The vapor pressure of nonane may be approximated by the following expression (2):

$$\log_{10} P_R'' = 5.22152 - \frac{2571.860}{330.914 + t} \qquad (1)$$

in which P_R'' is the reference pressure in pounds per square inch and t is the temperature in ° F.

The values of vapor pressure determined by Young (6), Wibaut (4, 5), and the authors have been placed on a residual basis by using Equation 1 as a reference. The residual vapor pressures are shown in Figure 2. P'' and P_R'' are the vapor pressure and the reference pressure, respectively. For temperatures below 340° F. all the experimental data agree with Equation 1 within the uncertainty of the respective measurements. At higher temperatures the deviation of the present measurements is more marked. The pairs of points shown from the authors' work represent the extremes of variation of the vapor pressure that were encountered with changes in volume from 0 to 0.3 weight fraction of gas.

LITERATURE CITED

(1) Bridgeman, O. C., J. Am. Chem. Soc., 49, 1174–83 (1927).
(2) Rossini, F. D., "Selected Values of Properties of Hydrocarbons," Washington, D. C., Natl. Bur. Standards, 1947.
(3) Sage, B. H., and Lacey, W. N., Trans. Am. Inst. Mining Met. Engrs., 136, 136–57 (1940).
(4) Wibaut, J. P., Hoog, H., Langedijk, S. L., Overhoff, J., and Smittenberg, J., Rec. trav. chim., 58, 329–77 (1939).
(5) Wibaut, J. P., and Langedijk, S. L., Ibid., 59, 1220–51 (1940).
(6) Young, S., Proc. Roy. Irish Acad., 38B, 65–92 (1928).

Volumetric Behavior of Nitric Acid

H. H. REAMER, W. H. CORCORAN, AND B. H. SAGE

California Institute of Technology, Pasadena, Calif.

NITRIC acid has been the subject of many investigations, only a few of which are mentioned here. Yost and Russell (16) reviewed its physicochemical properties and Taylor (14) reported its fugacity in aqueous solutions. Forsythe and Giauque (3) investigated a number of its thermodynamic properties in aqueous solution. Veley and Manley (15) determined the specific volume and the electrolytic conductance of this compound at atmospheric pressure. Recently Sibbitt et al. (12) summarized the physical properties of concentrated nitric acid and gave some data on the pure compound. This information is primarily related to the behavior of concentrated nitric acid at physical equilibrium. Reference was made to the effect of the relative volume of the gas phase upon the "vapor pressure" at temperatures above 200° F.

Experimental information concerning the volumetric behavior of nitric acid at either physical or chemical equilibrium at elevated pressures did not appear to be available. Volumetric and phase behavior was determined at chemical and physical equilibrium (6) for samples of commercial red and white fuming nitric acid. These measurements indicated a marked effect of small quantities of nitrogen dioxide upon the equilibrium bubble point pressures. For example, a decrease in the weight fraction of nitrogen dioxide from 0.15 to 0.03 resulted in approximately a tenfold increase in bubble point pressure. It was the purpose of the present investigation to determine the volumetric behavior of nitric acid throughout the heterogeneous region from bubble point to a specific volume of 0.2 cubic foot per pound and the characteristics of the condensed liquid for pressures up to 5000 pounds per square inch.

METHODS AND APPARATUS

The equipment used for this investigation was similar, in principle, to that developed by Beattie (1). Its general arrangement is shown schematically in Figure 1.

A sample of nitric acid was confined within a glass piston–cylinder combination at A. This vessel was enclosed within the heavy-walled metal container, B, which was connected through the small steel tubing, D, with the fluid injector, C. A polymerized, fluorinated hydrocarbon filled the space surrounding the glass piston–cylinder combination, A, in the metal vessel, B. The tubing, D, and the injector, C, also were filled with this fluorinated hydrocarbon. The pressure within the system was determined by means of the mercury-in-steel U-tube shown at F. A pressure balance, E (10), in conjunction with the manually operated fluid injector, J, was used to measure the pressure within the fluid-filled portion of the system. J was employed in order to adjust the interfaces in the mercury-in-steel U-tube, F, to a predetermined fixed level.

B was immersed in an agitated silicone bath, I (6, 9), the temperature of which could be controlled within 0.02° F. The lower part of C was immersed in an agitated air bath in order to keep the fluorinated hydrocarbon at a constant temperature
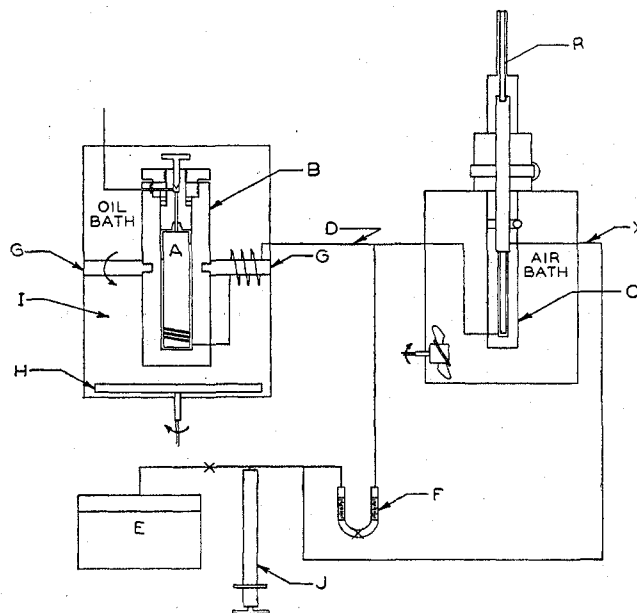

Figure 1. Schematic Diagram of Apparatus

Adjustment of the position of C changed the effective volume of A and thus permitted the equilibrium pressure of the sample of nitric acid to be measured as a function of volume.

A sectional view of B with the glass piston–cylinder combination in place is shown in Figure 2.

Unsupported area seals with lead gaskets were employed at M. The valve assembly, K, and the stem, N, were constructed of titanium for the closure, L. All other parts of the vessel were constructed of stainless steel containing 8% nickel and 18% chromium.

A was attached to valve K by means of stem N. The glass was kept sealed against the lower part of this stem by means of the spring, O. The tapered joint between N and A remained relatively free of leaks throughout a wide range of temperatures. Vessel B of Figure 2 was connected to injector C of Figure 1 by means of stainless steel tubing with an outside diameter of 0.072 inch and a wall thickness of 0.009 inch. The tubing was arranged in a spiral in order to allow B to be oscillated mechanically about the axis GG of Figure 1. For some of the measurements a glass ball was placed in A in order to provide additional agitation of the contents of the equilibrium chamber.

The agitated silicone bath, I, of Figure 1 was provided with an adiabatic radiation shield (6, 9) in order to decrease thermal transfer from the bath. Agitation was provided by means of the centrifugal impeller, H, located in the lower part of the bath.

Figure 2. Details of Equilibrium Chamber

It was found (7, 11) that variations in temperature from one part of the bath to another were less than 0.03° F. and that the variation in temperature with time at one point was less than 0.005° F. The temperature was measured with a platinum resistance thermometer of the strain-free type (5). A similar instrument controlled the temperature through a modulating electronic circuit (8, 11). A review of the characteristics of the temperature-measuring and control circuits and their calibration leads to the conclusion that the temperature of the contents of vessel A was known with a probable error of 0.02° F. relative to the international platinum scale.

The pressure within the piston-cylinder combination was measured by means of a balance (10) which had been calibrated against the vapor pressure of purified carbon dioxide at the ice point (2). The mercury-in-steel U-tube, F, Figure 1, was provided with an electrical contact so that the level of the mercury-oil interface could be reproduced within small limits by adjustment of the displacement cylinder, J. A review of the calibration and reproducibility of the balance indicates that the pressure of the fluid surrounding A was known within 0.1 pound per square inch or 0.05%, whichever was the larger measure of uncertainty. The glass piston-cylinder combination did not introduce an added uncertainty of more than 0.2 pound per square inch in the measurement of pressure of the sample within it.

Some of the details of injector C of Figure 1 are evident in the shortened sectional view of Figure 3.

The position of the plunger, S, was controlled by means of the large lead screw, V, and nut assembly shown in the central part of the figure. The worm was driven by a motor through an appropriate gear reduction unit and a counter was attached which permitted the position of plunger S to be determined with accuracy.
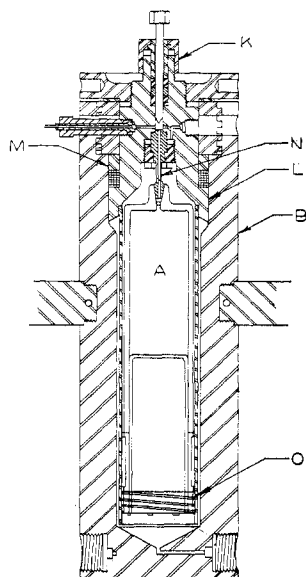
For calibration the actual relative movements of S and C were determined by use of a cathetometer which established the relative position of the reference member, R, to its surrounding case, B'. This case was connected directly to the lower part of C by means of the unstressed rods,. Such an arrangement permitted a check upon the deformation of the gear housing as a result of stress when the equipment was operated at high pressure.

A compensated packing shown at T in Figure 3 was interconnected, by means of the small tubing, X, depicted in Figures 1 and 3, with the oil-filled system leading to the pressure balance, E, of Figure 1. Polymerized, fluorinated hydrocarbon was used in the injector and no difficulties were experienced in obtaining a quantitatively tight system. The agitated air bath which surrounded C, as shown in Figure 1, was maintained at a constant temperature of 100° F. with a variation of less than 0.1° F.

Experience with the equipment indicated that the variations in temperature of the liquid-filled portions of the system contributed less than 0.1% uncertainty in the predicted volume of the sample within A of Figure 1. It was not found necessary to make a correction for deviation in the linear variation of displaced volume with change in counter reading for these measurements. Calibrations indicated that such effects were much less than 0.1% even at the highest pressures investigated.

In order to establish the volume of the sample in cylinder A of Figure 1 as a function of temperature and pressure, direct calibration was employed. The equilibrium chamber was filled with a known weight of water and the readings of the counter were determined as a function of pressure for three different temperatures. These measurements were repeated with a second and somewhat different weight of water sample. From these two series of measurements and the volumetric data of Smith and Keyes (4, 13) the necessary small corrections were calculated for the effects of pressure and temperature upon the counter readings for a fixed quantity of the fluorinated hydrocarbon in the system. In addition, these two sets of measurements established the volumetric behavior of the fluorinated hydrocarbon. The details of such calculations have been described by Beattie (1) and others (10). The volumetric behavior of the fluorinated hydrocarbon
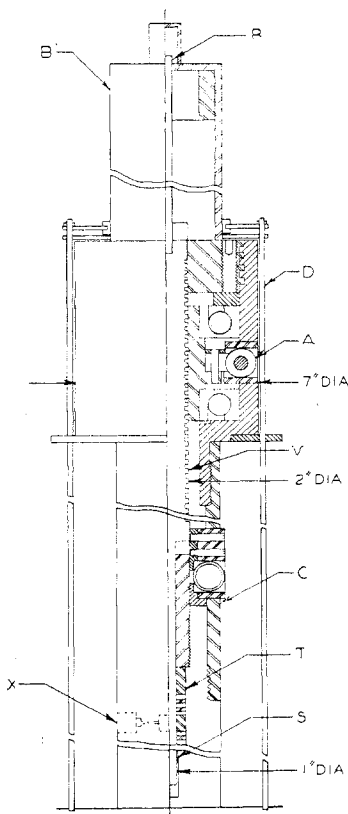

Figure 3. Sectional View of Injector

is recorded in Table I. The sample was obtained from Hooker Electrochemical Co. under the trade name of Fluorolube and had a viscosity of 243 centistokes at a temperature of 100° F. and atmospheric pressure.

In the present study the total quantity of fluorinated hydrocarbon in the system for a particular measurement was determined from a knowledge of the quantity of pure nitric acid added to the equilibrium chamber and measurements of counter reading as a function of pressure at a temperature of 70° F. Extrapolation of these measurements to atmospheric pressure permitted

TABLE I. SPECIFIC VOLUME OF A POLYMERIZED, FLUORINATED HYDROCARBON

Pressure, Lb./Sq. Inch Abs.	Specific Volume, Cu. Feet/Lb. × 10³						
	70° F.	100° F.	160° F.	190° F.	220° F.	280° F.	340° F.
0	8.167[a]	8.282	8.507	8.620	8.735	8.963	9.189
200	8.161[a]	8.275	8.497	8.612	8.725	8.951	9.176
400	8.155[a]	8.269	8.491	8.603	8.715	8.940	9.163
600	8.150[a]	8.262	8.482	8.594	8.706	8.929	9.151
800	8.144[a]	8.256	8.474	8.585	8.696	8.918	9.138
1000	8.138[a]	8.249	9.466	9.577	9.687	8.905	9.125
1250	8.132[a]	8.242	8.456	8.566	8.675	8.892	9.109
1500	8.128[a]	8.234	8.446	8.555	8.663	8.878	9.093
1750	8.118[a]	8.226	8.437	8.544	8.651	8.864	9.077
2000	8.111[a]	8.218	8.427	8.534	8.639	8.850	9.061
2250	8.105[a]	8.210	8.417	8.523	8.628	8.836	9.045
2500	8.098[a]	8.202	8.408	8.513	8.616	8.822	9.030
2750	8.091[a]	8.194	8.398	8.502	8.604	8.809	9.014
3000	8.089[a]	8.186	8.388	8.492	8.593	8.795	8.998
3500	8.071[a]	8.171	8.368	8.470	8.570	8.767	8.967
4000	8.057[a]	8.155	8.350	8.449	8.546	8.741	8.936
4500	8.044[a]	8.139	8.331	8.428	8.523	8.714	8.904
5000	8.031[a]	8.125	8.312	8.407	8.500	8.687	8.874

[a] Actual specific volume = 0.008167 cu. foot/lb.

the quantity of fluorinated hydrocarbon to be determined from the calibrations described and from the volume of nitric acid added.

INTRODUCTION OF SAMPLE

The sample of pure nitric acid was introduced into the glass piston–cylinder combination, A of Figure 1, by the equipment shown in Figure 4. A was connected to the glass equipment by means of titanium-to-glass tapered seals, Q. Glass tubing led from this seal to the calibrated cylindrical vessel, Y, which was provided with a frangible glass tip, Z. The entire assembly was evacuated to a pressure less than 0.0001 pound per square inch through tubing W. This pressure was determined with a conventional McLeod gage. The special valve and tubing W adjacent to Q and valve K were closed and Z was broken. After physical equilibrium had been obtained, the elevation of the acid in vessel Y was determined with a cathetometer, and the desired quantity of acid was introduced into A by opening valve K. The change in level of the acid in Y was determined with this cathetometer and the temperature was noted. Y was calibrated by determining the weight of mercury withdrawn from it as a function of the elevation of the interface as measured from an established reference. A comparison of calibration and a gravimetric check of the quantity of acid withdrawn between known levels indicated a probable error of 0.2% in the weight of acid added.

After the introduction of the acid and closing of K, the entire upper part of B was flushed with water through tubing seals Q around the stem of the valve. This flushing was necessary in order to avoid corrosion of the metal parts during subsequent use of the apparatus. No difficulty developed in introducing the nitric acid by the above described procedure; nor was there significant corrosion of the metal parts of the equipment.
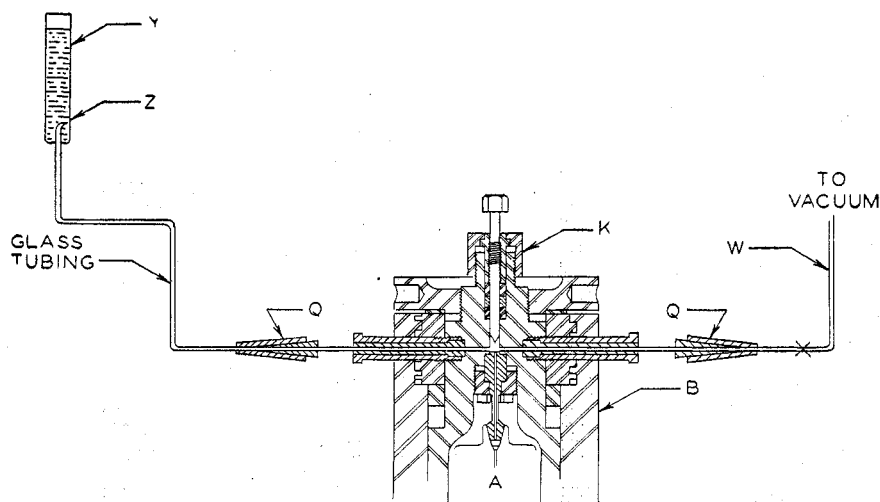
MATERIALS

The nitric acid employed in these studies was prepared from recrystallized potassium nitrate and pure sulfuric acid in accordance with the procedures described by Forsythe and Giauque (3). The nitric acid was recovered by distillation and was condensed at a pressure of less than 0.01 inch of mercury at liquid air temperature. The purified acid had a specific weight of 94.188 pounds per cubic foot at 70° F. and atmospheric pressure, which may be compared with a value of 94.250 pounds per cubic foot determined by Veley and Manley (15) for the same state. The specific conductance of samples prepared in the same fashion was 3.77 reciprocal ohms at 32° F. (9). These measurements indicated that there was less than 0.005 weight fraction of materials other than nitric acid in the sample.

BEHAVIOR AT PHYSICAL EQUILIBRIUM

The volumetric behavior of two samples of nitric acid which were prepared independently was studied at physical equilibrium for temperatures of 70° and 100° F. The results of these measurements are shown in Figure 5 as a function of pressure. It was
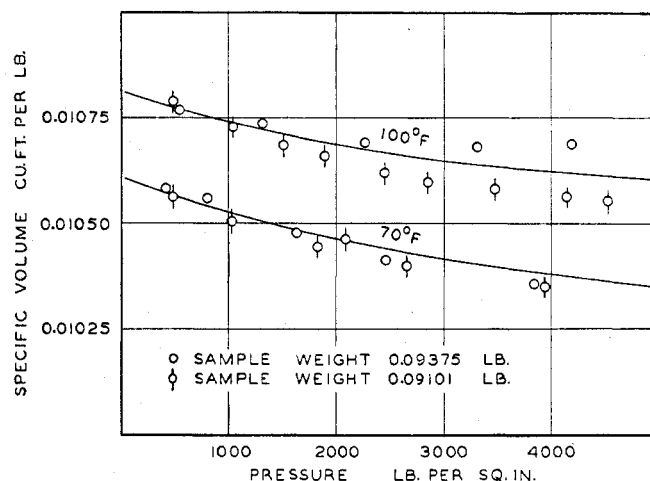
Figure 5. Specific Volume of Nitric Acid in the Liquid Phase at Physical Equilibrium

not possible to measure the low bubble point pressure, as at these temperatures it was a function of time. Such behavior indicated that small changes in chemical composition were occurring even at these relatively low temperatures. The reaction rate at 70° and 100° F. was not great enough to result in a detectable change in the specific weight of the liquid phase during the period of these measurements. The standard deviation from the smoothed curves of the experimental measurements on both samples was 0.00002 cubic foot per pound. It is believed that the specific volumes recorded in Table II do not involve a standard error greater than 0.0004 cubic foot per pound.

BEHAVIOR AT PHYSICAL AND CHEMICAL EQUILIBRIUM

It was found that the system approached physical equilibrium within a few minutes, but that at a temperature of 190° F. a longer period was required to reach chemical equilibrium. Figure 6 depicts the specific volume of two samples of nitric acid at physical and chemical equilibrium for six
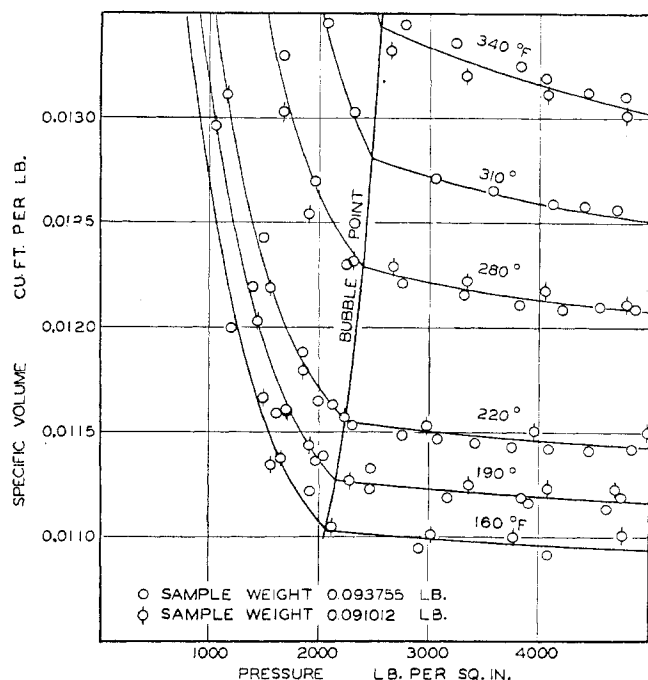
Figure 4. Equipment for Introduction of Nitric Acid

Figure 6. Specific Volume of Nitric Acid near Bubble Point at Physical and Chemical Equilibrium
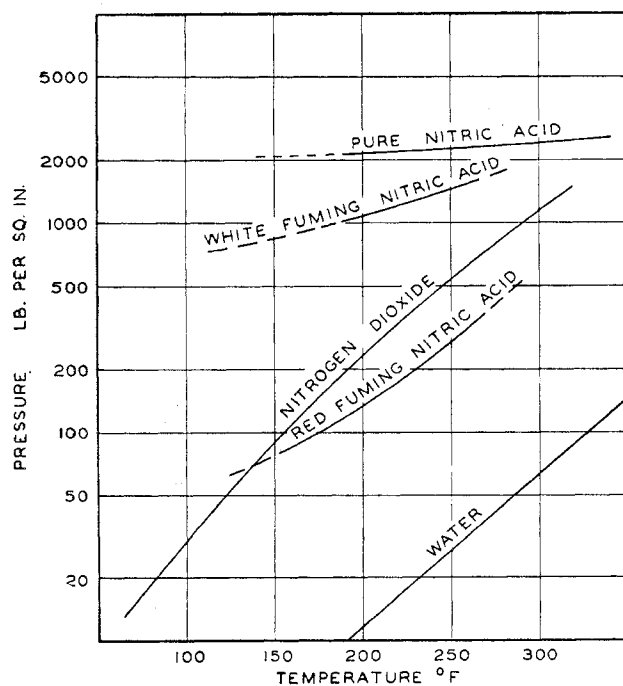
Figure 8. Bubble Point Pressures in the Nitric Acid–Nitrogen Dioxide–Water System

Figure 7. Specific Volume of Nitric Acid in the Heterogeneous Region at Physical and Chemical Equilibrium

cedure was desirable, as the absolute uncertainty within which the weight of the small sample could be directly determined was larger than that realized by this comparison procedure. The standard deviation of the experimental measurements for the two larger samples which are shown in both Figures 5 and 6 was 0.000026 cubic foot per pound. This deviation is slightly larger than that found for nitric acid at physical equilibrium.

Table III records the specific volume of nitric acid at physical and chemical equilibrium for temperatures between 160° and 340° F. The data for specific volumes less than twice that at bubble point do not involve standard errors greater than 0.00005 cubic foot per pound. However, at larger specific volumes the standard error may be as large as 2% of the value recorded. The equilibrium bubble point pressures for each of the temperatures investigated were included in this table. The effect of temperature upon bubble point pressure is shown in Figure 8. The bubble point pressures of nitrogen dioxide (11), of water (4), and of red and white fuming nitric acid (6) were included in this diagram. The white fuming nitric acid contained 0.0337 weight fraction of nitrogen dioxide, whereas the red fuming nitric acid contained 0.1430 weight fraction of nitrogen dioxide. For tem-

temperatures near bubble point. Many of the points shown were taken upon increase and others upon decrease of the total volume of the system. The volumetric behavior at 190° F. was reproduced with negligible differences from the original measurements after studies at higher temperatures were completed. The volumetric behavior at larger specific volumes for four temperatures between 190° and 340° F. is shown in Figure 7. In this figure the characteristics of a third much smaller sample have been included, so that the behavior at higher specific volumes might be measured. The weight of the small sample was established by comparison with the volumetric behavior of the larger samples. This pro-
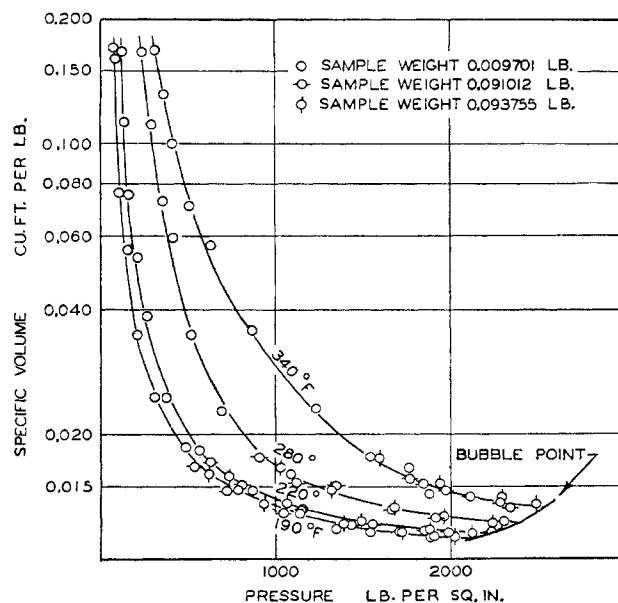
TABLE II. SPECIFIC VOLUME OF NITRIC ACID AT PHYSICAL EQUILIBRIUM

Pressure, Lb./Sq. Inch Abs.	Specific Volume, Cu. Foot/Lb.	
	70° F.	100° F.
0	....	....
200	0.010591	0.010799
400	0.010575	0.010780
600	0.010559	0.010769
800	0.010545	0.010755
1000	0.010529	0.010743
1250	0.010510	0.010729
1500	0.010494	0.010716
1750	0.010479	0.010702
2000	0.010464	0.010691
2250	0.010451	0.010679
2500	0.010439	0.010667
2750	0.010428	0.010658
3000	0.010417	0.010649
3500	0.010398	0.010634
4000	0.010380	0.010621
4500	0.010365	0.010612
5000	0.010354	0.010608

TABLE III. SPECIFIC VOLUME OF NITRIC ACID AT PHYSICAL AND CHEMICAL EQUILIBRIUM

Pressure, Lb./Sq. Inch Abs.	Specific Volume, Cu. Foot/Lb.					
	160° F.[a] (2054)[b]	190° F. (2148)	220° F. (2234)	280° F. (2391)	310° F. (2463)	340° F. (2535)
Bubble point	0.011028	0.011273	0.011557	0.012289	0.012813	0.013453
0	...	...	...	...	...	...
200	...	0.03680	0.05380	...	...	...
400	...	0.02115	0.02358	0.05965	...	...
600	...	0.01641	0.01770	0.02725	...	0.06165
800	0.01340	0.01411	0.01509	0.01995	...	0.03995
1000	0.01260	0.01312	0.01379	0.01665	...	0.02955
1250	0.01199	0.01237	0.01285	0.01490	...	0.02230
1500	0.01158	0.01185	0.01223	0.01385	0.01548	0.01815
1750	0.01128	0.01153	0.01185	0.01305	0.01424	0.01590
2000	0.01110	0.01137	0.01165	0.01261	0.01355	0.01469
2250	0.011022	0.011266	0.011549	0.01237	0.01308	0.01400
2500	0.011009	0.011251	0.011531	0.012276	0.012809	0.01355
2750	0.010998	0.011238	0.011515	0.012246	0.012763	0.013403
3000	0.010989	0.011224	0.011501	0.012214	0.012720	0.013346
3500	0.010974	0.011207	0.011474	0.012177	0.012649	0.013243
4000	0.010959	0.011191	0.011458	0.012134	0.012587	0.013162
4500	0.010947	0.011178	0.011437	0.012105	0.012540	0.013088
5000	0.010939	0.011168	0.011426	0.012080	0.012509	0.013026

[a] Volumes at 160° F. are extrapolated.
[b] Figures in parentheses are bubble point pressures expressed in lb./sq. inch.

peratures between 70°. and 300° F. the bubble point pressure at physical and chemical equilibrium of the sample of red fuming nitric acid was less than that of nitrogen dioxide.

The mixtures shown in Figure 8 may be treated as a part of the ternary system nitric acid–nitrogen dioxide–water. The relative quantities of each of the molecular species can be described in terms of the fraction of each of these three components. There exist substantial quantities of oxygen, oxides of nitrogen, and water when a sample of pure nitric acid is brought to physical and chemical equilibrium.

RATES OF ATTAINMENT OF EQUILIBRIUM

At temperatures below 160° F. the rates of attainment of equilibrium for pure nitric acid were too low for effective investigation with the equipment available, but at 160° and 190° F.
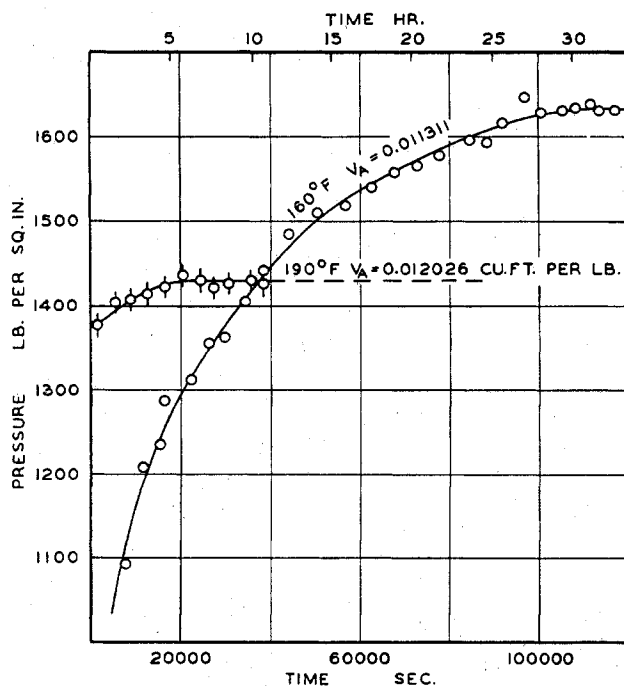
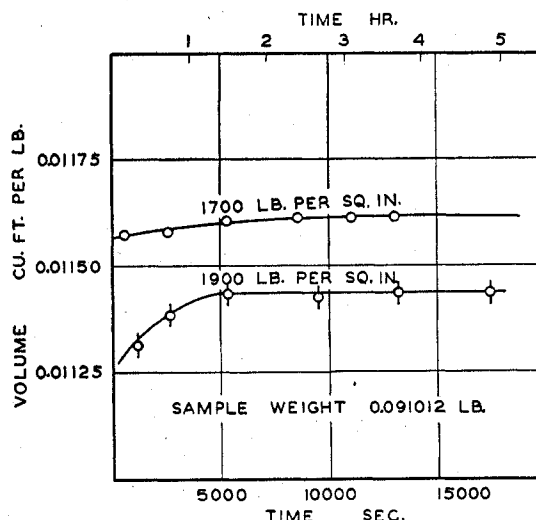Figure 9. Pressure as a Function of Time under Isochoric Conditions

Figure 10. Specific Volume as a Function of Time under Isobaric Conditions at 190° F.

equilibrium could be reached in a day or two. Figure 9 shows the pressure at physical equilibrium as a function of time at a constant specific volume, V_A, of the heterogeneous system for temperatures of 160° and 190° F. Chemical equilibrium is approximated at 160° F. in 18 hours, whereas only 2 hours are required to reach the same approach to equilibrium at 190° F. Similar information is presented in Figure 10 for an approach to equilibrium under isobaric conditions. In this instance the specific volume was indicated as a function of time for pressures of 1700 and 1900 pounds per square inch. The time reference was taken as that at which the sample reached the indicated temperature. During all the nonequilibrium measurements reported in Figures 9 and 10 the sample was agitated in order to assure a close approximation to physical equilibrium between the phases.

DISCUSSION

The marked difference in behavior of nitric acid under conditions at physical equilibrium and those obtained under both physical and chemical equilibrium is apparent from this work. Sibbitt et al. (12) reported a vapor pressure of 24.8 pounds per square inch at a temperature of 212° F. at physical equilibrium. For the same temperature, experimental data at physical and chemical equilibrium indicate a bubble point pressure of 2211 pounds per square inch. The time required below 160° F. to obtain pressures at chemical equilibrium was such as to preclude their effective measurement with the present equipment.

To establish the equilibrium pressures that would be achieved in the storage of nitric acid at various ullages and temperatures below 160° F., it is believed that extrapolation of the present data may be employed. Such a procedure shows that bubble point pressures many times those of the vapor pressures of nitric acid at physical equilibrium prevail throughout the change of temperatures of interest in the storage of this compound. The slow rate of attainment of equilibrium probably will permit the effective venting of isochoric storage vessels without difficulty, and the gradual accumulation of oxides of nitrogen in the acid as decomposition proceeds under vented conditions probably will decrease the equilibrium bubble point pressure of the liquid remaining.

LITERATURE CITED

(1) Beattie, J. A., Proc. Am. Acad. Arts Sci., 69, 389–405 (1934).
(2) Bridgeman, O. C., J. Am. Chem. Soc., 49, 1174–83 (1927).
(3) Forsythe, W. R., and Giauque, W. F., Ibid., 64, 48–61 (1942).
(4) Keenan, J. H., and Keyes, F. G., "Thermodynamic Properties of Steam," New York, John Wiley & Sons, 1936.

(5) Myers, C. H., *J. Research Natl. Bur. Standards*, **9**, 807–15 (1932).

(6) Reamer, H. H., Mason, D. M., and Sage, B. H., IND. ENG. CHEM., **45**, 1094–7 (1953).

(7) Reamer, H. H., and Sage, B. H., *Ibid.*, **44**, 185–7 (1952).

(8) Reamer, H. H., and Sage, B. H., *Rev. Sci. Instr.*, **24**, 362–6 (1953).

(9) Robertson, G. D., Jr., Mason, D. M., and Sage, B. H., IND. ENG. CHEM., **44**, 2928–30 (1952).

(10) Sage, B. H., and Lacey, W. N., *Trans. Am. Inst. Mining and Met. Engrs.*, **136**, 136–57 (1940).

(11) Schlinger, W. G., and Sage, B. H., IND. ENG. CHEM., **42**, 2158–63 (1950).

12) Sibbitt, W. L., St. Clair, C. R., Bump, T. R., Pagerey, P. F.,

Kern, J. P., and Fyfe, D. W., Natl. Advisory Comm. Aeronaut., *Tech. Note* **2970** (1953).

(13) Smith, L. B., and Keyes, F. G., *Proc. Am. Acad. Arts Sci.*, **69**, 285–312 (1934).

(14) Taylor, G. B., IND. ENG. CHEM., **17**, 633–5 (1925).

(15) Veley, V. H., and Manley, J. J., *Phil. Trans. Roy. Soc. (London)*, **A191**, 365–98 (1898).

(16) Yost, D. M., and Russell, H., Jr., "Systematic Inorganic Chemistry," New York, Prentice-Hall, Inc., 1944.

Thermal Cracking of Alkyl Phenols

CONVERSION OF HIGH BOILING PHENOLS

B. W. JONES AND M. B. NEUWORTH

Research and Development Division, Pittsburgh Consolidation Coal Co., Library, Pa.

INCREASING demand for phenol and its alkylated derivatives has prompted consideration of new sources of supply for these chemicals. Synthesis of phenol from benzene has satisfied a large part of the increased consumption in recent years and undoubtedly will continue to do so as long as adequate supplies of the hydrocarbon are available. The production of *p*-cresol from isopropyltoluene is growing in industrial importance, but developments such as this are not likely to lessen the demand for the other cresol isomers and cresylic acids.

In a previous publication (*2*), data were presented for the rates of cracking of a number of model alkyl phenols together with the product distributions. The study indicated that low boiling phenols produced during carbonization of coal resulted from thermal dealkylation of higher boiling types. In this paper, the results of an investigation of the thermal cracking of high boiling phenols from low temperature tar are presented.

A review of the literature shows that no systematic study has been made in which the thermal cracking variables have been correlated with yield and composition of the cracked products. Sensemann (*5*) made some cracking experiments with coal tar acids from Scotch blast furnace tar in an apparatus similar to the one used in this laboratory, except that no steam dilution was used. The practicability of the method that he used is in doubt because of the deposition of considerable pitch and carbon in the reactor, resulting in plugging. A similar approach was made by Katkovskil *et al.* (*3*) who cracked a 230° to 300° C. fraction of high boiling tar acids at 600° to 675° C. in the presence of superheated steam. They obtained maximum yields of 10% of lower boiling tar acids, but they did not explore the possibilities of short residence time.

The design and operation of the cracking unit have been described (*2*).

MATERIALS

High boiling phenols were prepared from the tar produced in the Disco process of low temperature carbonization of bituminous coal (*4*). Three phenolic fractions were selected for study as feedstocks to the cracking unit. The atmospheric distillation range of each sample was as follows: 230° to 260° C., 260° to 300° C., and 230° to 300° C.

Precautions were taken in the preparation of the feedstocks to exclude all phenols boiling below 230° C. This was done by efficient fractional distillation at 50 mm. by removal of any distillable product boiling below 147° C. Since the highest boiling xylenol isomer boils at 225° C. at 760 mm. or 142° C. at 50 mm., the feedstocks contained only traces of xylenols.

CRACKED-PRODUCT ANALYSIS

Cracked-product analysis followed a conventional pattern. After separation of the water and organic layers, the water and contents of the dry ice traps were extracted exhaustively with ethyl ether. The ether extract was freed of ether in an efficient column. The solvent-free extract was combined with the previously separated organic phase and vacuum distilled in a Claisen flask to determine nondistillable residue. The distillate from this separation was then distilled analytically under vacuum in a Cannon packed column 1.9 × 100 cm. and carried to a vapor temperature of 147° C. at 50 mm.

The distillate from this step, containing a mixture of low boiling phenols and hydrocarbons, was analyzed for total phenols by determination of the loss in weight on extraction with 10% sodium hydroxide. The distillate was diluted about twofold with Decalin prior to the extraction step to reduce contamination of the caustic soda extract. In cases where the composition of the low boiling phenolic mixture was to be determined it was recovered from solution in caustic soda by springing with 30% sulfuric acid followed by separation from the sulfate liquor.

EFFECT OF TEMPERATURE, RESIDENCE TIME, AND STEAM DILUTION

THERMAL CRACKING OF 230° to 260° C. PHENOLIC FRACTION. The effect of cracking temperature was studied by making three cracking runs on a once-through basis at temperatures of 746°, 775°, and 850° C. with a phenolic feedstock boiling from 230° to 260° C. The results are shown in Table I. Residence time was held at 0.05 second and ratio of steam to feedstock was held constant at 1.7.

Aside from the deeper levels of cracking obtained with an increase in temperature, it is significant that a greater destruction of the hydroxyl group occurs resulting in an increase in low boiling neutral hydrocarbons. The optimum conversion to low boiling phenols occurred in the temperature range of 750° to 775° C.

Using the same feedstock, three runs were carried out at residence times of 0.05, 0.08, and 0.15 second at 746° C. and steam to feedstock ratio of 1.7 in all cases. The results are summarized in Table I. An increase in residence time results in increased cracking levels, although this effect was not so pronounced as the effect of cracking temperature over the range explored in this study.

Three runs were made to check the effect of steam to feedstock ratio. The cracking temperature was held at 746° C. and resi-