detrimental effect upon the oil and should be removed as far as possible.

The above analysis would seem to indicate that the chief difference between the Californian and Australian oils is in the exceedingly high content of pinene found in the Californian oil; this would account for the high rotation and low specific gravity of this oil. In order to determine the effect of the pinene upon the solubility in alcohol, pure pinene and cineol were mixed in definite proportions and the solubility in alcohol determined. Fig. III shows the effect of varying concentrations of pinene upon the solubility of cineol. It is readily seen that above certain percentages of pinene the mixture would become practically insoluble in 70 per cent alcohol.

SUMMARY

The above investigation has brought out the following facts:

I—The oil from the *Eucalyptus globulus*, from trees grown in California, has the same constituents as the oil of the Australian trees but in different proportions.

II—The reason why the Californian oil does not fulfil the U. S. P. requirements is probably due in great part to the exceptionally high pinene content.

Since Eucalyptus oil could be easily produced in large quantities in various parts of California and other Pacific coast states, a method of refining the oil so as to bring it up to the U. S. P. specifications would be particularly valuable. The investigation is being continued by the present authors with this idea in view.

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THE SEPARATION OF GASES BY FRACTIONAL DISTILLATION IN A VACUUM AT LOW TEMPERATURES¹

By G. A. BURRELL AND I. W. ROBERTSON

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The authors have separated many gaseous mixtures by means of fractional distillation in a vacuum at low temperatures, and have found the method useful, accurate and applicable to a wide range of mixtures. Some of the latter are impossible to separate by other methods and some are exceedingly difficult. Hence there is presented in this paper a summary of the results so far obtained, with a discussion of the application of the method to mixtures other than those experimented with. To date three papers on the subject have been presented by the Bureau, as follows:

1—Gas analysis by fractional distillation at low temperatures.² In this paper was shown the separation of the paraffin hydrocarbons in natural gas.

2—The separation of the illuminants of mixed coal and water gas.³ In this paper was shown the method of separating the paraffin hydrocarbons, olefine hydrocarbons and benzene in mixed coal and water gas.

3—The determination of gasoline vapor in air.⁴

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² J. A. C. S., **36** (1914), 1537.

³ THIS JOURNAL, **7** (1915), 17.

⁴ *Ibid.*, **7** (1915), 112.

In this paper was shown a method for separating gasoline vapor from air.

PARAFFIN HYDROCARBONS—Any combination of the gaseous hydrocarbons, methane, ethane, propane and the two butanes, can be separated by first liquefying the mixture at the temperature of liquid air, removing the methane at that temperature, the ethane at a temperature not higher than -140° C., the propane at a temperature not higher than -120° C., the butanes at a temperature not higher than -95° C. leaving the pentanes or higher paraffins as a final residue.

OLEFINE HYDROCARBONS—Any combination of the gaseous olefine hydrocarbons, ethylene, propylene, and the butylenes, can be separated. The ethylene can be removed at a temperature not higher than -140° C., the propylene at a temperature not higher than -120° C., leaving the butylenes as a residue.

PARAFFIN AND OLEFINE HYDROCARBONS—Any combination of the paraffin and olefine gaseous hydrocarbons can be separated. The methane can be removed at the temperature of liquid air. The ethane and ethylene can be removed at a temperature not higher than -140° C. The propylene and propane can be removed at a temperature not higher than -120° C., leaving the butanes and butylene as a residue. The pairs of constituents can be analyzed as such by combustion in oxygen, and from this data the percentage of each one determined. The authors have separated ethylene and ethane, boiling point only 10° C. apart, but the operation is too tedious to be of practical value.

BENZENE VAPOR in air or in mixture with other gases, such as coal gas, can be separated at the temperature of liquid carbon dioxide (-78° C.). In the case of benzene vapor and other gases that represent the final or the only separation desired in mixtures, it is most convenient to measure their pressure after the removal of the other constituents. The volume present can be calculated from this pressure. For instance in the case of benzene vapor in air or coal gas, the mixture is introduced into the liquefaction bulb at atmospheric pressure. It is then cooled by surrounding the liquefaction bulb with liquid carbon dioxide and removing as much gas as is possible with a vacuum pump. Next the stopcock on the liquefaction bulb is closed, the refrigerant removed, and the pressure of the benzene read on a manometer attached to the liquefaction bulb. If a represents the pressure of the atmosphere and b the partial pressure of the benzene vapor, the percentage of benzene by volume becomes $100\ b/a$: water vapor is removed by absorbing same in phosphorus pentoxide.

GASOLINE VAPOR IN AIR—It was found necessary to adopt a temperature lower than that of liquid carbon dioxide in order to separate gasoline vapor from air, hence liquid air was used since it has to be used and time is consumed in obtaining temperatures between those of liquid carbon dioxide and liquid air. The partial pressure of the gasoline is determined in the same way as is that of the ben-

zene. From the partial pressure of the gasoline its volume is computed.

WATER VAPOR IN AIR can be determined in the same manner as gasoline or benzene vapor. A temperature of -78°C . (the temperature of liquid carbon dioxide) can be employed. At this temperature the vapor pressure of ice is practically nil.

APPLICATION OF METHOD TO OTHER MIXTURES—Aside from the separation of natural gases, illuminants in coal gas, gasoline, benzene and water vapor in air, the method should be useful in examining the various mixtures produced in the destructive distillation of different fuels, concerning which a large amount of experimental work is performed each year. The authors are coöperating with Dr. W. F. Rittman, of the petroleum laboratory of the Bureau, in the cracking of oils. The different gases produced by cracking oils and the pure liquid paraffins are being examined by the method of fractional distillation. In this way facts of fundamental importance regarding the "cracking" of oils will be learned.

In the case of fractional distillation of liquids at ordinary or elevated temperatures, the distillations have to be repeated several times in order to obtain the different fractions in a fairly free condition. The same is true of the fractional distillation of gases in a vacuum at low temperatures. The Bureau has redistilled some fractions four and five times to obtain gases that were analytically pure.

The apparatus required is such as can be easily obtained by many laboratories. A vacuum pump for withdrawing the gases, glass vessels for trapping them, a gas burette for measuring them, and pentane thermometers for measuring temperatures are easily procurable. Liquid air can be obtained at several different places in the United States, and liquid carbon dioxide in all large cities. The only special part of the apparatus is the liquefaction bulb and this is very simple. Precise thermometric measurements are not necessary and pentane thermometers accurate to 1 or 2°C . can be used.

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A RAPID METHOD OF FRACTIONATING GASES AT LOW TEMPERATURES¹

By G. A. BURRELL AND I. W. ROBERTSON

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In this paper is shown a more rapid method of fractionating gases in a vacuum at low temperatures than hitherto used by the Bureau of Mines. The particular gas worked with was the artificial illuminating gas of New York City.

In previous experiments the authors continued to refractionate a particular fraction until the gases obtained were analytically pure. For instance, in working with natural gas, the first distillate was obtained at the temperature of liquid air. The distillate and residue were then refractionated until methane and

nitrogen were obtained pure. The same procedure was followed in fractionating coal gas. At the temperature of liquid air, the first fraction consisted of methane, nitrogen, carbon monoxide, hydrogen, and oxygen with small quantities of ethane and ethylene. Also the residue contained some of the five gases first mentioned. Hence the distillate and residue were refractionated until the distillate was freed of ethane and ethylene, and none of the five gases remained in the final residue.

The procedure now adopted, which is faster and more economical of liquid air, consists, in the case of coal gas, for instance, of first removing as much gas as possible at the temperature of liquid air. Call this fraction *A*. The residue is then subjected to distillation at a temperature not higher than -140°C . Call the distillation so obtained *B*. Next fractionate the residue from *B* at a temperature not higher than -120°C . Call the distillate so obtained *C*. Then fractionate the residue from *C* at a temperature not higher than -78°C . and call the distillate so obtained *D*. There are thus obtained four fractions, *A*, *B*, *C* and *D*, each containing some gases that belong properly to other fractions and which must be purified by further fractionating. As each distillate was obtained it was removed from the pump and transferred to another container. The residue in each case was left in the liquefaction bulb. For instance, after the first distillate was removed (at the temperature of liquid air), the liquid air was removed and the bulb surrounded with light gasoline of a temperature not higher than -140°C ., and so on.

The following data show the results of fractionating the artificial illuminating gas of New York City:

FRACTIONATION ANALYSIS OF NEW YORK ILLUMINATING GAS	
Original volume of gas.....	Cc. 1007.6
CO ₂ removed by caustic potash.....	32.3
Volume taken for fractionation.....	975.3
975.3 cc. Liquefied at temperature of liquid air	
<i>A</i> —Distillate 817.4 cc.	Residue 157.9 cc. Liquefied at -140°C .
<i>B</i> —Distillate 106.5 cc.	Residue 51.4 cc. Liquefied at -120°C .
<i>C</i> —Distillate 25.3 cc.	Residue 26.1 cc. Liquefied at -78°C .
<i>D</i> —Distillate 13.8 cc.	12.3 cc.

The above diagram shows the method of obtaining the first four distillates, *A*, *B*, *C* and *D*. Next the distillate *A* was reliquefied at the temperature of liquid air and the distillate from it removed. The residue, which was very small, was left in the liquefaction bulb and the distillate *B* added to it. The latter was then refractionated at a temperature not higher than -140°C . The distillate and residue so obtained were both refractionated again, because the pressure manometer showed that one fractiona-

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