution were placed in the apparatus and the catalyst pellets in the side arm. The apparatus was immersed in a thermostatically controlled water bath and allowed to reach temperature equilibrium. It was then purged with argon until analysis showed that all traces of air had been removed. Argon was also used as the carrier gas in the gas chromatograph. The catalyst pellets were dropped into the hydrazine solution by rotating the side arm through 180°. To follow the progress of the reaction the volume of gas produced was measured at regular intervals, using a gas burette. Each run was terminated before the concentration of hydrazine had changed appreciably. All traces of ammonia were removed using a molecular sieve filter. The gas produced by the decomposition reaction was analysed for nitrogen and hydrogen content, using the gas chromatograph, the columns of which were packed with a Linde molecular sieve, Type 5A. Calibration was by nitrogen and hydrogen from cylinders of compressed gas. The apparent rates of reaction were calculated from the volume of gas produced in unit time and were expressed in moles of hydrogen and nitrogen produced per unit time per unit mass of catalyst.

3 RESULTS

Fig. 2 shows the variation in the apparent rate of decomposition of hydrazine on the supported ruthenium catalyst at 24°C with respect to hydrazine concentration. These data are also presented in Table 1 together with the results of the gas chromatographic analysis for nitrogen and hydrogen. The apparent rate of decomposition is a linear function of the hydrazine concentration and the composition of the gas produced is independent of hydrazine concentration at 24°C. A product gas composition of 25% hydrogen and 75% nitrogen corresponds to an overall reaction stoichiometry at 24°C of:

$$8\,N_2H_4 \rightarrow 3N_2 + H_2 + 10NH_3 \; .$$

The effects of temperature on the rates of decomposition of 19.6% w/w and 58.5% w/w hydrazine solutions on the supported ruthenium catalyst are shown in Fig . 3 and 4 respectively in the form of Arrhenius plots. The results are also presented in Tables 2 and 3 together with the results of the gas chromatographic analysis. The product gas composition changes with temperature, the percentage of nitrogen increasing with increasing temperature.

Tables 4 to 8 and Fig. 5 to 10 show the results of an analysis of the data in Tables 1 to 3, which are discussed later.

4 DISCUSSION

Possible overall reactions which may be used to represent the decomposition of hydrazine under various experimental conditions are[10]:

$$(1) \quad 3N_2H_4 \rightarrow N_2 + 4NH_3$$
$$(2) \quad 2N_2H_4 \rightarrow N_2 + H_2 + 2NH_3$$
$$(3) \quad 3N_2H_4 \rightarrow 2N_2 + 3H_2 + 2NH_3$$
$$(4) \quad N_2H_4 \rightarrow N_2 + 2H_2 \; .$$

In general, reactions (1) and (2) have been found to predominate in the heterogeneous decomposition of hydrazine[4]. The decomposition on a supported iridium catalyst follows reaction (1)[1,11,12], while the use of a supported rhodium catalyst results in reaction (2)[2,3].

Studies of the decomposition of hydrazine on tungsten[4] and molybdenum[5] films have shown that the manner in which hydrazine is adsorbed appears to determine the reaction path of the decomposition. The associative adsorption of hydrazine on the metal surface results in an activated complex which breaks down in accordance with reaction (1) to form nitrogen and ammonia. Alternatively, hydrazine may be dissociatively adsorbed as NH_2 radicals on metals which are capable of the dissociative adsorption of nitrogen and/or hydrogen. With tungsten and molybdenum further surface dissociation of the NH_2 radicals occurs to form NH , N and H adsorbed on the surface. The hydrogen atoms combine to form molecules which are desorbed, while the nitrogen atoms remain chemisorbed on the surface owing to the strong metal to nitrogen triple bond.

Although both iridium and rhodium catalysts decompose hydrazine in accordance with only one simple reaction stoichiometry, a supported ruthenium catalyst decomposes hydrazine at 24°C to form a gas in which the hydrogen to nitrogen ratio does not correspond to any of reactions (1) to (4) but gives an overall stoichiometry of:

$$8N_2H_4 \rightarrow 3N_2 + H_2 + 10NH_3 .$$

The effect of temperature on the overall rate of reaction and on the product gas composition is presented in Fig. 3 and 4 and in Tables 2 and 3, for 19.6 and 58.5% w/w hydrazine solutions respectively. The percentage of nitrogen in the product gas increases with increasing temperature, indicating that the overall reaction comprises two or more simultaneous reactions with different activation energies. The overall activation energies calculated from the Arrhenius plots in Fig. 3 and 4 are 47,700 ± 1,190 and 40,800 ± 1,380 J $mole^{-1}$ (11,415 ± 285 and 9,766 ± 330 cal $mole^{-1}$) for 19.6% and 58.5% hydrazine respectively. Various temperature ranges were covered for both hydrazine concentrations. As the contribution of each different reaction to the overall rate varies with temperature, the effect of different temperature ranges is to vary the activation energy of the overall reaction. Over a wide temperature range the Arrhenius plot would result in a curve, but over the limited temperature ranges covered in Fig. 3 and 4 the experimental error masks any tendency for the Arrhenius plot to give a curve instead of a straight line.

As reactions (1) and (2) occur during the decomposition of liquid hydrazine on supported iridium and rhodium catalysts respectively, and as the amount of hydrogen in the products is between 0% for reaction (1) and 50% for reaction (2) (the ammonia remains in solution), the results of the decomposition of liquid hydrazine on the supported ruthenium catalyst are considered in terms of the simultaneous occurrence of these two reactions. The overall reaction rates are given in terms of moles of nitrogen and hydrogen produced per gram of catalyst per second. The percentages of nitrogen and hydrogen are also given in Tables 1 to 3. Reaction (1) produces no hydrogen, while reaction (2) produces equimolar quantities of nitrogen and hydrogen. Therefore the contribution of reaction (2) to the overall rate is 2 × percentage of hydrogen produced in the product gas, while that of reaction (1) is 100 − 2 × %H_2 . The rates of reaction (1) shown in Tables 4, 5 and 7 are given in moles of nitrogen produced per gram of catalyst per second. The rates of reaction (2) shown in Tables 4, 6 and 8 are given in moles of nitrogen and hydrogen produced per gram of catalyst per second.

The calculated variation in the rate of reaction (1) for the decomposition of hydrazine on a supported ruthenium catalyst at 24°C with respect to hydrazine concentration is shown in Fig. 5 and the data are also given in Table 4. The linear relationship between rate of reaction and hydrazine concentration shows that the reaction is first order with respect to hydrazine concentration. The effect of temperature on the rate of reaction (1) is shown in the form of Arrhenius plots in Fig. 7 and 9 for 19.6% w/w and 58.5% w/w hydrazine solutions respectively. The calculated activation energies are 55,400 ± 2,030 J mole^{-1} and 51,500 ± 2,060 J mole^{-1} (13,252 ± 485 cal mole^{-1} and 12,318 ± 495 cal mole^{-1}) and the pre-exponential factors are 1.3×10^4 and 2.4×10^3 litre gm^{-1} sec^{-1} respectively. Combining the two sets of results gives an activation energy of 54,400 ± 500 J mole^{-1} (13,022 ± 120 cal mole^{-1}) and a pre-exponential factor of 8.7×10^3 litre gm^{-1} sec^{-1}.

A linear relationship between the rate of reaction and the reactant concentration may be due to the reaction being either first order chemically controlled or diffusion controlled. However, diffusion controlled reactions normally have activation energies of less than 16,000 J mole^{-1} (4,000 cal mole^{-1}). The reaction is therefore more likely to be first order chemically controlled. For a first order reaction the rate equation is:

$$v = kc$$

where v is the rate of reaction, k is the rate constant and c is the concentration of reactant, and as

$$k = Ae^{-E/RT} ,$$

the rate equation for reaction (1) is:

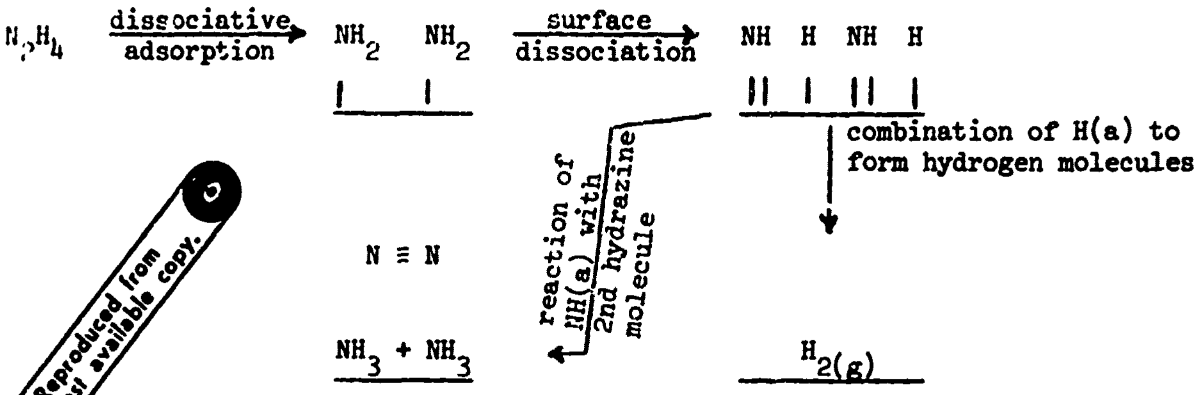
$$v_1 = 8.7 \times 10^3 \times e^{-54,400/8.314T} \times c \text{ mole } N_2 \text{ , gm}^{-1} \text{ sec}^{-1} .$$

The decomposition of hydrazine on tungsten[4] and molybdenum[5] films by reaction (1) was postulated to follow the associative adsorption of hydrazine on the metal and each hydrazine molecule appears to be attached to one metal atom. It has been suggested that the hydrazine molecule is bonded to the metal atom through one of its hydrogen atoms and that there is also lateral interaction, possibly hydrogen bonding, between adjacent hydrazine molecules. Assuming therefore that the associative adsorption of hydrazine molecules on the ruthenium metal surface occurs during reaction (1) it is neccesary to consider how the first order kinetics agree with this theory. The rate controlling step of the reaction must involve only one hydrazine molecule and probably consists of the reaction between one hydrazine molecule in the liquid phase and two associated hydrazine molecules adsorbed on the metal surface. If each adsorbed hydrazine molecule is bonded to the metal through one of its hydrogen atoms then the nitrogen lone pair electrons are directed away from the metal surface and are available to form a hydrogen bond with the hydrogen atoms of the incoming hydrazine molecule. This forms the activated complex which may then break down to form nitrogen and ammonia.

Fig. 6 shows that the rate of reaction (2) is also a linear function of hydrazine concentration for the decomposition of hydrazine on the supported ruthenium catalyst at 24°C. The variation in the rate of reaction (2) according to temperature is shown in Fig. 8 and 10 for 19.6% w/w and 58.5% w/w hydrazine solutions respectively. The calculated activation energies are 34,900 ± 1,150 J mole^{-1} and 33,800 ± 1,440 J mole^{-1} (8,341 ± 275 and 8,076 ± 345 cal mole^{-1}) and the pre-exponential factors are 3.0 and 1.8 litre gm^{-1} sec^{-1} respectively. Combining the two sets of data gives a calculated activation energy of 34,100 ± 375 J mole^{-1} (8,350 ± 90 cal mole^{-1}) and a pre-exponential factor of 3.0 litre gm^{-1} sec^{-1}. An activation energy of this order means that the linear relationship between the rate of reaction (2) and the hydrazine concentration results from the reaction being first order chemically controlled. The rate equation may be represented as:

$$v_2 = 3.0 \times e^{-34,100/8.314T} \times c \text{ moles } (N_2 + H_2) \text{ gm}^{-1} \text{ sec}^{-1} .$$

Reaction (2) occurs in the decomposition of hydrazine on a supported rhodium catalyst and the complex kinetics are assumed to involve the dissociative adsorption of hydrazine. The Langmuir adsorption isotherm was used to derive the rate equation. Both rhodium and ruthenium are capable of dissociatively adsorbing hydrogen, and nitrogen is dissociatively adsorbed on ruthenium. Ruthenium may therefore be expected to dissociatively adsorb hydrazine. However, when hydrazine is decomposed on ruthenium the first order kinetics preclude the possibility of the dissociative adsorption being the rate controlling step, because this would require a half order reaction going to a zero order reaction at high concentrations of hydrazine, as was found for the rhodium catalyst[3]. It is therefore postulated that the rate controlling step involves the second hydrazine molecule and is probably the reaction between this and the radicals on the ruthenium surface formed by the dissociative adsorption of the primary hydrazine molecule. The overall reaction mechanism is postulated to be:



5 CONCLUSIONS

The decomposition of liquid hydrazine on a supported ruthenium catalyst is a complex reaction which is postulated to consist of the two simultaneous reactions:

$$(1) \quad 3N_2H_4 \rightarrow N_2 + 4NH_3$$

$$(2) \quad 2N_2H_4 \rightarrow N_2 + H_2 + 2NH_3 \quad .$$

Both reactions are first order with respect to hydrazine concentration (c).

The activation energy and pre-exponential factor for reaction (1) were calculated to be 54,400 ± 500 J mole^{-1} (13,022 ± 120 cal mole^{-1}) and 8.7×10^3 litre gm^{-1} sec^{-1} respectively, and the rate equation is:

$$v_1 = 8.7 \times 10^3 \times e^{-54,440/8.314T} \times c \text{ mole } N_2 \text{ gm}^{-1} \text{ sec}^{-1} \quad .$$

It is suggested that the mechanism of reaction (1) involves the associative adsorption of hydrazine molecules on the catalyst surface, and that the rate controlling step is the reaction between one molecule in the liquid phase and two adsorbed molecules, to form an activated complex which breaks down to form nitrogen and ammonia.

The activation energy and pre-exponential factor for reaction (2) were calculated to be 34,100 ± 375 J $mole^{-1}$ (8,350 ± 90 cal $mole^{-1}$) and 3.0 litre gm^{-1} sec^{-1} respectively and the rate equation is:

$$v_2 = 3.0 \times e^{-34,100/8.314T} \times c \text{ mole } (N_2 + H_2) \text{ gm}^{-1} \text{ sec}^{-1} \quad .$$

The initial step in reaction (2) is postulated to be the dissociative adsorption of hydrazine molecules as NH_2 radicals on the catalyst surface. The NH_2 radicals may dissociate further to produce adsorbed NH and H species, the latter combining to produce hydrogen molecules which are desorbed. The rate controlling step is the reaction between one hydrazine molecule in the liquid phase and the adsorbed NH radicals to form nitrogen and ammonia.

TABLE 1

The effect of hydrazine concentration on the apparent rate of reaction and product gas composition at 24°C

Hydrazine concentration		Rate of reaction	Gas composition	
% w/w	mole 1^{-1}	moles sec^{-1} gm^{-1}	% H_2	% N_2
3.9	1.2	7.2×10^{-6}	24.1	75.9
9.8	3.1	1.43×10^{-5}	25.6	74.4
19.6	6.1	2.83×10^{-5}	25.1	74.9
29.6	9.3	3.9×10^{-5}	26.5	73.5
39.4	12.3	5.2×10^{-5}	23.0	77.0
47.0	14.7	6.4×10^{-5}	25.1	74.9
58.5	18.3	8.2×10^{-5}	25.0	75.0
68.6	21.4	9.6×10^{-5}	25.7	74.3
78.0	24.4	1.01×10^{-4}	25.1	74.9
84.4	26.4	1.16×10^{-4}	24.9	75.1

TABLE 2

The effect of temperature on the rate of decomposition and product gas composition of 19.6% w/w hydrazine solution

Temp (T) K	$^1/_T \times 10^3$	Rate of reaction mole $sec^{-1} gm^{-1} \times 10^6$	$k \times 10^6$ litre $sec^{-1} gm^{-1}$	$6 + \log_{10} k$	Gas composition % H_2	% N_2
290.5	3.442	20.6	3.38	0.529	25.5	74.5
297.0	3.367	28.3	4.74	0.676	25.1	74.9
309.0	3.236	62.0	10.2	1.009	18.6	81.4
317.0	3.155	102.0	16.7	1.223	18.3	81.7
324.0	3.086	138.0	22.6	1.354	16.1	83.9
331.0	3.021	267.0	43.7	1.640	14.0	86.0
336.0	2.976	293.0	48.0	1.681	12.0	88.0
342.0	2.924	339.0	55.4	1.744	12.5	87.5

TABLE 3

The effect of temperature on the rate of decomposition and product gas composition of 58.5% w/w hydrazine solution

Temp (T) K	$1/T \times 10^3$	Rate of reaction mole $gm^{-1}sec^{-1} \times 10^7$	$k \times 10^7$ litre $gm^{-1}sec^{-1}$	$7 + \log_{10}k$	Gas composition % H_2	% N_2
263.0	3.802	102.5	5.60	0.748	34.4	65.6
267.0	3.745	131.9	7.20	0.857	35.7	64.3
273.0	3.663	190.1	10.41	1.017	30.1	69.9
278.0	3.597	313.5	17.09	1.233	30.5	69.5
280.0	3.571	267.5	14.65	1.166	30.7	69.3
285.0	3.509	469.0	25.66	1.409	27.8	72.2
290.5	3.442	582.0	31.80	1.502	25.0	75.0
297.0	3.367	820.0	45.00	1.653	25.0	75.0

TABLE 4

The effect of hydrazine concentration on the rates of reactions (1) and (2) at 24°C

Hydrazine concentration % w/w	Overall rate of reaction mole $gm^{-1}sec^{-1} \times 10^6$	$\%H_2$ in the product gas	Rate of reaction (1) mole $gm^{-1}sec^{-1} \times 10^6$	Rate of reaction (2) mole $gm^{-1}sec^{-1} \times 10^6$
3.9	7.2	24.1	3.72	3.48
9.8	14.3	25.6	7.0	7.3
19.6	28.3	25.1	14.1	14.2
29.6	39.0	26.5	18.4	20.6
39.4	52.0	23.0	28.0	24.0
47.0	64.0	25.1	31.8	32.2
58.5	82.0	25.0	41.0	41.0
68.6	96.0	25.7	46.5	49.5
78.0	101.0	25.1	50.2	50.8
84.4	116.0	24.9	58.2	57.8

Note: Rate of reaction (1) is the overall rate of reaction × $\frac{(100 - 2 \times \%H_2)}{100}$;

Rate of reaction (2) is the overall rate of reaction × $\frac{2 \times \%H_2}{100}$.

TABLE 5

The effect of temperature on the rate of reaction (1) for 19.6% w/w hydrazine solution

Temp (T) K	$^1/_T \times 10^3$	Overall rate mole $sec^{-1} gm^{-1} \times 10^6$	% of overall rate due to reaction (1)	Rate of reaction (1) mole $gm^{-1} sec^{-1} \times 10^6$	$K_1 \times 10^6$ litre $gm^{-1} sec^{-1}$	$6 + \log_{10} K_1$
290.5	3.442	20.6	49.0%	10.1	1.66	0.220
297.0	3.367	28.3	49.8%	14.1	2.31	0.364
309.0	3.236	62.0	62.8%	39.0	6.4	0.806
317.0	3.155	102.0	63.4%	64.8	10.6	1.025
324.0	3.086	138.0	67.8%	93.5	15.3	1.185
331.0	3.021	267.0	72.0%	192.5	31.5	1.498
336.0	2.976	293.0	76.0%	222.5	36.4	1.561
342.0	2.924	339.0	75.0%	254.0	41.5	1.618

Note: The contribution of reaction (1) to the overall rate is (100 - 2 × $\%H_2$) for that temperature given in Table 2.

TABLE 6

The effect of temperature on the rate of reaction (2) for
19.6% w/w hydrazine solution

Temp (T) K	$^1/_T \times 10^3$	Overall rate mole $sec^{-1} gm^{-1} \times 10^6$	% of overall rate due to reaction (2)	Rate of reaction (2) mole $sec^{-1} gm^{-1} \times 10^6$	$K_2 \times 10^6$ litre $gm^{-1} sec^{-1}$	$6 + \log_{10} K_2$
290.5	3.442	20.6	51.0%	10.5	1.72	0.236
297.0	3.367	28.3	50.2%	14.2	2.43	0.386
309.0	3.236	62.0	37.2%	23.0	3.80	0.580
317.0	3.155	102.0	36.6%	37.2	6.1	0.785
324.0	3.086	138.0	32.2%	44.5	7.3	0.863
331.0	3.021	267.0	28.0%	74.5	12.2	1.086
336.0	2.976	293.0	24.0%	70.5	11.6	1.065
342.0	2.924	339.0	25.0%	85.0	13.9	1.143

Note: The contribution of reaction (2) to the overall rate is 2 × $\%H_2$ at that temperature in Table 2.

TABLE 7

The effect of temperature on the rate of reaction (1) for 58.5% w/w hydrazine solution

Temp (T) K	$^1/_T \times 10^3$	Overall rate mole $gm^{-1}sec^{-1} \times 10^7$	% of overall rate due to reaction (1)	Rate of reaction (1) mole $gm^{-1}sec^{-1} \times 10^7$	$K_1 \times 10^7$ litre $gm^{-1}sec^{-1}$	$7 + \log_{10} K_1$
263.0	3.802	102.5	31.2%	32.0	1.75	0.244
267.0	3.745	131.9	28.6%	37.9	2.07	0.316
273.0	3.663	190.1	39.8%	75.6	4.13	0.616
278.0	3.597	313.5	39.0%	122.0	6.64	0.822
280.0	3.571	267.5	38.6%	103.5	5.66	0.753
285.0	3.509	469.0	44.4%	208.0	11.4	1.057
290.5	3.442	582.0	50.0%	291.0	15.9	1.201
297.0	3.367	820.0	50.0%	410.0	22.5	1.352

Note: The contribution of reaction (1) to the overall rate is (100 - 2 × %H_2) for that temperature in Table 3.

TABLE 8

The effect of temperature on the rate of reaction (2) for
58.5% w/w hydrazine solution

Temp (T) K	$1/T \times 10^3$	Overall rate mole $gm^{-1}sec^{-1} \times 10^7$	% of overall rate due to reaction (2)	Rate of reaction (2) mole $gm^{-1}sec^{-1} \times 10^7$	$K_2 \times 10^7$ litre $gm^{-1}sec^{-1}$	$7 + \log_{10}K_2$
263.0	3.802	102.5	68.8	70.5	3.85	0.585
267.0	3.745	131.9	71.4	94.0	5.13	0.710
273.0	3.663	190.1	60.2	114.5	6.28	0.798
278.0	3.597	313.5	61.0	191.5	10.45	1.019
280.0	3.571	267.5	61.4	164.0	8.99	0.954
285.0	3.509	469.0	55.6	261.0	14.26	1.154
290.5	3.442	582.0	50.0	291.0	15.9	1.201
297.0	3.367	820.0	50.0	410.0	22.5	1.352

Note: The contribution of reaction (2) to the overall rate is 2 × %H_2
for that temperature in Table 3.

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10	I.J. Eberstein I. Glassman	Consideration of hydrazine decomposition. ARS Propellants, Combustion and Liquid Rockets Conference, Columbus, Ohio, 1960, Paper 1247-60 Prog. Astron. Rocketry 2, 351-366 (1960)
11	J.P. Contour G. Pannetier	Catalytic properties of iridium deposited on γ-alumina. IV. Adsorption and description of hydrazine studied by thermodesorption and infra-red spectroscopy. Bull Soc. chim. fr. 1970 (12) 4260-4
12	E. Santacesaria L. Giuffre D. Gelosa	Catalytic decomposition of hydrazine Riv. Combust. 24 (3), 101-118, 1970

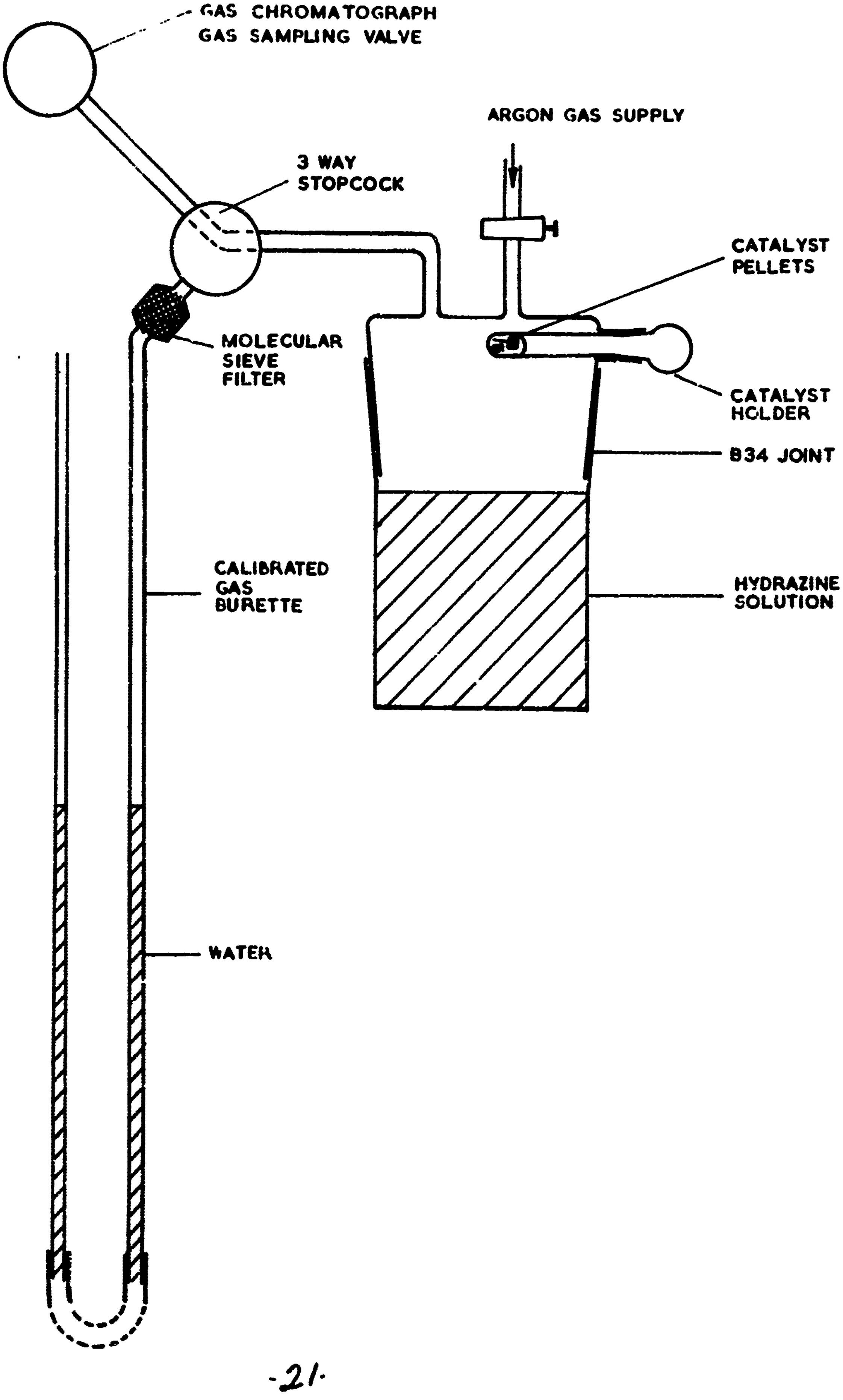

FIG. 1 APPARATUS USED TO MEASURE THE RATE OF DECOMPOSITION OF HYDRAZINE ON SUPPORTED RUTHENIUM CATALYST PELLETS

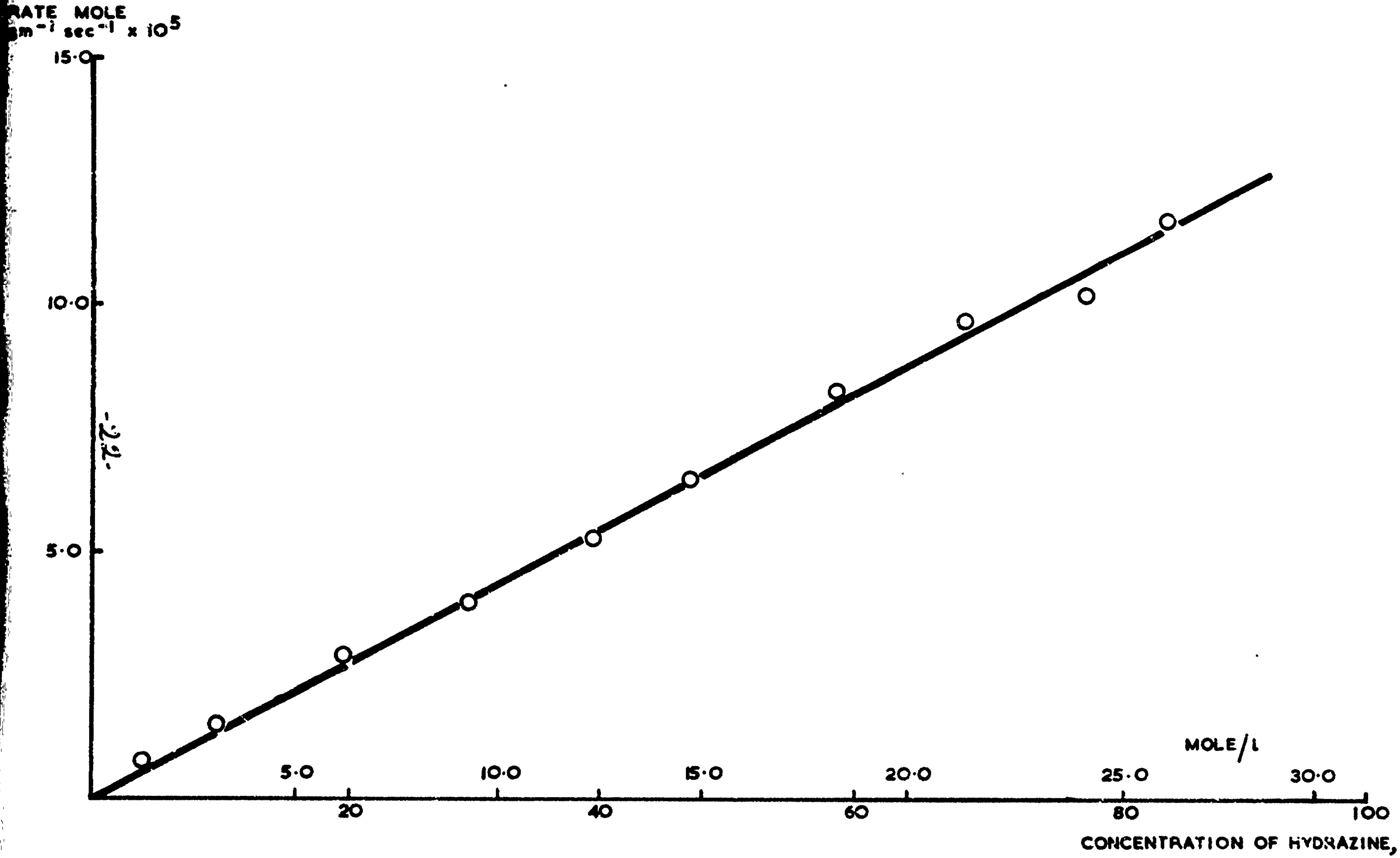

FIG. 2 THE OVERALL RATE OF DECOMPOSITION OF HYDRAZINE ON THE SUPPORTED RUTHENIUM CATALYST AT 24°C WITH RESPECT TO HYDRAZINE CONCENTRATION

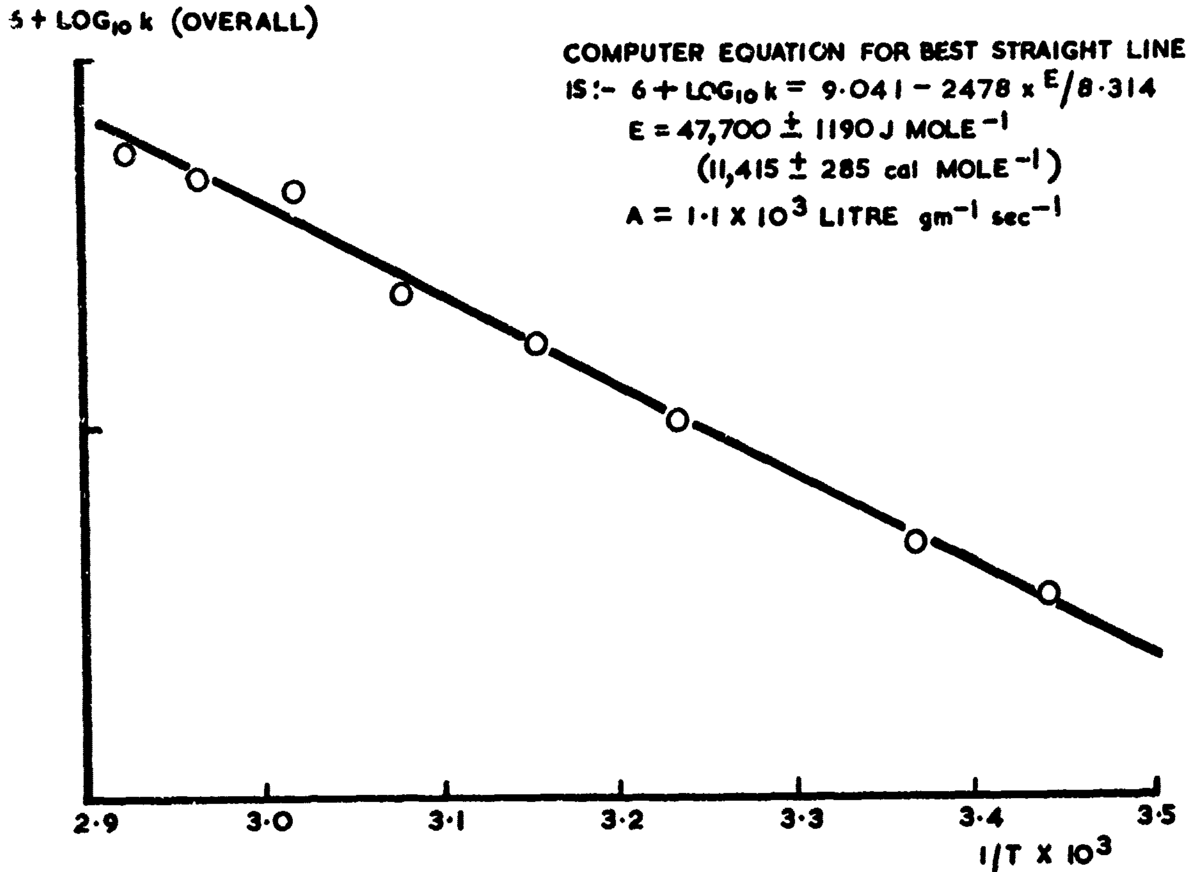

FIG. 3 ARRHENIUS PLOT OF LOG_{10} k (OVERALL) AGAINST 1/T FOR 19·6 % w/w HYDRAZINE SOLUTION

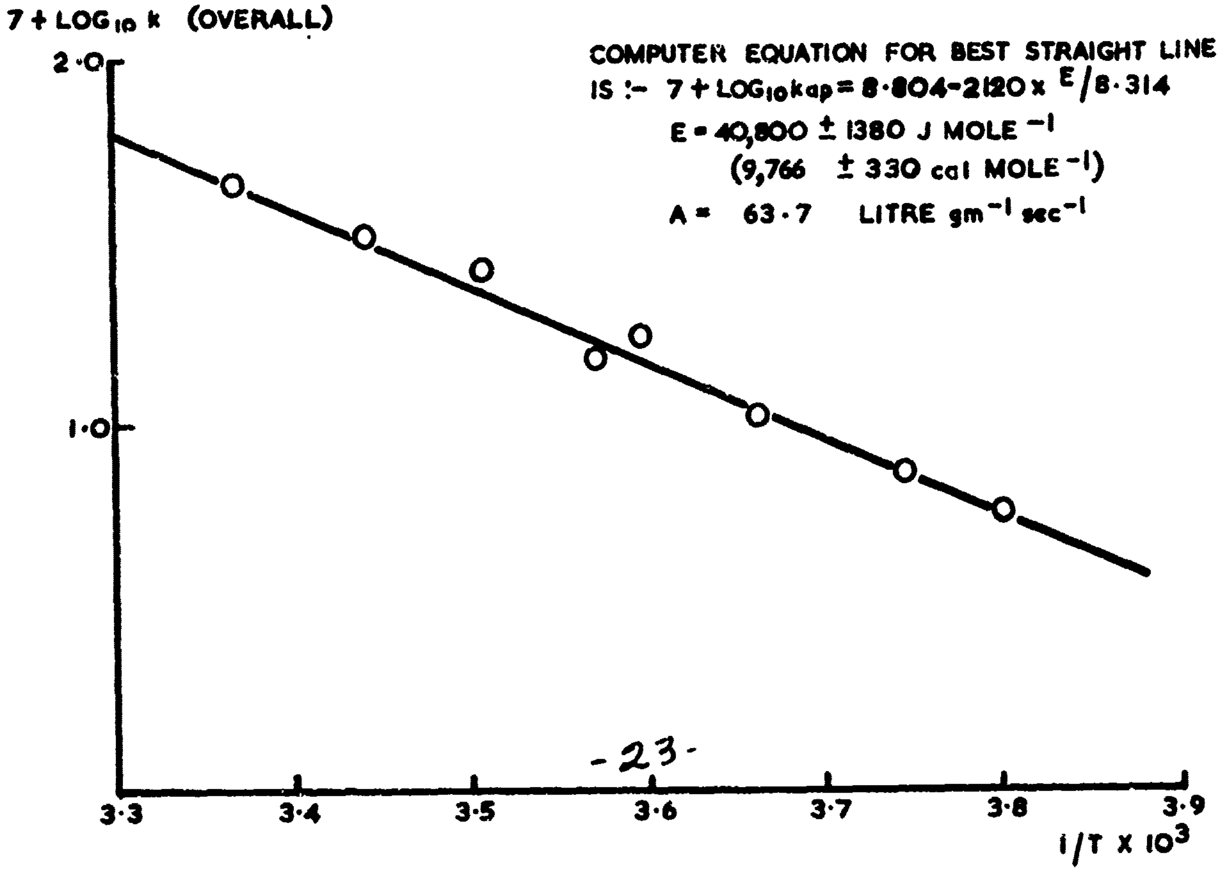

FIG. 4 ARRHENIUS PLOT OF LOG_{10} k (OVERALL) AGAINST 1/T FOR 58·5 % w/w HYDRAZINE SOLUTION

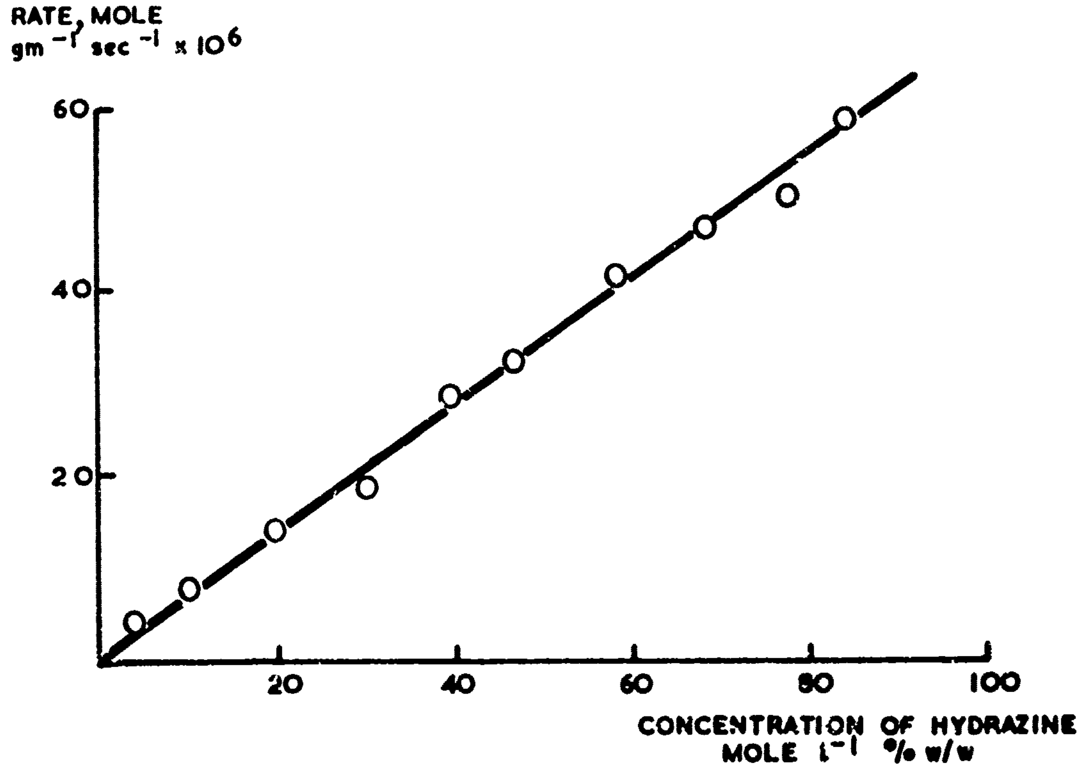

FIG. 5 THE RATE OF DECOMPOSITION OF HYDRAZINE BY REACTION (1) ON THE SUPPORTED RUTHENIUM CATALYST AT 24°C WITH RESPECT TO HYDRAZINE CONCENTRATION

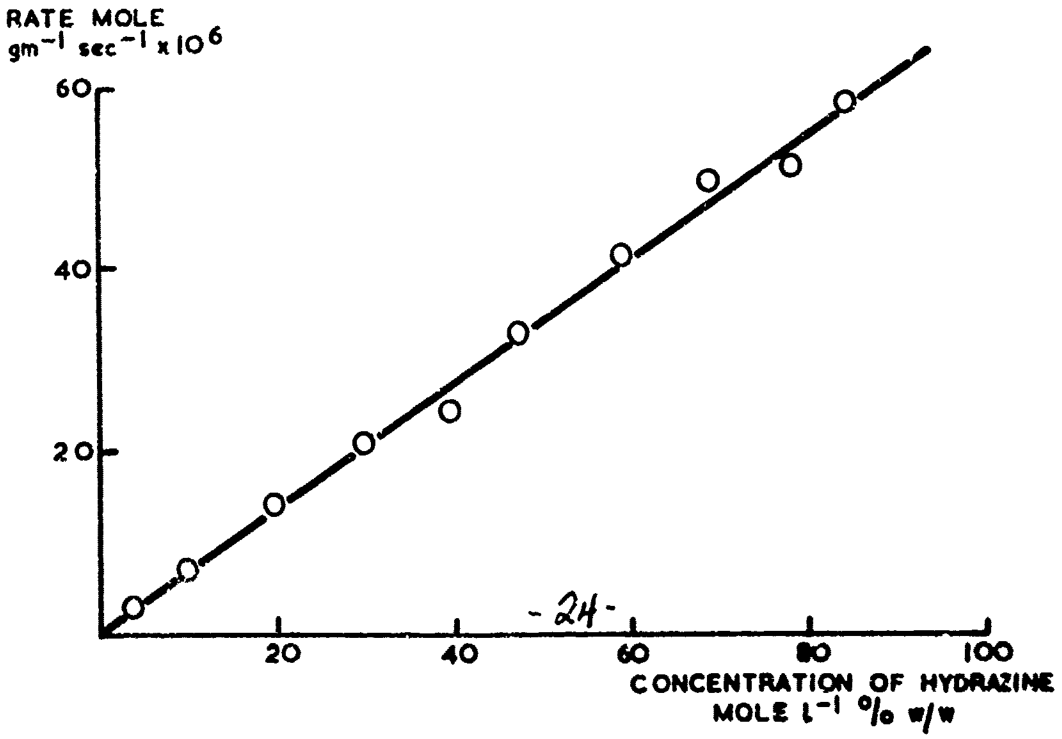

FIG. 6 THE RATE OF DECOMPOSITION OF HYDRAZINE BY REACTION (2) ON THE SUPPORTED RUTHENIUM CATALYST AT 24°C WITH RESPECT TO

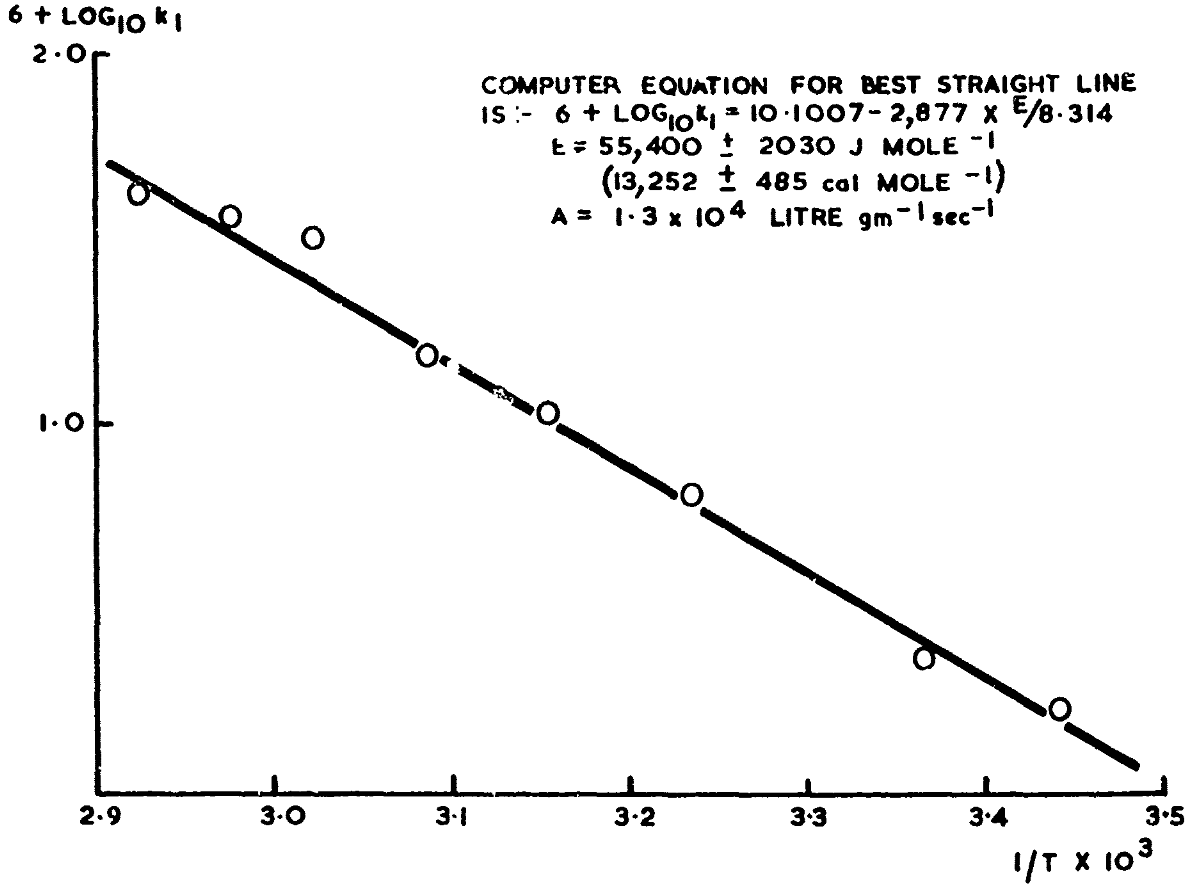

FIG. 7 ARRHENIUS PLOT OF $\mathrm{LOG}_{10}\, k_1$ AGAINST 1/T FOR 19·6 % w/w HYDRAZINE SOLUTION

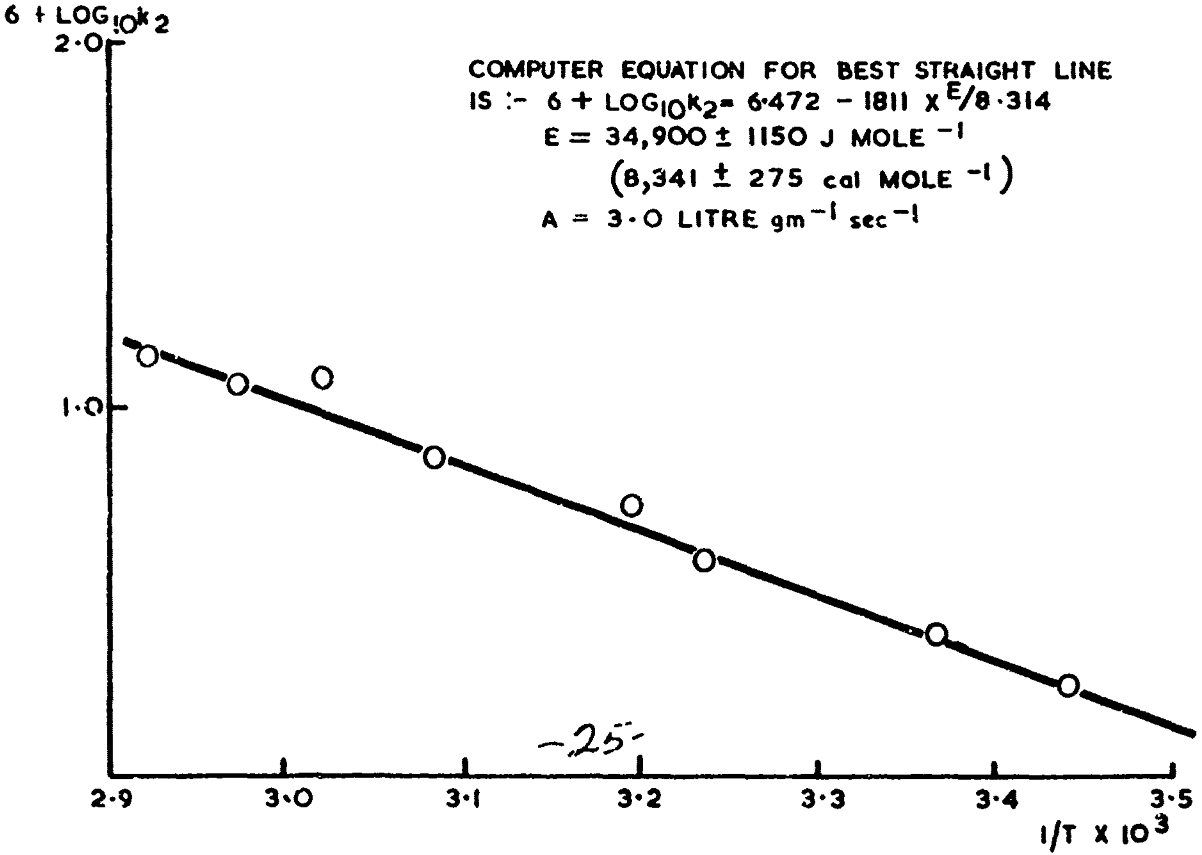

FIG. 8 ARRHENIUS PLOT OF $\mathrm{LOG}_{10}\, k_2$ AGAINST 1/T FOR 19·6 % w/w HYDRAZINE SOLUTION

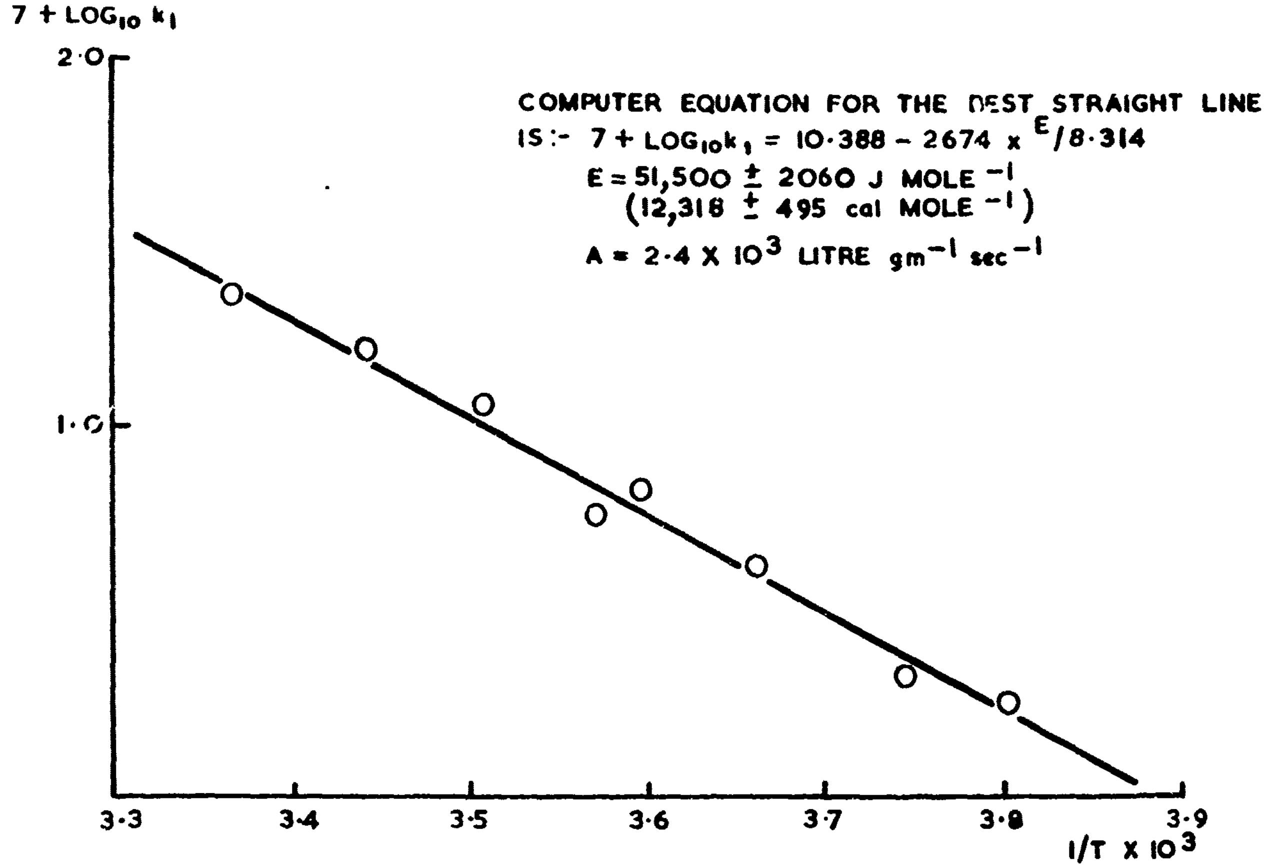

FIG. 9 ARRHENIUS PLOT OF LOG_{10} K_1 AGAINST 1/T FOR 58·5% w/w HYDRAZINE SOLUTION

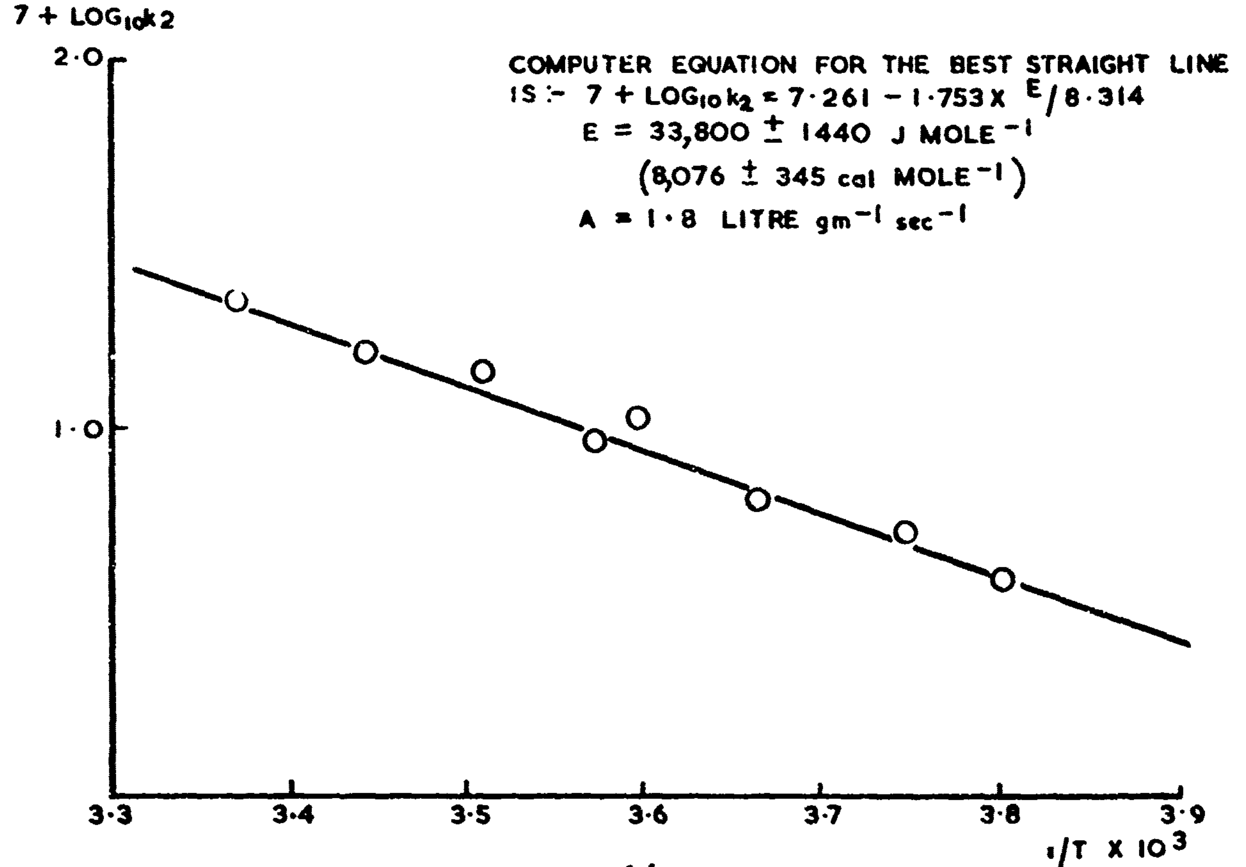

FIG. 10 ARRHENIUS PLOT OF $LOG_{10}k_2$ AGAINST 1/T FOR 58·5% w/w HYDRAZINE SOLUTION