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Rates of Methane Formation from Carbon Dioxide and Hydrogen Over a Ruthenium Catalyst*

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The Sabatier Reaction,

$$4H_2 + CO_2 \rightleftharpoons 2H_2O + CH_4 + 43 \text{ kcal}$$

was examined experimentally at 1 atm using a 0.5% ruthenium on alumina catalyst. Data are given from 62 experimental runs made in a 4.15 cm^3 isothermal reactor with from 0 to 85% conversion in the inlet feed gases and feed flow ratios (H_2 to CO_2) of 1.9 to 3.9, and temperatures from 400 to 680°F. Empirical correlations, based on modified gas phase kinetics, were made to describe the reaction rate over the experimental range.

INTRODUCTION

The catalytic hydrogenation of carbon dioxide to methane,

$$4H_2(g) + CO_2(g) \rightarrow CH_4(g) + 2H_2O(g) + 43 \text{ kcal}, \quad (1)$$

sometimes called the Sabatier reaction (*1*), is of commercial interest for the manufacture of synthetic natural gas from the products of coal gasification. This paper developed from work performed under NASA Contract NAS 9-9844 to investigate the Sabatier reaction as a step in reclaiming oxygen within closed cycle aerospace life support systems.

The Sabatier reaction is a reversible, highly exothermic reaction which proceeds at a useful rate at the low temperatures required for high yields only when a catalyst is used. Dew, White, and Sliepcevitch (*2*) studied this reaction using a nickel catalyst. Other investigators have looked at this reaction at elevated pressures (*3*). A review of earlier work is given by Emmett (*4*). This work describes an experimental investigation of the reaction using a ruthenium catalyst, and derives a correlation describing the kinetics of this catalysis in the 400 to 700°F experimental temperature range.

Thermodynamics

Equilibrium compositions for hydrogen and carbon dioxide mixtures at 1 atm are shown in Fig. 1 using free energies from Wagman *et al.* (*5*). Carbon and carbon monoxide are possible products, as well as methane and water vapor. The reaction proceeds as shown in Eq. (1) for molar feed ratios (H_2 to CO_2) of over 3.5:1 at temperatures from 400 to 700°F. Low temperatures favor high conversions while temperatures above 700 allow carbon monoxide formation. As the molar feed ratio falls below 3.5:1, carbon becomes thermodynamically stable at increasingly higher temperatures.

Catalyst Selection

Thompson (*6*) conducted a Sabatier catalyst screening program experimentally evaluating four catalysts:

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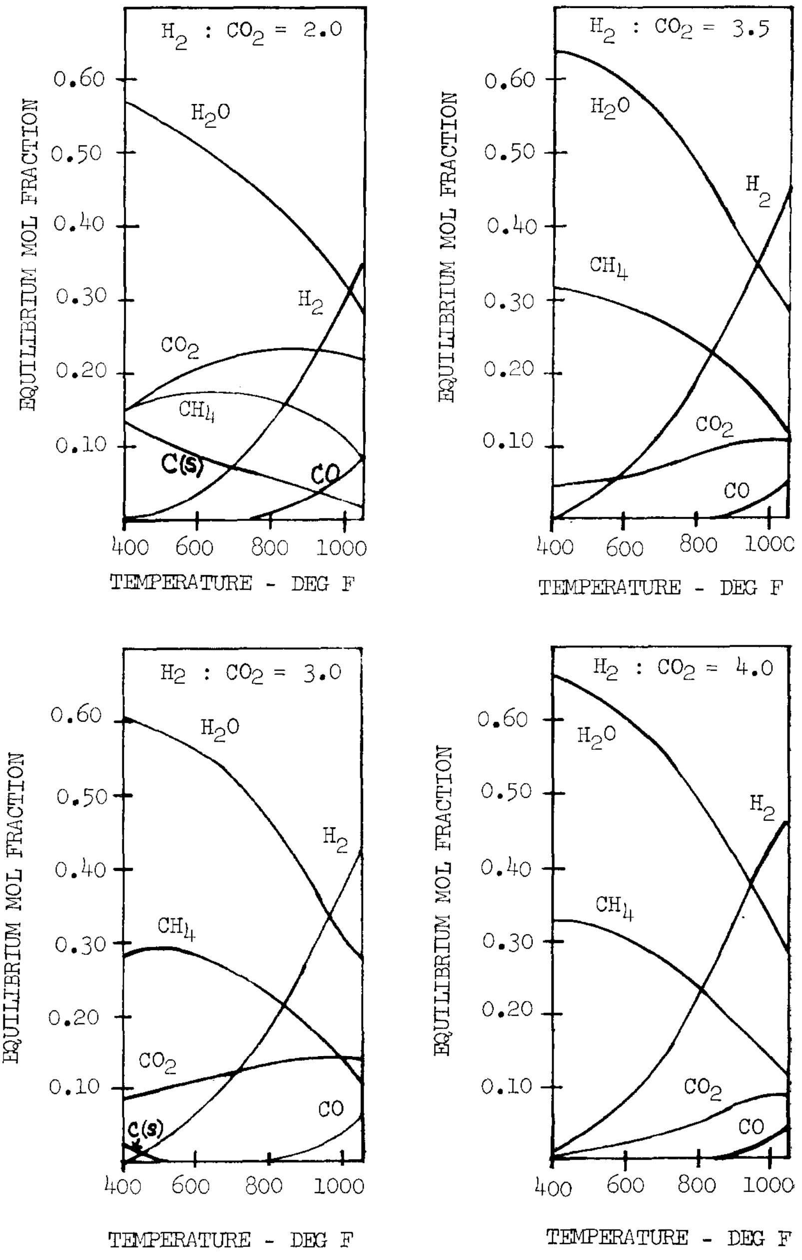

FIG. 1. Thermodynamic equilibrium products as a function of temperature for various H_2:CO_2 mole ratios.

1. Nickel (80% Ni and NiO) (on kieselguhr);
2. 0.5% ruthenium (on alumina);
3. 0.5% rhodium (on alumina);
4. 0.5% cobalt (on alumina).

Thompson found ruthenium and nickel to be the most active catalysts for promoting the Sabatier reaction. Nickel, however, presented the following operating problems not present with ruthenium:

1. Slow deterioration over the test period, attributed to trace level sulfur poisoning.

2. Reactor startup in hydrogen was advisable to assure reduction of nickel to its most active form.
3. Carbon deposition was reported at 650 to 700°F.

Consequently a 0.5% ruthenium catalyst on $\frac{1}{8} \times \frac{1}{8}$ in. cylindrical alumina pellets was selected for further investigation.[‡] Superficial examination of the pellets indicated the ruthenium did not penetrate more than 0.1 mm into the alumina, indicating that pore diffusion was not likely to be important in the performance of this catalyst. The bulk density of the pellets was measured as 1.0 g/cc.

Experimental Methods

The test reactor was a tube filled with catalyst which was held isothermal by immersion in a molten salt bath. It was made small so that the conversion of unreacted feed was low but measurable at the lowest operating temperature, minimizing the reaction heat released. At higher temperatures part of the hydrogen and carbon dioxide feed was passed through another reactor to provide a partly reacted feed thus minimizing reaction heat in the test reactor. In this manner the temperature differential between reactor wall and center was held to 20°F and usually much less.

Mass flow to the reactor was held steady for runs at several temperatures, giving data for calculation of the reaction activation energy. Additional runs were made at two temperatures to allow more precise determination of the basic reaction rate constant.

Feed flow ratios (H_2 to CO_2) of 2:1 and nearly 4:1 were investigated. Temperatures of 400 to 700°F were selected for data accumulation since at temperatures over 700°F the reaction is complicated by carbon monoxide formation, while 400°F is low enough to allow virtually complete conversion of the feed in a practical reactor.

A process gas chromatograph analyzed feed and effluent gases. The chromatograph was calibrated by using pure CO_2, H_2, and CH_4 at several pressures in the 0–1 atm range. Since equal volume samples were used, the chromatographic peak heights corresponded to partial pressures of the calibrated constituents. Water was calibrated indirectly using Sabatier reactor effluent, in which the partial pressure of water vapor was necessarily exactly twice that of the methane which was already calibrated.

The test reactor used for the kinetic study was made from $\frac{1}{2}$ in. stainless steel tubing (0.43 in. i.d. × 1.75 in.). The catalyst charge of 3.58 g (about eighty $\frac{1}{8} \times \frac{1}{8}$ in. cylindrical alumina pellets coated with 0.5% ruthenium) filled the 4.15 cc reactor tube.

Table 1 shows the complete experimental data after preliminary processing. Table 2 shows the results of activation energy and reaction rate constant calculations using selected runs made at several temperatures. Table 3 shows the results of integration of other runs made at two bath temperatures to calculate a rate constant.

The lower inlet flow ratios of H_2 to CO_2 in each test series were within the range for which carbon deposition was thermodynamically stable (Fig. 1). No evidence for such deposition was observed in these tests in either performance degradation or posttest catalyst examination.

Discussion

The actual mechanism of ruthenium catalysis in CO_2 methanation was not investigated in correlation of the data. Instead an empirical correlation was made using ordinary gas phase kinetics, but modified by an additional catalyst coefficient n. Thus:

$$-\frac{dP_{CO_2}}{dt} = k\exp(-E_a/RT)\left\{[P_{CO_2}]^n[P_{H_2}]^{4n} - \frac{[P_{CH_4}]^n[P_{H_2O}]^{2n}}{[K_e(T)]^n}\right\}, \quad (2)$$

where $K_e(T) = \exp[(1.0/1.987)(56{,}000/T_k^2 + 34{,}633/T_k - 16.4 \ln T_k + 0.00557T_k) +$

[‡] Englehard type "E," Englehard Minerals and Chemicals Corp., Newark, NJ.

TABLE 1

SUMMARY OF ALL EXPERIMENTAL TEST RUNS

SUMMARY OF EXPERIMENTAL DATA AFTER PRELIMINARY PROCESSING
3.58 GRAMS CATALYST USED IN 4.15 ML REACTOR
INLET/OUTLET PARTIAL PRESSURES SUM TO INLET/OUTLET TOTAL PRESSURE
SPACE VELOCITY CALCULATED AT REACTOR TEMP AND PRESSURE
INLET FLOW (CUBIC FT/HR) MEASURED AT 19 PSIA AND 73 DEG F

TEST NUMBER	REACTOR TEMP. (DEG F)	WALL TEMP (DEG F)	SPACE VELOCITY (1/HR)	INLET FLOW (CFH)	INLET CO2 (ATM)	OUTLET CO2 (ATM)	INLET H2 (ATM)	OUTLET H2 (ATM)	INLET H2O (ATM)	OUTLET H2O (ATM)	INLET CH4 (ATM)	OUTLET CH4 (ATM)
519.00	404.	404.	2854.	0.2117	0.2036	0.2002	0.8033	0.7894	0.0	0.0115	0.0	0.0058
520.00	433.	433.	3005.	0.2117	0.1978	0.1911	0.8091	0.7828	0.0	0.0220	0.0	0.0110
520.10	433.	433.	5585.	0.4172	0.2047	0.2015	0.8022	0.7893	0.0	0.0107	0.0	0.0054
521.00	443.	443.	5649.	0.4169	0.2034	0.1993	0.8035	0.7870	0.0	0.0137	0.0	0.0069
521.10	462.	462.	7766.	0.4172	0.1386	0.1305	0.8683	0.8427	0.0	0.0225	0.0	0.0112
521.40	469.	469.	6175.	0.4239	0.2036	0.1970	0.8034	0.7767	0.0	0.0222	0.0	0.0111
522.30	505.	505.	6337.	0.4243	0.2055	0.1899	0.8050	0.7422	0.0	0.0453	0.0	0.0226
523.30	500.	500.	5828.	0.4256	0.1714	0.1575	0.6814	0.6257	0.1060	0.1454	0.0517	0.0714
524.00	527.	520.	5801.	0.4231	0.1790	0.1645	0.6818	0.6224	0.0987	0.1480	0.0475	0.0720
525.00	552.	543.	5874.	0.4231	0.1799	0.1573	0.6826	0.5896	0.0968	0.1739	0.0476	0.0861
525.10	545.	537.	5835.	0.4231	0.1799	0.1600	0.6800	0.5979	0.0994	0.1675	0.0476	0.0816
526.00	553.	548.	5319.	0.4231	0.1487	0.1331	0.5370	0.4721	0.2141	0.2678	0.1071	0.1340
527.00	576.	567.	5357.	0.4231	0.1485	0.1272	0.5298	0.4409	0.2197	0.2932	0.1090	0.1457
527.10	559.	551.	5300.	0.4231	0.1485	0.1316	0.5298	0.4595	0.2197	0.2778	0.1090	0.1380
527.20	569.	560.	5334.	0.4231	0.1485	0.1291	0.5298	0.4490	0.2197	0.2865	0.1090	0.1424
528.10	600.	587.	5426.	0.4227	0.1477	0.1181	0.5305	0.4071	0.2197	0.3217	0.1090	0.1600
529.20	598.	589.	5125.	0.4223	0.1243	0.0983	0.4362	0.3280	0.2965	0.3859	0.1499	0.1946
530.70	623.	612.	5150.	0.4223	0.1255	0.0916	0.4299	0.2878	0.3004	0.4178	0.1510	0.2097
531.00	652.	639.	5235.	0.4223	0.1229	0.0846	0.4202	0.2598	0.3059	0.4380	0.1579	0.2245
532.00	652.	648.	4660.	0.4223	0.0714	0.0594	0.1805	0.1298	0.5023	0.5441	0.2526	0.2735
533.00	677.	670.	4764.	0.4223	0.0714	0.0591	0.1805	0.1287	0.5023	0.5450	0.2526	0.2740
534.00	700.	694.	4855.	0.4223	0.0714	0.0582	0.1805	0.1248	0.5023	0.5482	0.2526	0.2756
538.50	400.	400.	5302.	0.4352	0.3893	0.3874	0.6175	0.6078	0.0	0.0055	0.0	0.0027
539.50	423.	423.	4956.	0.4063	0.3415	0.3374	0.6654	0.6463	0.0	0.0109	0.0	0.0054
540.10	430.	430.	4967.	0.4063	0.3435	0.3393	0.6633	0.6427	0.0	0.0120	0.0	0.0060
540.20	440.	440.	5016.	0.4063	0.3435	0.3388	0.6633	0.6392	0.0	0.0147	0.0	0.0073
540.80	450.	450.	5062.	0.4063	0.3435	0.3382	0.6633	0.6340	0.0	0.0185	0.0	0.0093
541.10	485.	480.	5192.	0.4063	0.3455	0.3379	0.6613	0.6117	0.0	0.0336	0.0	0.0168
541.10	485.	480.	5192.	0.4063	0.3455	0.3380	0.6613	0.6121	0.0	0.0333	0.0	0.0166
542.00	490.	485.	5276.	0.4070	0.3434	0.3359	0.6634	0.6146	0.0	0.0330	0.0	0.0165
542.10	505.	498.	5324.	0.4070	0.3434	0.3336	0.6634	0.5955	0.0	0.0472	0.0	0.0236
543.00	495.	491.	4741.	0.4070	0.3305	0.3264	0.5117	0.4762	0.1051	0.1314	0.0595	0.0728
544.00	512.	505.	4782.	0.4070	0.3312	0.3241	0.5124	0.4507	0.1081	0.1539	0.0552	0.0781
544.10	520.	514.	4815.	0.4070	0.3312	0.3236	0.5124	0.4466	0.1081	0.1570	0.0552	0.0796
544.20	528.	521.	4818.	0.4070	0.3312	0.3208	0.5124	0.4221	0.1081	0.1752	0.0552	0.0888
544.30	534.	525.	4839.	0.4070	0.3312	0.3202	0.5124	0.4170	0.1081	0.1790	0.0552	0.0907
545.00	519.	512.	4577.	0.4070	0.3302	0.3226	0.4476	0.3872	0.1543	0.1973	0.0782	0.0997
545.10	528.	519.	4624.	0.4073	0.3302	0.3220	0.4476	0.3822	0.1543	0.2010	0.0782	0.1016
545.30	534.	524.	4626.	0.4070	0.3302	0.3209	0.4476	0.3722	0.1543	0.2085	0.0782	0.1053
546.10	541.	532.	4668.	0.4078	0.3276	0.3182	0.4427	0.3593	0.1587	0.2206	0.0779	0.1088
547.00	572.	558.	4726.	0.4070	0.3275	0.3125	0.4428	0.3086	0.1583	0.2578	0.0783	0.1280
548.00	560.	555.	4177.	0.4070	0.2647	0.2581	0.1527	0.1021	0.3941	0.4320	0.2024	0.2215
549.00	587.	581.	4276.	0.4070	0.2647	0.2568	0.1526	0.0914	0.3941	0.4400	0.2024	0.2255
549.10	590.	581.	4404.	0.4070	0.2865	0.2729	0.2477	0.1379	0.3164	0.3984	0.1632	0.2045
550.00	616.	604.	4497.	0.4070	0.2855	0.2686	0.2502	0.1146	0.3154	0.4167	0.1627	0.2137
551.00	640.	628.	4560.	0.4066	0.2855	0.2659	0.2494	0.0916	0.3161	0.4342	0.1627	0.2221
560.00	624.	589.	5483.	0.4067	0.3417	0.2998	0.6686	0.3220	0.0	0.2590	0.0	0.1295
561.00	610.	588.	4909.	0.4067	0.3237	0.2943	0.4848	0.2412	0.1375	0.3184	0.0663	0.1563
562.00	602.	583.	4721.	0.4059	0.3151	0.2923	0.4142	0.2214	0.1865	0.3302	0.0944	0.1664
563.00	596.	581.	4587.	0.4059	0.3017	0.2824	0.3468	0.1880	0.2400	0.3587	0.1217	0.1813
564.00	588.	578.	4361.	0.4059	0.2855	0.2721	0.2362	0.1268	0.3214	0.4031	0.1638	0.2048
565.00	588.	579.	4566.	0.4321	0.1708	0.1509	0.3028	0.2014	0.3542	0.4340	0.1803	0.2204
566.00	593.	579.	4548.	0.4321	0.1960	0.1654	0.3599	0.1964	0.3248	0.4556	0.1274	0.1894
567.00	598.	580.	5022.	0.4321	0.2143	0.1800	0.4990	0.3213	0.1981	0.3372	0.0988	0.1684
568.00	601.	580.	5234.	0.4321	0.2258	0.1860	0.5672	0.3622	0.1456	0.3066	0.0717	0.1521
569.00	617.	583.	5872.	0.4321	0.2600	0.2027	0.7482	0.4515	0.0	0.2351	0.0	0.1175
570.00	531.	520.	5670.	0.4311	0.2623	0.2436	0.7514	0.6561	0.0	0.0737	0.0	0.0368
571.00	527.	520.	4971.	0.4311	0.2226	0.2078	0.5567	0.4820	0.1567	0.2142	0.0776	0.1063
572.00	526.	519.	4932.	0.4311	0.2011	0.1887	0.5043	0.4459	0.2052	0.2479	0.1030	0.1244
573.00	519.	520.	4552.	0.4311	0.1924	0.1807	0.4154	0.3571	0.2692	0.3136	0.1367	0.1589
574.00	524.	520.	4358.	0.4311	0.1755	0.1584	0.3404	0.2555	0.3308	0.3965	0.1670	0.1999
575.00	524.	520.	4231.	0.4311	0.1604	0.1523	0.2654	0.2263	0.3895	0.4186	0.1984	0.2131
576.00	527.	520.	4347.	0.4082	0.2828	0.2755	0.2692	0.2179	0.3063	0.3430	0.1554	0.1738
577.00	528.	520.	4581.	0.4082	0.3000	0.2923	0.3700	0.3153	0.2288	0.2681	0.1149	0.1345
578.00	529.	520.	4754.	0.4082	0.3089	0.3003	0.4350	0.3728	0.1806	0.2255	0.0892	0.1116
579.00	529.	521.	5058.	0.4082	0.3223	0.3106	0.5442	0.4566	0.0993	0.1634	0.0478	0.0798
580.00	530.	520.	5382.	0.4082	0.3306	0.3195	0.6270	0.5453	0.0386	0.0983	0.0175	0.0473
581.00	531.	520.	5644.	0.4558	0.3377	0.3253	0.6760	0.5837	0.0	0.0675	0.0	0.0337

TABLE 2

SUMMARY OF CALCULATIONS FOR RUNS 520.1 - 551.

EACTIN= 0.30320E 05

CATALYST COEFFICIENT= 0.22500E 00

TEST NUMBER	ABSCISSA X(NP) (1/DEG R)	ORDINATE Y(NP)	REACTION RATE CONSTANT
520.10	0.001120	3.9713	0.1399E 10
521.00	0.001107	4.2306	0.1500E 10
521.40	0.001076	4.7937	0.1642E 10
522.30	0.001036	5.5539	0.1903E 10
523.30	0.001042	5.4613	0.1883E 10
524.00	0.001013	5.6478	0.1469E 10
525.00	0.000988	6.1293	0.1623E 10
525.10	0.000995	5.9929	0.1573E 10
526.00	0.000987	5.8519	0.1212E 10
527.00	0.000965	6.2189	0.1252E 10
527.10	0.000981	5.9478	0.1220E 10
527.20	0.000972	6.1079	0.1238E 10
528.10	0.000943	6.6091	0.1325E 10
529.20	0.000945	6.6274	0.1387E 10
530.70	0.000923	7.0069	0.1453E 10
531.00	0.000899	7.2669	0.1305E 10
532.00	0.000899	7.3220	0.1378E 10
533.00	0.000880	7.7087	0.1501E 10
538.50	0.001163	3.3132	0.1395E 10
539.50	0.001133	3.9248	0.1620E 10
540.10	0.001124	4.0167	0.1550E 10
540.20	0.001111	4.2528	0.1623E 10
540.80	0.001099	4.4918	0.1711E 10
541.10	0.001058	5.1035	0.1695E 10
541.10	0.001058	5.0846	0.1663E 10
542.00	0.001053	5.0928	0.1540E 10
542.10	0.001036	5.4771	0.1762E 10
543.00	0.001047	4.9328	0.1207E 10
544.00	0.001029	5.5029	0.1613E 10
544.10	0.001020	5.5874	0.1545E 10
544.20	0.001012	5.9222	0.1903E 10
544.30	0.001006	5.9862	0.1848E 10
545.00	0.001021	5.5024	0.1441E 10
545.10	0.001012	5.6042	0.1385E 10
545.30	0.001006	5.7672	0.1485E 10
546.10	0.000999	5.9260	0.1563E 10
547.00	0.000969	6.4725	0.1708E 10
548.00	0.000980	6.4450	0.1977E 10
549.00	0.000955	6.7867	0.1892E 10
549.10	0.000952	6.8709	0.1974E 10
550.00	0.000929	7.2473	0.2025E 10
551.00	0.000909	7.6323	0.2184E 10

THE AVERAGE REACTION RATE CONSTANT IS

0.1585E 10

TABLE 3

SUMMARY OF CALCULATIONS FOR RUNS 560 - 581

EACTIN= 0.30320E 05

CATALYST COEFFICIENT= 0.22500E 00

TEST NUMBER	ABSCISSA X(NP) (1/DEG R)	ORDINATE Y(NP)	REACTION RATE CONSTANT
560.00	0.000923	7.4153	0.2157E 10
561.00	0.000935	7.1887	0.2068E 10
562.00	0.000942	7.0268	0.1958E 10
563.00	0.000947	6.9666	0.2000E 10
564.00	0.000954	6.9201	0.2132E 10
565.00	0.000954	6.7169	0.1740E 10
567.00	0.000945	6.8889	0.1801E 10
568.00	0.000943	6.9717	0.1878E 10
569.00	0.000929	7.2710	0.2046E 10
570.00	0.001009	5.9441	0.1856E 10
571.00	0.001013	5.7676	0.1656E 10
572.00	0.001014	5.5660	0.1375E 10
573.00	0.001021	5.6628	0.1692E 10
575.00	0.001016	5.6175	0.1494E 10
576.00	0.001013	5.7555	0.1636E 10
577.00	0.001012	5.5894	0.1364E 10
578.00	0.001011	5.6253	0.1392E 10
579.00	0.001011	5.6801	0.1796E 10
580.00	0.001010	5.7625	0.1572E 10
581.00	0.001009	5.8908	0.1760E 10

THE AVERAGE REACTION RATE CONSTANT IS

0.1769E 10

33.165]. T_k is the gas temperature (°K).** The forward rate constant k, the activation energy E_a, and catalyst coefficient n are constants to be determined from the experimental data.

To find these constants Eq. (2) was rewritten and integrated over the reactor length, expressing space velocity as $S_v = 1/\tau$ with τ the contact time. Rearrangement gave,

$$k \exp(-E_a/RT) = S_v \int_{P_{\mathrm{CO}_2}\,\mathrm{in}}^{P_{\mathrm{CO}_2}\,\mathrm{out}} \frac{-dP_{\mathrm{CO}_2}}{[P_{\mathrm{CO}_2}]^n[P_{\mathrm{H}_2}]^{4n} - \{[P_{\mathrm{CH}_4}]^n[P_{\mathrm{H}_2\mathrm{O}}]^{2n}/[K_e(T)]^n\}} \equiv \exp Y, \quad (3)$$

which was evaluated with a digital computer by using small values of $d\,P_{\mathrm{CO}_2}$ (i.e., ΔP_{CO_2}) and stepping through the reactor using a trial value for n. After each increment corrected partial pressures P'_i were calculated using, $P'_i = P_{i_{\mathrm{old}}} + a_i \Delta P_{\mathrm{CO}_2}$, where $i = \mathrm{CO}_2$, H_2, CH_4, and $\mathrm{H}_2\mathrm{O}$, and

$$a_{\mathrm{CO}_2} = -1,$$
$$a_{\mathrm{H}_2} = -4,$$
$$a_{\mathrm{CH}_4} = +1,$$
$$a_{\mathrm{H}_2\mathrm{O}} = +2.$$

The partial pressures were then normalized so that the sum equaled the total pressure,

$$P_{i_{\mathrm{new}}} = P_i' \frac{\sum\limits_i P_{i_{\mathrm{old}}}}{\sum\limits_i P_i'} \quad (i = \mathrm{CO}_2, H_2, \mathrm{CH}_4, \mathrm{H}_2\mathrm{O}). \quad (4)$$

** This equation for equilibrium constant was derived from data in NBS Research Paper RP 1634 [Ref. (5)].

This technique will not work if there is any pressure drop through the reactor. In such cases the very small pressure drop was eliminated mathematically by ratioing the outlet partial pressures upward to make the total outlet pressure equal to the total inlet pressure.

After exp(Y) has been evaluated, the rate expression for a particular run is then of the form

$$\exp(Y) = k \exp(-E_a/RT). \qquad (5)$$

Taking logarithms of both sides,

$$Y = -\frac{E_a}{R}\left[\frac{1}{T}\right] + \ln k, \qquad (6)$$

which is of the form $Y = mX + b$, so that a plot of Y vs $1/T$ for several runs forms a line with a slope $-E_a/R$ and a $1/T = O$ intercept of ln$k$. If the correlation is good the plot will show minimum scatter and good linearity when a proper value of n has been chosen.

Experimental Data Reduction

Reduced run data were further processed in Table 2 and 3 to determine values of the activation energy E_a, catalyst coefficient n, and reaction rate coefficient k. (Runs 519, 520, 521.1, 534, 566, 574 were deleted due to poor analyses or undesirable reaction conditions.)

The listed values of Y were calculated by the computer program according to Eq. (3), and a least squares fit made according to Eq. (6) to determine the activation energy E_a. A plot of Eq. (6) for runs of Table 2 is shown as Fig. 2. A catalyst coefficient of 0.225 was used because it gave the most linear plot and the least scatter. The activation energy of 30,320 btu/lb mol CO_2 was determined from the slope $(-E_a/R)$ in Fig. 2. The individual reaction rate constants tabulated in Table 2 were calculated from Eq. (3) using this activation energy. An arithmetic average of these values for rate constant was 0.1585×10^{10}, which compares with 0.15664×10^{10} determined by extrapolation to the ordinate of the line in Fig. 2 according to Eq. (6).

Table 3 summarizes the identical processing of the constant bath temperature runs used for reaction rate determination, using the catalyst coefficient of 0.225 and

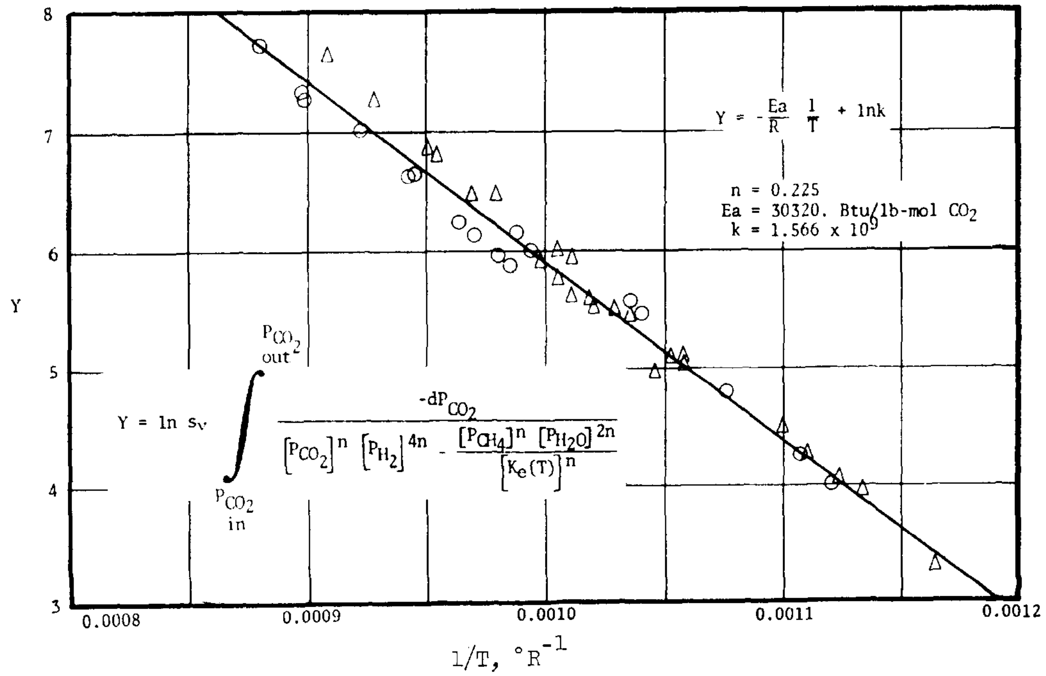

FIG. 2. Activation energy determination using runs from Table 2.

activation energy of 30,320 btu/lb mol CO_2 as determined above. The average rate constant for these runs was found to be 0.1769×10^{10} and this is taken as the preferred value since these runs were over a wider range of compositions than the runs used for activation energy determination.

Conclusion

The Sabatier Reaction,

$$4H_2 + CO_2 \rightleftharpoons 2H_2O + CH_4 + 43 \text{ kcal}$$

was examined experimentally at 1 atm using a 0.5% ruthenium on alumina catalyst. Data are given from 62 experimental runs made in a 4.15 cm^3 isothermal reactor with from 0 to 85% conversion in the inlet feed gases and feed flow ratios (H_2 to CO_2) of 1.9 to 3.9, and temperatures from 400 to 680°F.

The reaction rate was found to be described by

$$-\frac{dP_{CO_2}}{dt} = k \exp(-E_a/RT) \left\{ [P_{CO_2}]^n [P_{H_2}]^{4n} - \frac{[P_{CH_4}]^n [P_{H_2O}]^{2n}}{[K_e(T)]^n} \right\}$$

where $K_e(T) = \exp[(1.0/1.987)(56{,}000/T_k^2 + 34{,}633/T_k - 16.4 \ln T_k + 0.00557 T_k) + 33.165]$.

Correlation of the data gave

$$n = 0.225,$$
$$E_a = 16.84 \text{ kcal/gmol (30,320 btu/lb mol)},$$
$$k = 0.1769 \times 10^{10} \text{ hr}^{-1} \text{ atm}^{-0.125},$$

when P's are expressed in atmospheres.

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