With regard to the first assumption, it appears quite probable that the relationship mentioned holds quite accurately for ethane. If this be true, the equations that have been worked out would apply to natural gases where the average number of carbon atoms per molecule is less than 2, and most natural gases would be included in this class. The applicability of the formulas to rich natural gases and gasoline vapor is problematical, and experimental proof of the accuracy of the basic assumption is needed. It will be noted that the specific heat of the hydrocarbons that constitute gasoline ranges from 0.426 to 0.448. This is considerably less than the value of 0.5 that is generally employed for gasoline in liquid form.

The assumption as to the composition of the natural gas has been made purely for convenience. If analysis shows constituents other than paraffin gases, it is a simple matter to make the necessary corrections.

SUMMARY

I—Formulas have been developed to correlate the following characteristics of normal paraffin hydrocarbons:

- Calories per gram-molecule and number of carbon atoms per molecule (2)
- B. t. u. per lb. and number of carbon atoms per molecule (4)
- B. t. u. per cu. ft. and number of carbon atoms per molecule (6)
- B. t. u. per lb. and specific gravity in liquid form (8)
- B. t. u. per gal. and specific gravity in liquid form (10)
- Specific gravity in liquid form and number of carbon atoms per molecule (Note)
- Specific heat and number of carbon atoms per molecule (15)
- Specific heat and specific gravity in gaseous form (17)
- Volumetric specific heat and specific gravity in gaseous form (18)

II—The relationships between specific gravity and B. t. u. per lb. and per gal. may be expressed quite accurately by linear equations. The significance of this is that the specific gravity of a mixture of normal paraffin hydrocarbons determines its heating value, expressed either in B. t. u. per lb. or B. t. u. per gal., regardless of what variation may take place in the number and proportions of constituents. This statement applies to gasoline in so far as gasoline is a mixture of the normal paraffin hydrocarbons.

III—Probable values of the heating value and specific gravity of vapor, and volume of vapor per gallon have been computed for four different grades of gasoline.

IV—Figures have been prepared showing the change in the heating value and specific gravity as a result of the extraction of different amounts of 90° Bé. gasoline from different grades of natural gas.

ALKALI FUSIONS. II—THE FUSION OF SODIUM BENZENE *m*-DISULFONATE WITH SODIUM HYDROXIDE FOR THE PRODUCTION OF RESORCINOL¹

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In a paper² recently published from this laboratory, there were given results of a series of experiments

¹ Presented at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

² THIS JOURNAL, 12 (1920), 145.

ascertaining the proper conditions for obtaining the highest yield of carvacrol by the fusion of sodium *p*-cymene sulfonate with sodium hydroxide. In connection with these experiments an apparatus was devised especially suited to the study of alkali fusion of aromatic sulfonic acids. Using this apparatus we have now completed a similar study of the production of resorcinol by the fusion of sodium benzene *m*-disulfonate with sodium hydroxide.

Although this subject has received attention from a number of investigators, a survey of the literature shows quite conclusively that, with possibly one exception, no systematic study of this problem has been made. There appears to be no agreement among those who have contributed to this subject as to the proper method of conducting an alkali fusion of sodium benzene *m*-disulfonate in order to get the best yield of resorcinol. The recorded yields vary from about 20 to 100 per cent.

HISTORICAL REVIEW

Among the earliest contributions on this subject those of Garrick¹ and V. Meyer² may be mentioned. The former claimed to have obtained an almost quantitative yield of resorcinol by the fusion of sodium benzene *m*-disulfonate with potassium hydroxide for 2 to 3 hrs. at 230°. V. Meyer in his paper gives no details as to method or yield.

Barth and Senhofer³ obtained a 90 to 95 per cent yield of resorcinol by fusing sodium benzene *m*-disulfonate with potassium hydroxide, but failed to describe just how the fusion was conducted. The same authors in a second paper⁴ stated that an almost theoretical yield of resorcinol was obtained by fusing the potassium salt of benzene *m*-disulfonic acid with potassium hydroxide, but again failed to give any details as to their method.

Durand⁵ gave the following directions for making resorcinol: The sodium salt of benzene *m*-disulfonic acid is fused for from 24 to 36 hrs. with five times its weight of sodium hydroxide (35 moles) in an iron pot provided with a mechanical stirring device and heated in an oil bath. The melt is dissolved in water, acidulated with sulfuric acid, and extracted with ether. No data are given as to the yield or the temperature at which the fusion is conducted.

Binschedler and Busch⁶ gave a description of the process of making resorcinol then commercially in use. Sixty kilos of sodium benzene *m*-disulfonate were added to 150 kilos (17.6 moles) of molten sodium hydroxide, containing as little water as possible, and fused for from 8 to 9 hrs. at 270°. An almost theoretical yield of resorcinol was claimed.

Degener⁷ was the first to make a study of the various conditions affecting the yield of resorcinol, such as temperature and time of fusion, proportion of alkali to be used, and the effect of substituting sodium

¹ Z. Chem., 1869, 549.

² Ber., 7 (1874), 1308.

³ Ann., 174 (1874), 235.

⁴ Ber., 8 (1875), 1477.

⁵ Mon. Sci., 18 (1876), 696.

⁶ Ibid., 20 (1878), 1169.

⁷ J. prakt. Chem., [2] 20 (1879), 300.

hydroxide for the potassium compound. He came to the conclusion that potassium hydroxide was somewhat better than sodium hydroxide and that a mixture of one mole of each of these two alkalis was nearly as satisfactory as pure potassium hydroxide. The optimum temperature when potassium hydroxide was used for the fusion was from 250° to 255°, whereas with sodium hydroxide the best yields were obtained at from 270° to 280°. The results also indicated that 12 moles of alkali to one of sodium benzene *m*-disulfonate were sufficient, and that 20 min. was the most favorable fusion period. In general, the yields were low, the best being 25.94 per cent of the theory. The fact that all the fusions were conducted below 280° undoubtedly accounts, to some extent, for the low yields.

Mülhauser¹ described the commercial process for making resorcinol. Two hundred and fifty kilos of sodium hydroxide (14.1 moles), 10 kilos of water (4 per cent of the weight of the sodium hydroxide), and 125 kilos of sodium benzene *m*-disulfonate are fused in an open pot provided with a stirrer. The reaction is said to be complete when the mixture becomes quiet. A yield of 20 to 23 kilos of resorcinol (41 to 47.2 per cent of the theory) is obtained.

The commercial process for making resorcinol as described by Schoop² is essentially the same as the foregoing, the only difference being that he prescribes 230 kilos of sodium hydroxide to 125 kilos of sodium benzene *m*-disulfonate. He claims, however, that from 125 kilos of sodium benzene *m*-disulfonate, 48 to 50 kilos of resorcinol were obtained. Inasmuch as the theoretical yield is 48.7 kilos, his figures are obviously too high.

MATERIALS AND APPARATUS

SODIUM BENZENE *m*-DISULFONATE—This salt was prepared according to the method of Barth and Senhofer,³ save that the sodium salt was obtained through the barium salt instead of the lead salt. The product was dried in a vacuum oven at 140° for 48 hrs. About 800 g. were made and used in all of our fusion experiments. An analysis gave the following results:

- (I) 0.1989 g. substance gave 0.1846 g. CO₂ and 0.0302 g. H₂O
 (II) 0.2417 g. substance gave 0.2228 g. CO₂ and 0.0358 g. H₂O
 (I) 0.5086 g. substance gave 0.2572 g. Na₂SO₄
 (II) 0.5005 g. substance gave 0.2532 g. Na₂SO₄

	Found		Calculated for C ₆ H ₄ (SO ₃ Na) ₂
	I Per cent	II Per cent	Per cent
C.....	25.31	25.14	25.52
H.....	1.69	1.60	1.43
S.....	22.74	22.77	22.73
Na.....	16.36	16.37	16.30
O (by diff.)...	33.90	34.12	34.02

SODIUM HYDROXIDE—This was a good grade of the commercial article (not C. P.), assaying 93.5 per cent NaOH. It was used in powdered form.

APPARATUS—A full description of the apparatus used will be found in the earlier article.⁴

EXPERIMENTAL METHODS

ALKALI FUSIONS—The problem of determining the proper conditions for obtaining the maximum yield

of resorcinol resolved itself into a study of the four following factors:

- (1) Ratio of sodium hydroxide to sodium benzene *m*-disulfonate.
- (2) The proper fusion period.
- (3) The proper fusion temperature.
- (4) Effect of the addition of water to the sodium hydroxide upon the yield of resorcinol.

Temporarily adopting 310° and 2 hrs. as the proper fusion temperature and period, respectively, and keeping these constant, experiments were conducted in which the ratio of sulfonate to alkali was varied in each tube. At the end of the fusion the tubes were suddenly cooled and analyzed for resorcinol and unused sodium benzene *m*-disulfonate. To determine the proper fusion period, all six tubes were filled with the same amount of alkali and sodium benzene *m*-disulfonate, the two constituents being in the proportion found in the previous experiment to give the best yield of resorcinol, and the fusion again conducted at 310°. At certain intervals of time a tube was removed, suddenly cooled, and analyzed as before. Using the optimum conditions as to period of fusion and ratio of alkali to benzene *m*-disulfonate, experiments were then conducted at different temperatures. The effect of the addition of water to the fusion mixture upon the yield of resorcinol was determined in a similar manner by adding a known amount of water to each tube, under the optimum conditions of the other factors as previously determined.

RESORCINOL DETERMINATION—The cold fused mass was removed from the tube with hot water, filtered, and the filtrate concentrated on the steam bath. It was made up to 200 cc. in a volumetric flask (Solution A), and 50 cc. were measured out with a pipet and transferred to a separatory funnel. It was made distinctly acid with hydrochloric acid, and extracted with five 50-cc. portions of ether, shaking vigorously with each portion for about one minute. The ether was evaporated off at room temperature, with the aid of a small blast of air, the residue dissolved in 200 cc. of water, and an aliquot part analyzed for resorcinol, according to the method of Pence.¹ It was found preferable to standardize the bromine solution against specially purified resorcinol instead of making the standard solution as recommended by the author. The weight of resorcinol was expressed as per cent of the theory.

DETERMINATION OF THE UNUSED SODIUM BENZENE *m*-DISULFONATE—An aliquot part of Solution A (50 cc.) was acidified with hydrochloric acid, diluted with water, boiled until all of the sulfur dioxide had been expelled, neutralized with sodium hydroxide, filtered, and made up to 200 cc. in a volumetric flask (Solution B). An aliquot part (50 cc.) of this solution was transferred to a weighed beaker, evaporated to dryness, dried for 48 hrs. in a vacuum oven at 140°, and weighed. A sample of the residue was analyzed for sulfur, using the Parr fusion bomb for carrying out the sodium peroxide fusion. Another measured portion of Solution B was analyzed for sulfate sulfur by precipitating as barium sulfate with barium chloride in the usual

¹ Dingler's polytech. J., 263 (1887), 154.

² Z. Chem. Ind., 2 (1887), 1.

³ Ber., 8 (1875), 1477.

⁴ Loc. cit.

¹ THIS JOURNAL, 8 (1911), 820.

manner. The total sulfur in Solution B found by this determination was deducted from that found by the sodium peroxide fusion, and the result calculated as $C_6H_4(SO_3Na)_2$. The weight of salt thus found was expressed as per cent of the weight of sodium benzene *m*-disulfonate taken for the experiment.

EXPERIMENTAL DATA

EFFECT OF AMOUNT OF SODIUM HYDROXIDE UPON YIELD OF RESORCINOL—The results of the experi-

FIG. 1—CONCENTRATION, YIELD CURVE

ments in which the amount of sodium hydroxide was made the only variable are shown in Table I and graphically in Fig. 1.

TABLE I—EFFECT OF VARYING AMOUNT OF SODIUM HYDROXIDE¹

No.	Ratio $C_6H_4(SO_3Na)_2$: NaOH Moles	Yield of Resorcinol		$C_6H_4(SO_3Na)_2$ Found	
		Grams	Per cent	Grams	Per cent
1.....	1 : 2	0.2397	4.3	8.0450	57.0
2.....	1 : 4	1.5183	27.6	4.0702	28.8
3.....	1 : 6	2.7641	50.2	2.4533	17.4
4.....	1 : 8	2.5290	45.9	1.3473	9.6
5.....	1 : 10	3.0560	55.5	1.2367	8.7
6.....	1 : 12	3.2349	58.8	1.2023	8.5
7.....	1 : 14	3.3080	60.1	1.2607	9.0
8.....	1 : 16	3.4950	63.5	1.1675	8.3
9.....	1 : 20	3.6088	65.6	1.1367	8.0
10.....	1 : 24	3.5763	65.0	1.0692	7.6

¹ 14.1 g. (0.05 mole) of sulfonate were used in each experiment. Fusion temperature 310° C. Time of fusion 2 hrs.

The table shows that a rather large excess of sodium hydroxide over that required by the theory is neces-

FIG. 2—FUSION PERIOD, YIELD CURVES

sary for the best yields of resorcinol, which were obtained when from 20 to 24 moles of sodium hydroxide to 1 mole of sodium benzene *m*-disulfonate were used.

However, it is also evident that almost as good yields were obtained with 14 to 16 moles of sodium hydroxide, and in subsequent fusion experiments the ratio of 1 mole of sodium benzene *m*-disulfonate to 16 of sodium hydroxide was used.

EFFECT OF TIME OF FUSION ON RESORCINOL YIELD—

The results obtained with fusion periods of 1, 2, 3, 4, 6, and 7 hrs. are shown in Table II, and graphically in Fig. 2, Curve c.

TABLE II—EFFECT OF VARYING FUSION PERIOD¹

No.	Time of Fusion Hrs.	Yield of Resorcinol		$C_6H_4(SO_3Na)_2$ Found	
		Grams	Per cent	Grams	Per cent
1	1	3.2674	59.4	1.2114	8.6
2	2	3.4950	63.5	1.1675	8.3
3	3	3.4143	62.0	1.0099	7.2
4	4	3.4462	62.6	1.1497	8.1
5	6	3.4137	62.0	1.0914	7.7
6	7	3.3162	60.3	1.0511	7.5

¹ Ratio $C_6H_4(SO_3Na)_2$: NaOH = 1 : 16 (0.05 mole : 0.8 mole). Fusion temperature 310° C.

This table indicates that the maximum yield of resorcinol was obtained when the fusion was conducted for 2 hrs. A longer fusion period seems not only unnecessary but also quite undesirable.

FIG. 3—FUSION TEMPERATURE, YIELD CURVE

EFFECT OF THE TEMPERATURE OF FUSION ON YIELD OF RESORCINOL—The results of fusions at temperatures of 330°, 350°, 290°, and 270° C. are recorded in Table III, and shown graphically in Fig. 3.

TABLE III—EFFECT OF VARYING TEMPERATURE¹

No.	Temp. of Fusion ° C.	Yield of Resorcinol		$C_6H_4(SO_3Na)_2$ Found	
		Grams	Per cent	Grams	Per cent
1.....	330	3.1293	57.6	1.0030	7.1
2.....	350	2.9341	53.3	1.1850	8.4
3.....	270	2.5296	46.0	3.0807	21.9
4.....	290	3.2637	59.3	1.5501	11.0

¹ Ratio $C_6H_4(SO_3Na)_2$: NaOH = 1 : 16. Fusion period 2 hrs.

It appears from these results that 310° is the best fusion temperature. At 330° and 350° some destruction of resorcinol must have taken place, since the amount of unused sodium benzene *m*-disulfonate present was about the same or even less than that found in the fusion experiment conducted at 310°. At 290° and 270° the lower yields were due to the fact that the reaction had not gone to completion, as indicated by the somewhat higher per cent of sodium benzene *m*-disulfonate present in the fusion mixture, especially in the one where the fusion was conducted at 270°.

Since the results of the previous experiments showed considerable reduction in the yield of resorcinol when the fusion was conducted for 2 hrs. at temperatures below 310° , it was thought that by increasing the fusion period a corresponding increase in the yield of resorcinol might be obtained. Accordingly, the tubes were charged with the amount of sodium benzene *m*-disulfonate and sodium hydroxide used in the previous experiments, and the mixture fused at 270° . At the end of 4, 6, and 8 hrs., respectively, a tube was removed, suddenly cooled with water, and analyzed. An identical experiment was carried out at 290° and the results obtained are given in Table IV, and graphically in Fig. 2, Curves *a* and *b*.

TABLE IV—EFFECT OF VARYING FUSION PERIOD AT 270° AND 290° C.¹

No.	Temp. of Fusion °C.	Yield of Grams	Resorcinol Per cent	C ₆ H ₄ (SO ₃ Na) ₂ Found	
				Grams	Per cent
1.....	270	2.5296	46.0	3.0807	21.9
2.....	270	3.0675	55.7	1.9470	13.8
3.....	270	3.1983	58.1	1.4950	10.6
4.....	270	3.1820	57.9	1.3950	9.9
5.....	290	3.2637	59.3	1.5501	11.0
6.....	290	3.2311	58.7	1.3477	9.5
7.....	290	3.1443	57.1	1.3242	9.4
8.....	290	3.0560	55.5	1.3261	9.5

¹ Ratio C₆H₄(SO₃Na)₂ : NaOH = 1 : 16. Fusion period 2 hrs.

It appears from this table that even with longer fusion periods the yields, although improved, are not quite as good as those obtained at 310° . It is, therefore, reasonable to conclude that 310° is the optimum fusion temperature.

FIG. 4—CONCENTRATION OF WATER AS RELATED TO RESORCINOL YIELD

EFFECT OF WATER IN THE CHARGE UPON THE RESORCINOL YIELD—Since it is a common practice in making alkali fusions of aromatic sulfonic acids to add water to the sodium hydroxide, in order to make the melt less viscid and, therefore, more easily discharged from the fusion kettle, it was considered very important to study the effect of the presence of water upon the yield of resorcinol. The results of experi-

ments in which the amount of water was the only variable are given in Table V and graphically in Fig. 4.

TABLE V—EFFECT OF VARYING AMOUNT OF WATER¹

No.	Amount of Water Added Per cent of Total NaOH Used	Yield of Resorcinol		C ₆ H ₄ (SO ₃ Na) ₂ Found	
		Grams	Per cent	Grams	Per cent
1.....	10	2.8057	51.0	1.3279	9.4
2.....	20	2.4908	45.3	1.2600	9.0
3.....	30	1.9632	35.6	1.2182	8.7
4.....	40	1.4315	26.0	1.4470	10.2
5.....	50	0.7525	13.7	1.9765	14.0

¹ Ratio C₆H₄(SO₃Na)₂ : NaOH = 1 : 16. Temperature 310° C. Fusion period 2 hrs.

It is evident that water tends to cut down the yield of resorcinol. In conducting an alkali fusion of sodium benzene *m*-disulfonate for the production of resorcinol no water should be added, although judging from the nature of the curve from 2 to 4 per cent of water would not greatly reduce the yield. Our results on the effect of water bear out the statement of Binschedler and Busch¹ that the fusion must be conducted with the addition of as "little water as possible."

SUMMARY

Using an apparatus especially designed for carrying out of alkali fusions of aromatic sulfonic acids, a study was made of the various factors affecting the fusion of sodium benzene *m*-disulfonate with sodium hydroxide for the production of resorcinol, including temperature, time, ratio of sodium hydroxide to sodium benzene *m*-disulfonate, and concentration of water in the fusion mixture. The results indicate that 310° is the best fusion temperature, 2 hrs. the best fusion period, 14 to 16 moles of sodium hydroxide to 1 mole of sodium benzene *m*-disulfonate the best fusion mixture, and that water tends to reduce the yield of resorcinol.

THE PREVENTION OF SUGAR DETERIORATION BY THE USE OF SUPERHEATED STEAM IN CENTRIFUGALS

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The deterioration of manufactured cane sugar has been the subject of considerable investigation to which reference has already been made.² Following a study of the most important single group of micro-organisms, the molds, responsible for sugar deterioration, the writer prepared a chart whereby it was possible to predict the keeping quality of a sugar.³ It remained to devise some means of eliminating the causative organisms in order to prevent sugar deterioration. Shorey⁴ and others have suggested the use of superheated steam in the centrifugals, but so far as we have been able to ascertain no controlled experiments have been conducted to test out the efficiency of such an agent. Unfortunately, it was not possible to arrange for an equipment in our sugar house and mill which would permit of such a study, and it was due to Assistant Director W. G. Taggart, who devised an apparatus to be used in the laboratory

¹ Loc. cit.

² Kopeloff and Kopeloff, Louisiana Experiment Station, *Bulletin* 166 (1919).

³ Louisiana Experiment Station, *Bulletin* 170 (1920).

⁴ *J. Soc. Chem. Ind.*, 17 (1898), 555.