THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

EQUILIBRIUM WATER CONTENTS OF NATURAL GAS DEHYDRATED BY AQUEOUS DIETHYLENE AND TRIETHYLENE GLYCOL SOLUTIONS AT VARIOUS TEMPERATURES AND PRESSURES

A THESIS

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

By

FRANCIS MARK TOWNSEND

Norman, Oklahoma

1955

Downloaded from SHAREOK. Persistent Handle URL: https://hdl.handle.net/11244/154

EQUILIBRIUM WATER CONTENTS OF NATURAL GAS DEHYDRATED BY AQUEOUS DIETHYLENE AND TRIETHYLENE GLYCOL SOLUTIONS AT VARIOUS TEMPERATURES AND PRESSURES

APPROVED BY

R L Huntington

L O Reid

C. M. Sliepcevich

H H Rowley

T. O. Tuckard

THESIS COMMITTEE

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to:

Dr. R. L. Huntington, School of Chemical Engineering, University of Oklahoma, for supervision of this investigation and for many helpful suggestions during the course of this work.

Professor L. S. Reid, School of Chemical Engineering, University of Oklahoma, for direction of this work, and for his advice and encouragement.

Dr. L. F. Albright, School of Chemical Engineering, University of Oklahoma, for his constructive criticism.

Mr. J. J. Fox and Mr. E. G. Hopkins for their assistance in obtaining materials and construction of equipment.

Black, Sivalls, and Bryson, Inc., whose research fellowship grant supported a substantial portion of this project.

Carbide and Carbon Chemicals Corporation for contributing the glycols required.

Mr. B. L. Richards, graduate student, University of Oklahoma, for his assistance in this project.

FRANCIS MARK TOWNSEND

TABLE OF CONTENTS

	Page
LIST OF TABLES	v
LIST OF ILLUSTRATIONS	vii
Chapter	
I. INTRODUCTION AND STATEMENT OF PROBLEM	1
II. THERMODYNAMIC CONSIDERATIONS	5
III. EXPERIMENTAL APPARATUS	15
IV. PROCEDURE OF COLLECTING EXPERIMENTAL DATA	33
V. PROPERTIES OF MATERIALS AND EXPERIMENTAL DATA	40
VI. ANALYSIS OF DATA	60
VII. DISCUSSION	102
VIII. CONCLUSIONS	108
APPENDIX	110
BIBLIOGRAPHY	116

LIST OF TABLES

Table		Page
1.	Analysis of Natural Gas	42
2.	Physical Properties of Diethylene and Triethylene Glycol	43
3.	Physical Properties of "Dicol"	44
4.	Physical Properties of Hexylene Glycol	45
5.	Variation of Thermistor Circuit Resistance Ratio for Natural Gas Dehydrated with Anhydrous Magnesium Perchlorate and Phosphorous Pentoxide	47
6.	Variation of Thermistor Circuit Resistance Ratio with Water Content of Natural Gas	50
7.	Water Contents of Natural Gas Dehydrated by 99.8 Per Cent Diethylene Glycol	52
8.	Water Contents of Natural Gas Dehydrated by 98 Per Cent Diethylene Glycol	53
9.	Water Contents of Natural Gas Dehydrated by 95 Per Cent Diethylene Glycol	54
10.	Water Contents of Natural Gas Dehydrated by 100 Per Cent Triethylene Glycol. Measurement by Karl Fischer Reagent	55
11.	Water Contents of Natural Gas Dehydrated by 100 Per Cent Triethylene Glycol	56
12.	Water Contents of Natural Gas Dehydrated by 98 Per Cent Triethylene Glycol	57
13.	Water Contents of Natural Gas Dehydrated by 95 Per Cent Triethylene Glycol	58

LIST OF TABLES (continued)

Table		Page
14.	Water Contents of Natural Gas Dehydrated by "Dicol" and Hexylene Glycol	59
15.	Comparison of Calculated Water Contents of Methane Gas at Saturation with Experimental Water Contents	71
16.	Variation in the Terms of Equation (24), $y_2 = B_2 x_2 K_2 \gamma_2$, for the Methane-Water System with Pressure at 80°F.	73
17.	Calculated Values of $B_2 x_2$, Empirical Factor, for Aqueous Solutions of Diethylene Glycol at High Pressures	79
18.	Calculated Values of $B_2 x_2$, Empirical Factor, for Aqueous Solutions of Triethylene Glycol at High Pressures	82
19.	Smoothed Values of the Water Contents of Natural Gas Dehydrated with Diethylene and Triethylene Glycol Solutions at 80°F	92
20.	The Effect of Aqueous Solutions of Diethylene and Triethylene Glycol on Dew Points of Natural Gas at Various Contact Temperatures at Atmospheric Pressure	98
21.	Calculated Values of $B_2 x_2$, Empirical Factor, for Aqueous Solutions of Diethylene and Triethylene Glycols at Atmospheric Pressure	99

LIST OF ILLUSTRATIONS

Figure		Page
1.	Flow Diagram for Saturating Natural Gas with Water, and Filling of Equilibrium Cell	16
2.	View of Gas Saturating Equipment	17
3.	Details of Equilibrium Cell	21
4.	View of Equilibrium Cell	22
5.	Equipment for Measurement of the Water Content of Natural Gas by the Thermistor Bridge Circuit	25
6.	View of Thermistor Bridge Circuit Equipment	26
7.	Flow Diagram for Calibration of Thermistor Bridge Circuit	28
8.	Flow Diagram for Measurement of the Water Content of Natural Gas by Karl Fischer Reagent	30
9.	Graph of Calibration Data for Thermistor Bridge Circuit	64
10.	Water Content of Natural Gas Dehydrated with 99.8 Per Cent Diethylene Glycol	85
11.	Water Content of Natural Gas Dehydrated with 98 Per Cent Diethylene Glycol	86
12.	Water Content of Natural Gas Dehydrated with 95 Per Cent Diethylene Glycol	87
13.	Water Content of Natural Gas Dehydrated with 100 Per Cent Triethylene Glycol	88
14.	Water Content of Natural Gas Dehydrated with 98 Per Cent Triethylene Glycol	89

LIST OF ILLUSTRATIONS (continued)

Figure		Page
15.	Water Content of Natural Gas Dehydrated with 95 Per Cent Triethylene Glycol	90
16.	Effect of Glycol Concentration on the Water Content of Natural Gas Dehydrated with Diethylene Glycol at 80°F.	94
17.	Effect of Glycol Concentration on the Water Content of Natural Gas Dehydrated with Triethylene Glycol at 80°F.	95
18.	Comparison of Water Contents of Dehydrated Natural Gas Determined by Various Investigators	96

EQUILIBRIUM WATER CONTENTS OF NATURAL GAS DEHYDRATED BY AQUEOUS DIETHYLENE AND TRIETHYLENE GLYCOL SOLUTIONS AT VARIOUS TEMPERATURES AND PRESSURES

CHAPTER I

INTRODUCTION AND STATEMENT OF PROBLEM

Marketed production of natural gas has increased 83 per cent in the five-year period from 1946 through 1951[1], and present indications are that this increase in gas consumption will continue. To supply this great demand for natural gas, vast gas gathering and transmission systems have been constructed in the United States, Canada and Mexico. To insure maximum flow efficiency in these systems, gas dehydration has become an absolute necessity.

Gas dehydration is defined as the removal of all liquid water and enough of the water vapor present in the gas to prevent subsequent condensation of water under all operating conditions.[2] Virtually all natural gas, as produced, contains some moisture. The principal source is connate or interstitial water found in gas-and oil-producing strata[3] and the gas is saturated with water vapor at the temperature and pressure prevailing in the producing zone. Other sources of water are: (1) oil-field brine which is often produced in variable quantities with gas and/or

oil; (2) wet scrubbers which employ fresh water to remove traces of salt, pipe line dirt, and spent acid from gas prior to compression; (3) gas transmission lines in which liquid water has accumulated; (4) water-saturated absorption oils in gasoline plants.

The principal difficulties[3] caused by moisture in gas are: (1) formation of gas hydrates which plug pipe lines and pressure-control devices, (2) accumulation of liquid water in pipe lines, thus decreasing the transmission capacity, and (3) internal corrosion of well tubing, fittings, production equipment, and pipe lines. Proper moisture control is the simplest and most economical solution to these problems.[3]

The dehydration of natural gas has passed from the status of an art to that of an exact science through technical research and development in dehydration processes and equipment,[4] stimulated by an increasing demand for uninterrupted service from gas transmission lines operating at increasingly higher pressures. Extensive investigations of gas-hydrate-forming conditions have been reported and numerous dehydrating agents and methods have been evaluated.[5, 6, 7, 8]

Diethylene and triethylene glycols are widely used as water vapor absorbents in certain natural gas dehydration processes. In order to improve these processes and to establish their limitations, investigations have been conducted to determine the vapor-liquid equilibria of gas-water-glycol systems at temperatures ranging from 60°F. to 100°F.,

at pressures from atmospheric to 2500 pounds per square inch absolute, with water-glycol solutions of 95 per cent and 100 per cent by weight glycol. The vapor-liquid equilibrium data of Russell,[9] Porter,[10] Boyd[11] and Townsend[12] were obtained on a dynamic system in which a mixture of natural gas and glycol solution flowed concurrently through a 50- or 75-ft. coil of 5/16-in. copper tubing. It was believed that equilibrium was reached during the time of contact in the coil, and that the dew point of the gas was the minimum for all conditions of temperature and pressure investigated. However, field data taken by Campbell[13] on industrial dehydration units showed lower dew points were obtained than could be predicted from these sources, particularly in the higher pressure ranges.

Critical inspection of the dynamic system and the data obtained from it revealed that, while a fair approach to equilibrium was obtained at pressures ranging from atmospheric to 500 to 600 pounds per square inch, at progressively higher pressures this approach worsened due to inadequate mixing of the liquid and gas phases. The dynamic system has been replaced by a static equilibrium cell in which water-saturated natural gas, at a definite temperature and pressure, can be added to an excess of water-glycol solution of known concentration and the mixture agitated until true equilibrium is attained.

Statement of Problem and Method of Solution

This investigation was undertaken to determine the true effectiveness of glycol-water solutions in dehydrating water-saturated natural gas at atmospheric temperatures, relatively high pressures, and high glycol concentrations. The method consisted of saturating natural gas with water at temperatures of 70°F., 80°F., and 90°F.; at pressures varying from 500 to 2500 pounds per square inch absolute, and introducing this saturated gas into an equilibrium cell containing a substantial excess of 95 per cent to 100 per cent by weight diethylene glycol. The two phase mixture was agitated until equilibrium was reached and the water content of the dehydrated gas was then measured by a suitable means. The quantity of glycol present was in such great excess that the change in water concentration in glycol was negligible. The procedure was repeated for triethylene glycol. Spot checks were obtained with two relatively new materials, "Dicol", a relatively crude glycol mixture, and hexylene glycol. These data were compared with data obtained on diethylene and triethylene glycol in order to determine if these new materials were sufficiently effective to warrant future investigation.

CHAPTER II

THERMODYNAMIC CONSIDERATIONS

Vapor-Liquid Equilibrium

The study of vapor-liquid systems in equilibrium is aided by the Gibbs Phase Rule.[14] This rule may be written:

$$F = C - P + 2 \qquad (1)$$

where:

F = degrees of freedom at equilibrium

C = number of components in system

P = number of phases in equilibrium

If natural gas is assumed to be pure methane, then the system natural gas-water-glycol is a two phase, three component system. According to the Phase Rule there are then three degrees of freedom; that is, temperature, pressure and composition of the system must be specified before the system is fixed. The natural gas used in this investigation actually consisted of several components, but application of the Phase Rule indicates that temperature, pressure, and composition are still variables of the system in equilibrium.

This investigation is primarily concerned with the distribution

of water, the second component in the system natural gas-water-glycol, between the vapor and liquid phases. Therefore, the equations developed below will be applied to water as component 2, and will be changed to represent other components when required.

In a vapor-liquid system in equilibrium the chemical potentials of a component in the vapor and liquid phases must be equal; that is,

$$\mu_2 = \mu_2' \tag{2}$$

where:

μ_2 = chemical potential in the liquid phase

μ_2' = chemical potential in the vapor phase

Fugacity is directly related to chemical potential by the equation,

$$(d\mu_2 = R\ T\ d\ln f_2)_T \tag{3}$$

where:

μ_2 = chemical potential of component 2

R = gas constant

T = absolute temperature

f_2 = fugacity of component 2

It is evident that in a system in equilibrium at constant temperature the fugacities of a component in the vapor and liquid phases must be equal; that is,

$$f_2 = f_2' \tag{4}$$

where:

f_2 = fugacity of pure component 2 in the liquid phase

f_2' = fugacity of pure component 2 in the vapor phase

The fugacity of a pure gas at any temperature and pressure may be obtained most easily by the use of a fugacity coefficient graph.[15, 16] The ratio

$$\frac{f_2'}{\pi} = (\nu_2)_\pi \tag{5}$$

where:

π = total pressure of the system

ν = fugacity coefficient of component 2 at the temperature and pressure of the system

is plotted against reduced temperature and pressure. From the fugacity coefficient obtained at any reduced temperature and pressure the fugacity can be calculated as follows:

$$f_2' = (\nu_2)_\pi \pi \tag{6}$$

The fugacity of pure liquid at its vapor pressure is equal to the fugacity of its vapor in equilibrium with it. The fugacity of the vapor is calculated from the fugacity coefficient as follows:

$$\frac{(f_2')_{P_2}}{P_2} = (\nu_2)_{P_2} \tag{7}$$

or

$$(f_2')_{P_2} = (\nu_2)_{P_2} P_2 \tag{8}$$

where:

P_2 = vapor pressure of pure liquid component 2 at the temperature of the system

$(\nu_2)_{P_2}$ = fugacity coefficient of component 2 at P_2 and temperature of the system

The fugacity of a pure liquid at a pressure π different from its vapor pressure, P_2, is found as follows:

$$\ln \frac{(f_2)_\pi}{(f_2)_{P_2}} = \frac{V_m (\pi - P_2)}{R T} \qquad (9)$$

or

$$(f_2) = (f_2)_{P_2} e^{\frac{V_m(\pi - P_2)}{R T}} \qquad (10)$$

where:

V_m = mean molal volume of liquid component 2 between P_2 and π at the temperature of the system

The system methane-water-glycol is a mixture of three components, so a method for determining the fugacity of a component in a mixture must be considered. The fugacity of a component, either gaseous or liquid, in an ideal solution can be found by the Lewis-Randall Rule.[17] By this rule the fugacity of a component is proportional to its mole fraction. It can be written:

$$\bar{f}_2 = x_2 f_2 \qquad (11)$$

$$\bar{f}'_2 = y_2 f'_2 \qquad (12)$$

where:

$\bar{f}_2$ = fugacity of component 2 in the liquid phase of a mixture

$\bar{f}'_2$ = fugacity of component 2 in the vapor phase of a mixture

x_2 = mole fraction in the liquid phase

y_2 = mole fraction in the vapor phase

It is convenient, in the study of equilibrium involving solutions, to use a ratio of fugacities; the ratio of the fugacity in a given state to the fugacity in an arbitrarily defined state called the standard state. This ratio is called the activity. It is expressed as follows:

$$a_2 = \left[\frac{\bar{f}_2}{f^\circ_2}\right]_T \tag{13}$$

where:

a_2 = activity

$\bar{f}_2$ = fugacity in the given state

f°_2 = fugacity in the standard state at the same temperature

If the standard state of a component which is in solution is taken as the pure component at the temperature and pressure of the solution, the activity is directly related to composition. When ideal behavior cannot be assumed, as in this investigation, it is necessary to introduce an empirical factor which relates activity to composition. This factor is termed the activity coefficient, ϕ', which is the ratio of activity to a numerical expression of composition. Using mole fractions to represent compositions, the definition of the activity coefficient may be written:

$$\phi'_2 = \frac{a'_2}{y_2} \tag{14}$$

where:

ϕ'_2 = activity coefficient of component 2 in the vapor phase

a'_2 = activity of component 2 in the vapor phase referred to the pure component

y_2 = mole fraction of component 2 in the vapor phase

By combining Equations (13) and (14) the following equation is obtained:

$$\phi'_2 = \frac{\bar{f}'_2}{y_2 f^{\circ\prime}_2} \tag{15}$$

This equation permits the calculation of activity coefficients which may be used to correlate and check experimental data for consistency as a function of temperature, pressure and composition.

By rewriting Equation (4) to designate fugacities in a mixture, i. e., $\bar{f}_2 = \bar{f}'_2$, and combining with Equation (13), written for both the liquid and vapor phases, another relationship is obtained which may be used as a criterion of equilibrium. The equation is:

$$a_2 f^{\circ}_2 = a'_2 f^{\circ\prime}_2 \tag{16}$$

Equation (16) may be written:

$$\frac{a'_2}{a_2} = \frac{f^{\circ}_2}{f^{\circ\prime}_2} = K_2 \tag{17}$$

Here K_2 is termed the vaporization equilibrium constant of component 2.

The concept of the vaporization equilibrium constant was intro-

duced by Souders, Selheimer and Brown [18] who expressed it by the following equation resulting from combination of Equations (10) and (17) with the definition of the fugacity coefficient:

$$K_2 = \frac{f^\circ_2}{f^{\circ\prime}_2} = \frac{P_2 (\nu_2)_{P_2} e^{\frac{V_m (\pi - P_2)}{R T}}}{\pi (\nu_2)_\pi} \qquad (18)$$

Attempts to use Equation (18) above to evaluate vaporization constants for methane in the methane-water-glycol system are complicated by uncertainty as to the proper values of the molal volume, V_m, and vapor pressure of liquid methane, P_1, at room temperature, a temperature far above its critical temperature. Gamson and Watson[16] proposed that the molal volume be expressed as a function of temperature by the following equation:

$$V_m = (V_2 \omega_2)(5.7 + 3.0\, T_r) \qquad (19)$$

where $(V_2 \omega_2)$ is the product of the molal liquid volume V_2 and an expansion factor, ω_2, plotted as a function of reduced temperature and pressure at any selected condition.

The definition of (f°_2) at all conditions is completed by means of the vapor pressure equation:[19]

$$\log P = \frac{-A}{T_r} + B - e^{-20(T_r - b)^2} \qquad (20)$$

where A, B, and b are constants characteristic of the substance. It is claimed by Gamson and Watson[19] that this equation extrapolates logic-

cally above the critical point.

Equations (18), (19), and (20) permit the calculation of the equilibrium constant in an arbitrary but logical manner which is definite and reproducible. However, before this relationship is useful it is necessary to relate activities to mole fractions through the introduction of activity coefficients.

The following equation may be written for the vapor phase:

$$a_2' = \frac{\bar{f}_2'}{f^{\circ\,\prime}_2} = \phi_2' y_2 \qquad (21)$$

For ideal gaseous solutions of components which are not widely different in properties, ϕ_2' may be taken as equal to unity at moderate pressures and elevated temperatures. However, since the components of the methane-water-glycol system are widely different in their properties, and since the pressure range of this investigation is high, it is to be expected that the vapor phase would be a non-ideal solution, and that ϕ_2' would not equal unity.

In the liquid phase there are two different types of deviation from ideal solutions. It is convenient to replace the usual single activity coefficient by two separate activity coefficients to express each of these deviations. The following equation can be written for the liquid phase:

$$a_2 = \phi_2 \gamma_2 x_2 \qquad (22)$$

where the activity coefficient group $\phi_2\gamma_2$ consists of:

γ_2 = activity coefficient of component 2 in the liquid phase which takes into account deviations from ideal solutions caused by differences in molecular size or volatility.

ϕ_2 = activity coefficient in the liquid phase which accounts for deviations from ideal solutions caused by differences in molecular or chemical type.

For ideal systems ϕ_2 equals unity at all conditions. For non-ideal systems at low pressures where γ_2 may be taken as equal to unity, ϕ_2 may be determined by methods previously described. As the temperature and pressure in such a system are increased ϕ_2 tends to approach unity, while deviations of γ_2 from unity tend to increase.[15]

In the liquid phase of the methane-water-glycol system there are great differences in the molecular sizes, volatilities and chemical properties of the three components. It is then to be expected that values of ϕ_2 and γ_2 should deviate greatly from unity over the pressure range involved.

Combining Equations (17), (18), (21), and (22) gives:

$$\frac{y_2}{x_2} = \frac{\phi_2\gamma_2}{\phi_2'} K_2 = \frac{\phi_2\gamma_2 P_2 (\nu_2)_{P_2}}{\pi \, (\nu_2)_\pi} e^{\frac{V_m(\pi - P_2)}{RT}} = K_2' \quad (23)$$

It was suggested by Gamson and Watson[16] that the ratio K_2' of

the mole fractions in the vapor and liquid phases be termed the vaporization ratio of component 2. It is evident from Equation (23) that the vaporization ratio is equal to the thermody namic equilibrium constant only in ideal solutions where the activity coefficients are each equal to unity.

Equation (23) can be written as follows:

$$\frac{y_2}{x_2} = B_2 \gamma_2 K_2 \tag{24}$$

in which the ratio of activity coefficients $\frac{\phi_2}{\phi_2'}$ has been replaced by the single term B_2, thus decreasing the number of individual activity coefficients from three to two. Thus the amount of experimental data required to evaluate the activity coefficients is decreased.

The equations developed thus far furnish a means of correlating vapor-liquid equilibria data, and further use will be made of them in Chapter VI, Analysis of Data.

CHAPTER III

EXPERIMENTAL APPARATUS

Equipment for Saturating Natural Gas

The flow diagram for saturating natural gas with water at any predetermined temperature and pressure is shown in Figure 1. A photograph is shown in Figure 2.

The natural gas is compressed to the desired pressure by a three-stage, water-intercooled, Rix compressor. This compressor has a rated capacity of ten standard cubic feet of gas per minute at a maximum working pressure of 6000 pounds per square inch.

The compressed gas is then passed through a gas-liquid separator and a lubricating oil vapor adsorber. The separator is made from an 18-inch length of extra-heavy 2-inch steel pipe with welded caps. A 1/4 inch fitting for the inlet gas is welded into the side of the separator halfway between the ends, a 1/4 inch fitting for the outlet gas is welded at the top end of the separator, and a 1/4 inch drain is provided at the bottom end.

The oil vapor adsorber is made from an 18-inch length of extra-heavy 2-inch steel pipe. It has a 1/4-inch gas inlet fitting into a 1 1/4-

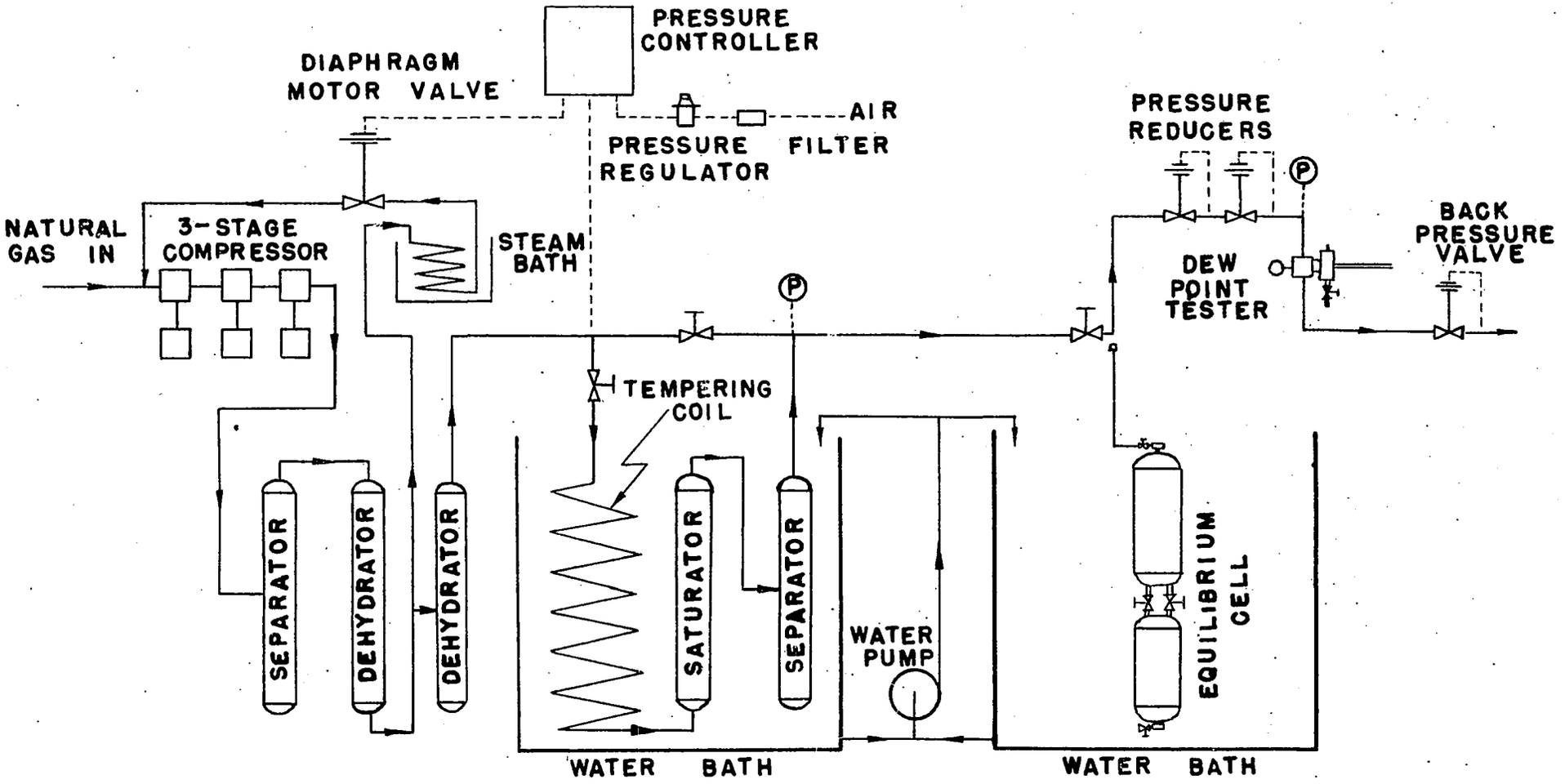


FIGURE 1. FLOW DIAGRAM FOR SATURATING NATURAL GAS WITH WATER, AND FILLING OF EQUILIBRIUM CELL.

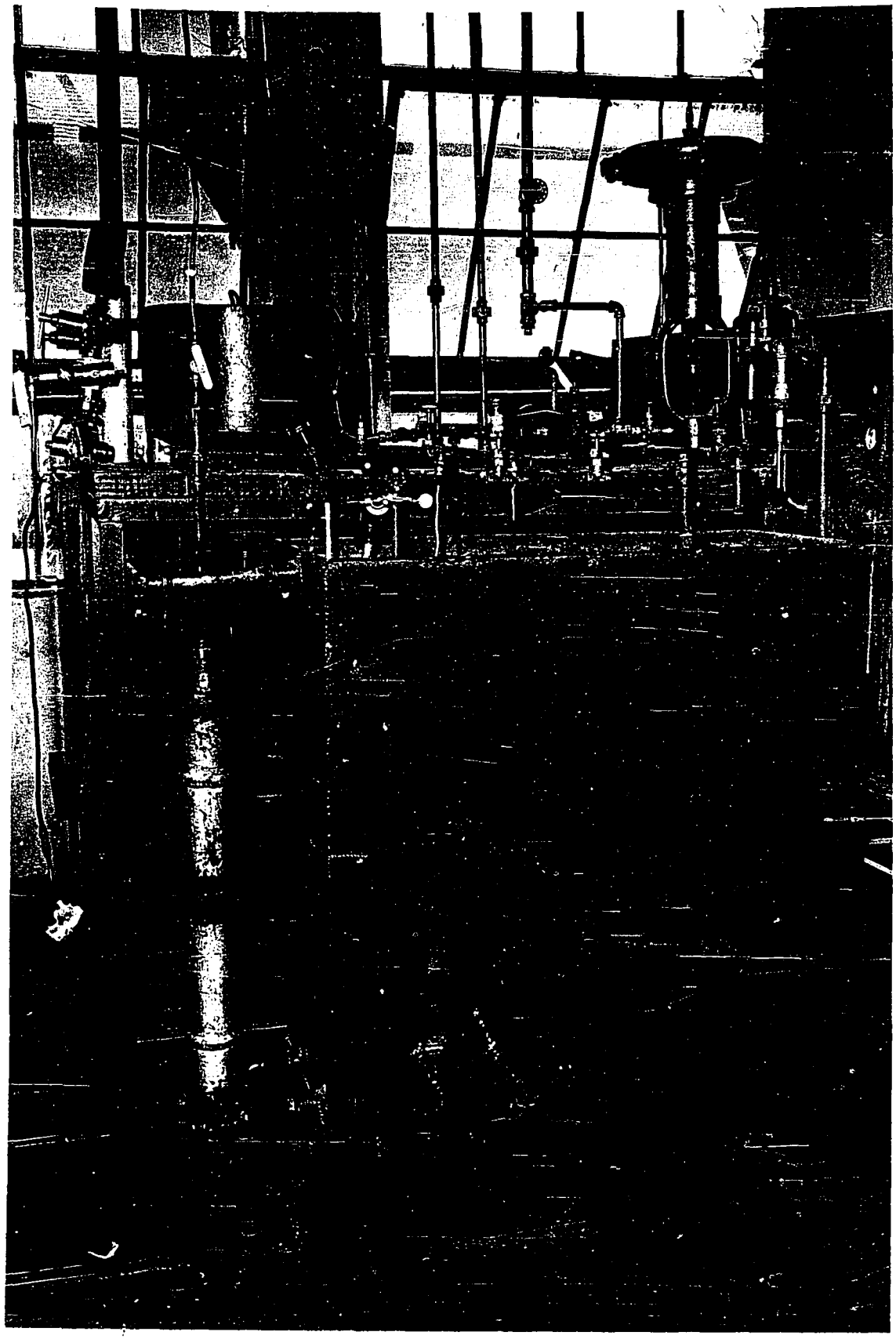


Fig. 2. View of Gas Saturating Equipment

inch threaded plug which screws into the top of the dehydrator. This 1 1/4-inch plug is removed for filling the adsorber with approximately one pound of "Sova Bead", a silica gel-alumina type of adsorbent manufactured by the Socony-Vacuum Oil Company. The bottom of the adsorber is closed by a welded cap with a 1/4 inch fitting for the outlet gas.

After leaving the adsorber the gas flow is split into two streams. One stream, amounting to all gas delivered by the compressor in excess of 25 standard cubic feet an hour, passes through a 25-foot length of 5/16-inch extra-heavy copper tubing immersed in a steam heated water bath which is maintained at 210°F. This excess gas is then released to the suction side of the compressor through a Fisher diaphragm motor back-pressure valve at the rate required to maintain the desired pressure on the system. The Fisher valve is actuated by a Taylor "Ful-scope" pressure controller which, in turn, is operated by a filtered, compressed air supply.

The second stream of natural gas, amounting to approximately 25 standard cubic feet per hour, passes through a dehydrator, a temperature stabilizing coil, a water saturator, and a separator where the moisture content of the gas is adjusted.

The dehydrator is made from a 24-inch length of extra-heavy 3-inch steel pipe with welded caps. A 1/4-inch fitting for the inlet gas is welded into the side of the dehydrator midway between the ends. In-

side the dehydrator and just above the gas inlet fitting there is a welded steel plate, perforated with 1/16-inch holes, which acts as a support for the desiccant. The top of the dehydrator is fitted with a 3/4 × 1/4-inch bushing which is removed for filling the dehydrator with two pounds of "Sova Bead". This bushing connects to the 1/4-inch gas outlet.

The temperature stabilizing coil, saturator, and separator are immersed in the first of two constant temperature baths constructed of 10-gauge sheet steel. This bath is 36 inches long, 18 inches wide, and 36 inches deep. The temperature stabilizing coil is a fifty-foot length of 5/16-inch O. D. × 0. 049-inch wall extra-heavy copper tubing. The saturator is made from an 18-inch length of extra heavy 2-inch steel pipe with welded caps and 1/4-inch fittings at each end. The saturator has a capacity of 900 milliliters, but is filled with only 500 milliliters when in service. The top half of the saturator is packed with three copper gauze "Chore Girl" scouring pads which serve as a mist extractor. The separator is identical in construction except that the 1/4-inch fitting for the inlet gas is welded into the side of the separator midway between the ends.

The saturated gas next passes through two Meco pressure-reducing regulators in series, a U. S. Bureau of Mines high-pressure dew point tester; and, finally, a third pressure-reducing regulator. The high pressure saturated gas is expanded through the two Meco regulators to an absolute pressure of 200 pounds per square inch at the dew point tester.

Here the dew point of the gas can be determined to check saturation of the gas. The third pressure regulator reduces the pressure to atmospheric and also regulates the rate of gas flow through the saturating system and the dew point tester.

Connections are so arranged that the saturated natural gas can be made to by-pass the pressure reducers and dew point tester, and pass directly to the equilibrium cell where the latter is charged.

Details of Equilibrium Cell

The details of the equilibrium cell are shown by Figure 3 and a photograph is shown in Figure 4. The upper cylinder is composed of a 16-inch long section of extra-heavy 6-inch steel pipe, fitted on each end with extra-heavy 2:1 elliptical welding caps. The top head is fitted with a 1/4-inch connection comprising extra-heavy steel pipe fittings and a 1/4-inch needle valve. The upper cylinder is joined to the lower cylinder by two 1/2-inch extra-heavy steel pipes each with a union and a 1/2-inch, 800-pound Hancock steel gate valve. For venting the cylinders so that liquid will flow easily from the upper cylinder to the lower cylinder, and vice versa, one of the 1/2-inch pipes extends into the upper cylinder for the full length of the cylinder. The other 1/2-inch pipe extends down into the lower cylinder for its full length. The lower cylinder is composed of a 10-inch long section of extra-heavy 6-inch seamless steel pipe fitted on each end with extra-heavy 2:1 elliptical

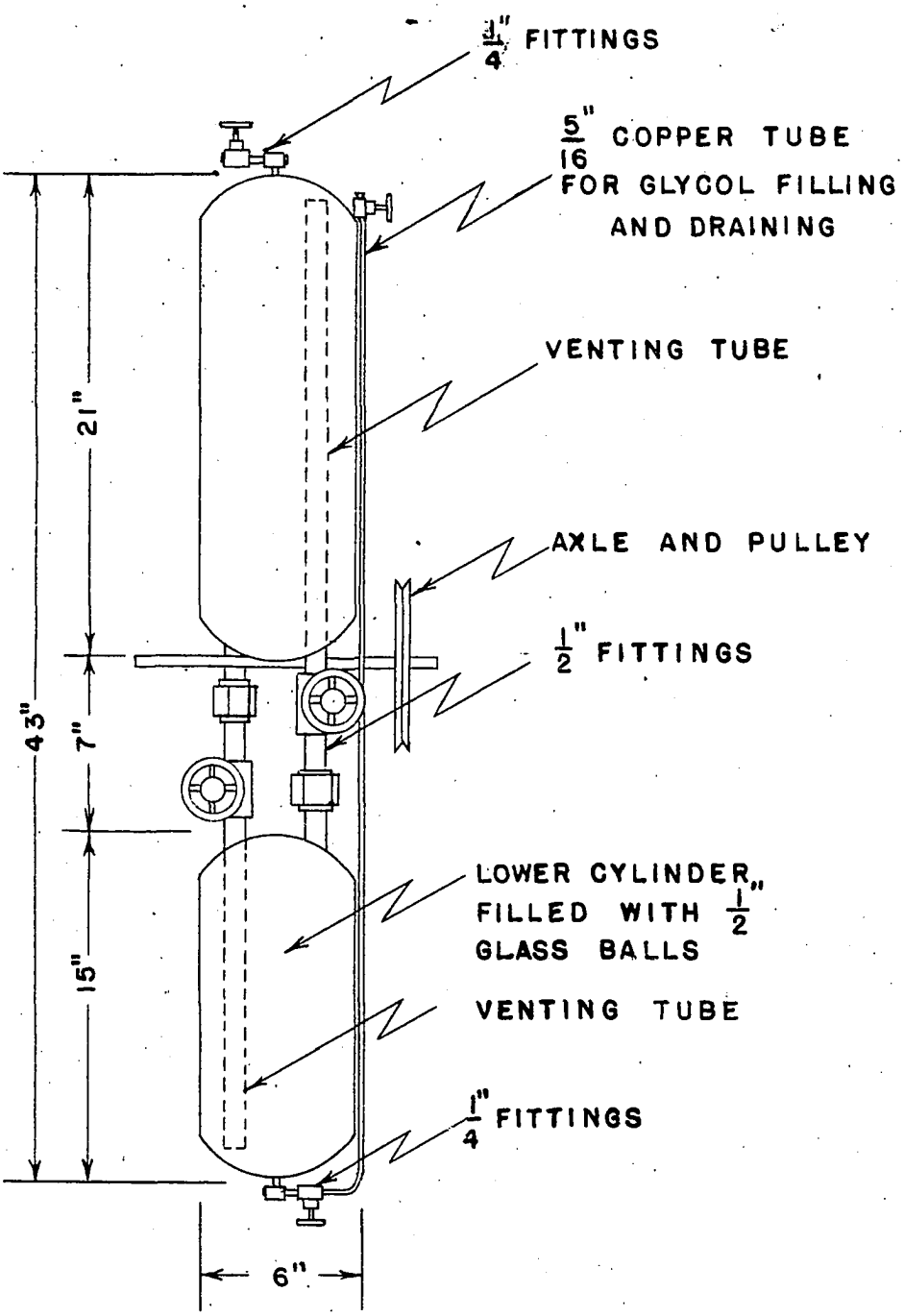


FIGURE 3. DETAILS OF EQUILIBRIUM CELL

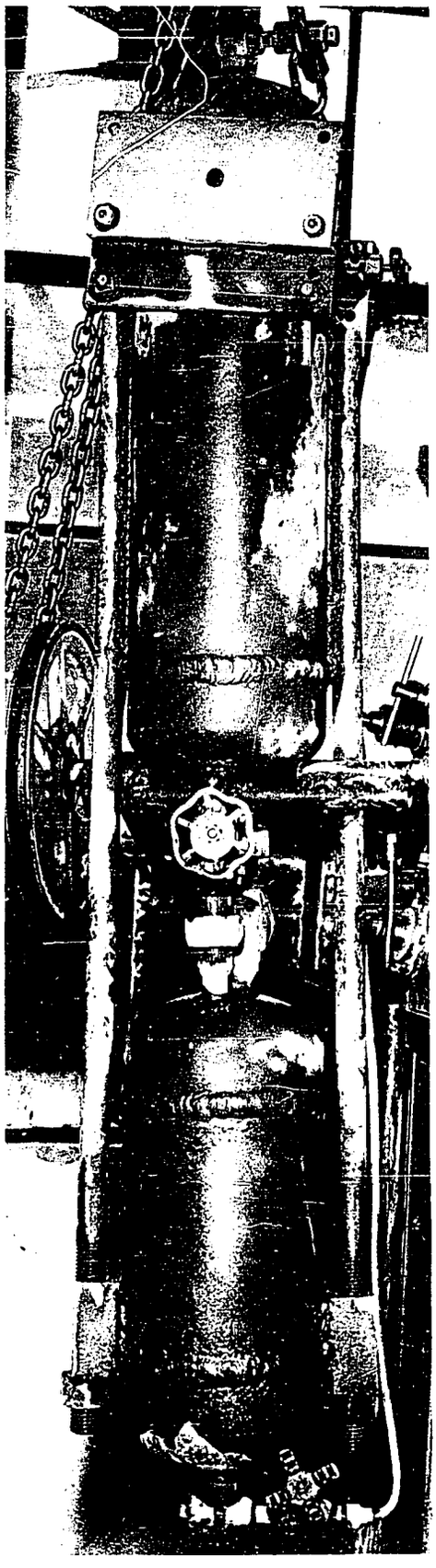


Fig. 4 View of Equilibrium Cell

welding caps. This lower cylinder is filled with 1/2-inch glass balls to act as a gas-liquid contact surface. The bottom head of the lower cylinder is fitted with a 1/4-inch high pressure steel connection and a 1/4-inch needle valve. For filling the cylinder with glycol and for draining, a 5/16-inch extra-heavy copper tubing is connected to the bottom fitting on the smaller lower cylinder. This tube extends upward to the top of the larger cylinder, and is strapped to the outside of both cylinders. At its upper end this copper tubing is fitted with a 1/4-inch needle valve for regulating the rate of glycol flow into or out of the cell.

The equilibrium cell is supported at its mid-point by a 1/2-inch trunnion shaft fitted with an 8-inch diameter V-belt pulley. The entire assembly is supported on this shaft in a second constant temperature water bath. This bath, constructed of 10-gauge steel plate, is 50-inches long, 18 inches wide, and 50-inches deep.

The cell is rotated in the water bath through an arrangement of two V-belts and four pulleys by a 1/3-horsepower 110 volt A.C. motor coupled to a variable-speed torque converter.

Figures 5 and 6 illustrate the apparatus for the measurement of the water content of natural gas by means of a thermistor bridge circuit, a modification of that described by Harris and Nash.[20] The reaction cell consists of a wide-mouth, one liter vacuum bottle or Dewar flask fitted with a large cork stopper. The gas flows into the reaction

cell through a 1/4-inch glass tee, one leg of which also acts as the inlet for the wires leading to the lower thermistor. The gas flows to the bottom of the vacuum bottle and then upward through a vertical glass tube, 12 inches long, 1/2-inch inside diameter, which is also fitted into the large cork stopper. At the mid-point of the glass tube there is a porous plug of glass wool which acts as a support for a two-inch layer of 4/18 mesh calcium hydride particles. A No. 17A Western Electric thermistor is suspended approximately one inch above the calcium hydride mass by wires entering the glass outlet tee fitted into the top of the 1/2 inch glass tube by means of a small cork stopper. A second thermistor of the same type is supported by its electrical leads in the 1/2-inch glass tube, being positioned one inch below the plug of glass wool. The gas flows from the upper end of the reaction cell to a Precision wet test meter.

The thermistor bridge circuit consists of two Wheatstone Bridges wired in parallel to two 1.5-volt dry cell A batteries. Each bridge consists of a 1000 ohm and a 1500 ohm fixed resistance, a Leeds and Northrup 1000 ohm decade box and a No. 17A Western Electric thermistor with a nominal resistance of 1000 ohms. The galvanometer circuit is wired through spring loaded switches so that a single galvanometer can be used for both circuits. The galvanometer is mounted in a Leeds and Northrup Portable Precision Potentiometer Model No. 8662.

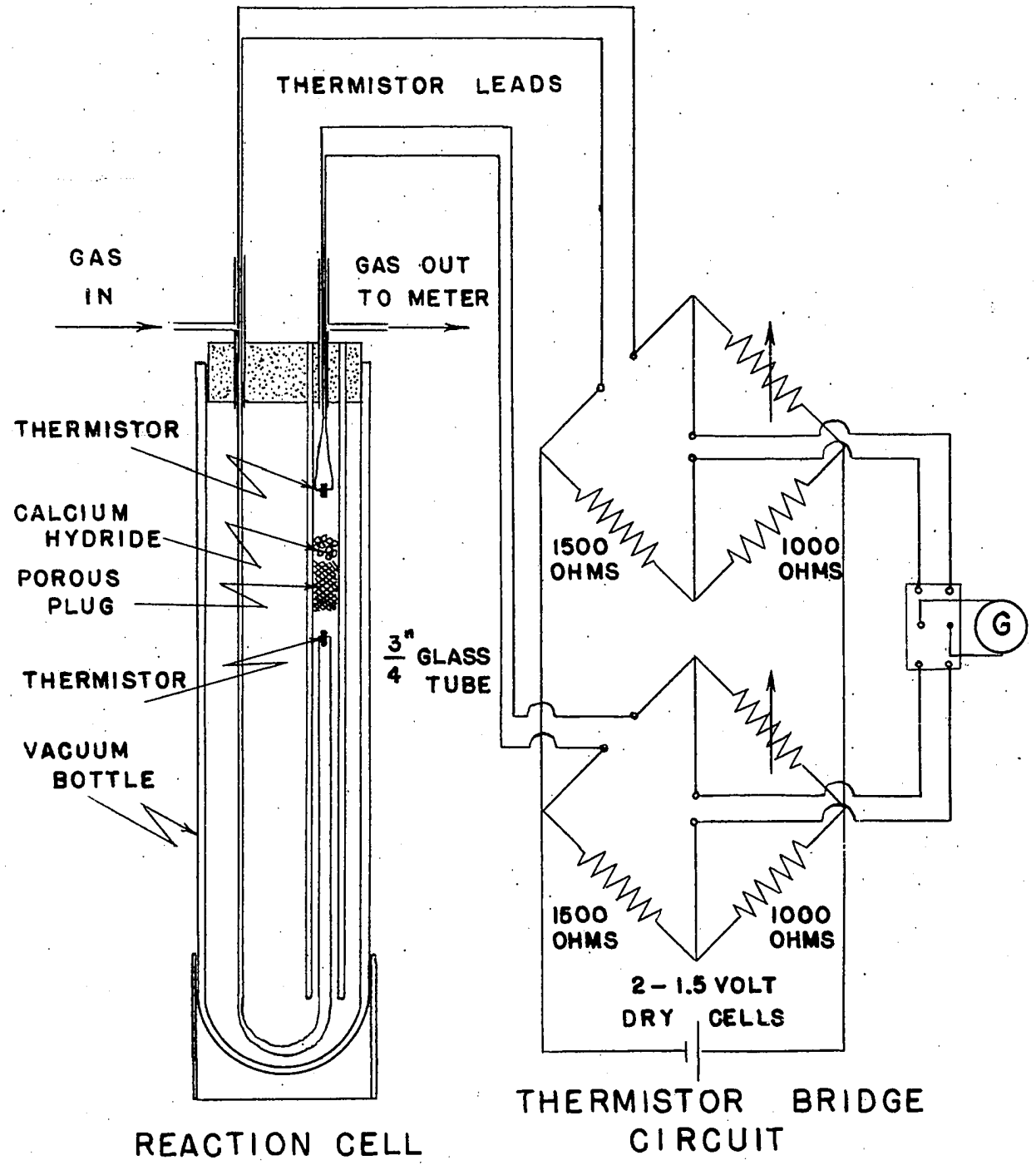


FIGURE 5. EQUIPMENT FOR MEASUREMENT OF THE WATER CONTENT OF NATURAL GAS BY THE THERMISTOR BRIDGE CIRCUIT

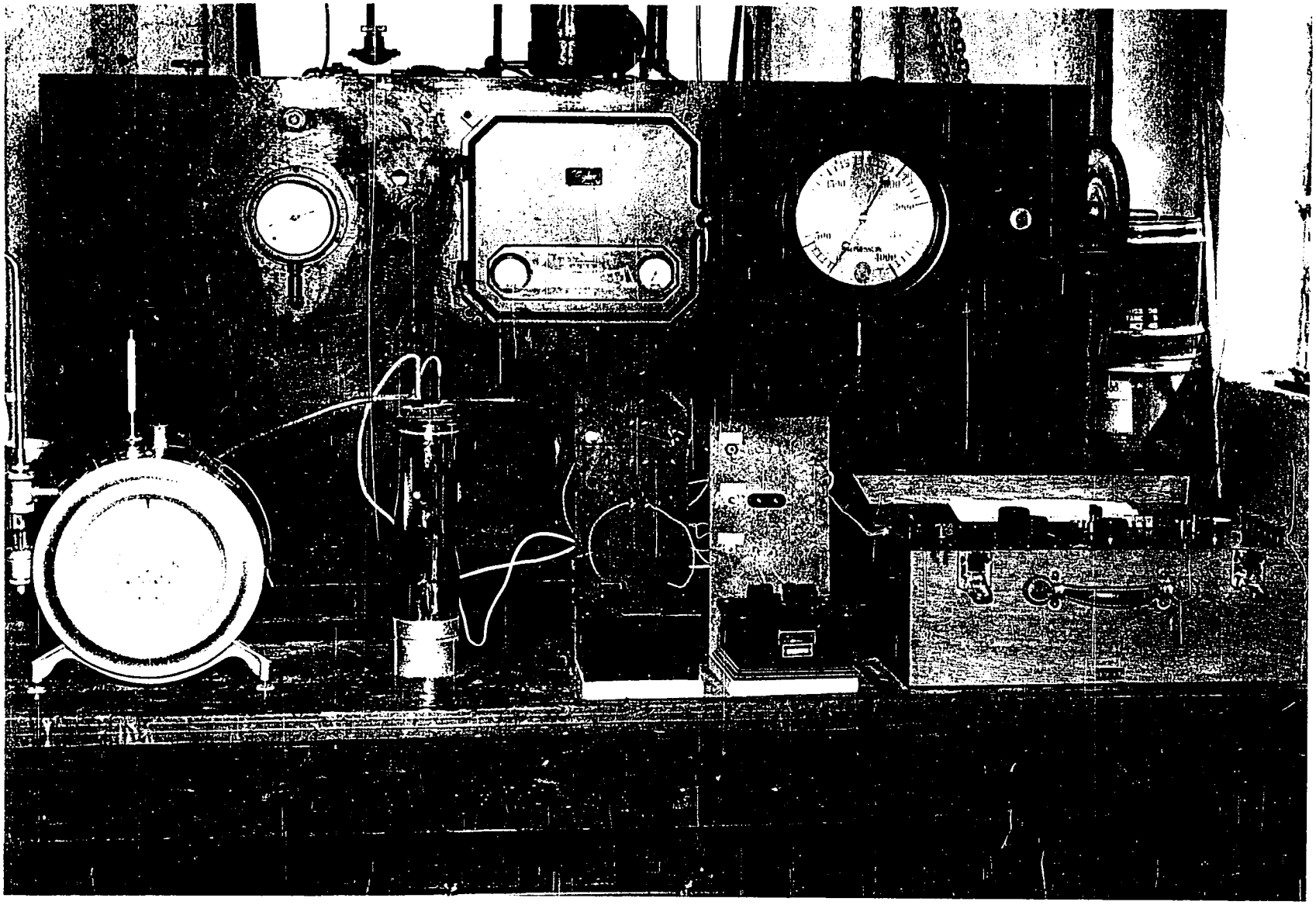


Fig. 6. View of Thermistor Bridge Circuit Equipment

Equipment for Calibration of the Thermistor Bridge Circuit

The thermistor bridge circuit is calibrated by use of the apparatus shown in Figure 7 in conjunction with the gas saturating equipment shown in Figure 1. The saturated natural gas is dropped to near-atmospheric pressure through the dew point tester equipment and is metered through a capillary flow meter filled with 100 per cent triethylene glycol as the manometer fluid. The gas then mixes with dehydrated natural gas which has passed through a "Sova Bead" dehydrator and a P_2O_5 drying tube. The mixture of wet and dry gas then flows to the reaction cell, and is finally metered in a Precision wet test meter. The "Sova Bead" dehydrator is constructed from a 36 inch length of standard two-inch pipe, and is completely filled with desiccant. The P_2O_5 dehydrator consists of a glass tube nine inches long, one-inch inside diameter, filled with a four-inch column of P_2O_5 contained by two glass wool plugs.

Equipment for Measurement of the Water Content of Natural Gas by Karl Fischer Reagent

The special apparatus used for measurement of the water content of natural gas by Karl Fischer reagent is shown in Figure 8. This method is described in the U.O.P. Laboratory Manual.[21] The 100 milliliter absorption flask has a 3/4-inch mouth and a stopcock drain. The 3/4-inch opening is fitted with a rubber stopper provided with suitable holes for admitting a 6-millimeter gas dispersion tube, a 6-millimeter

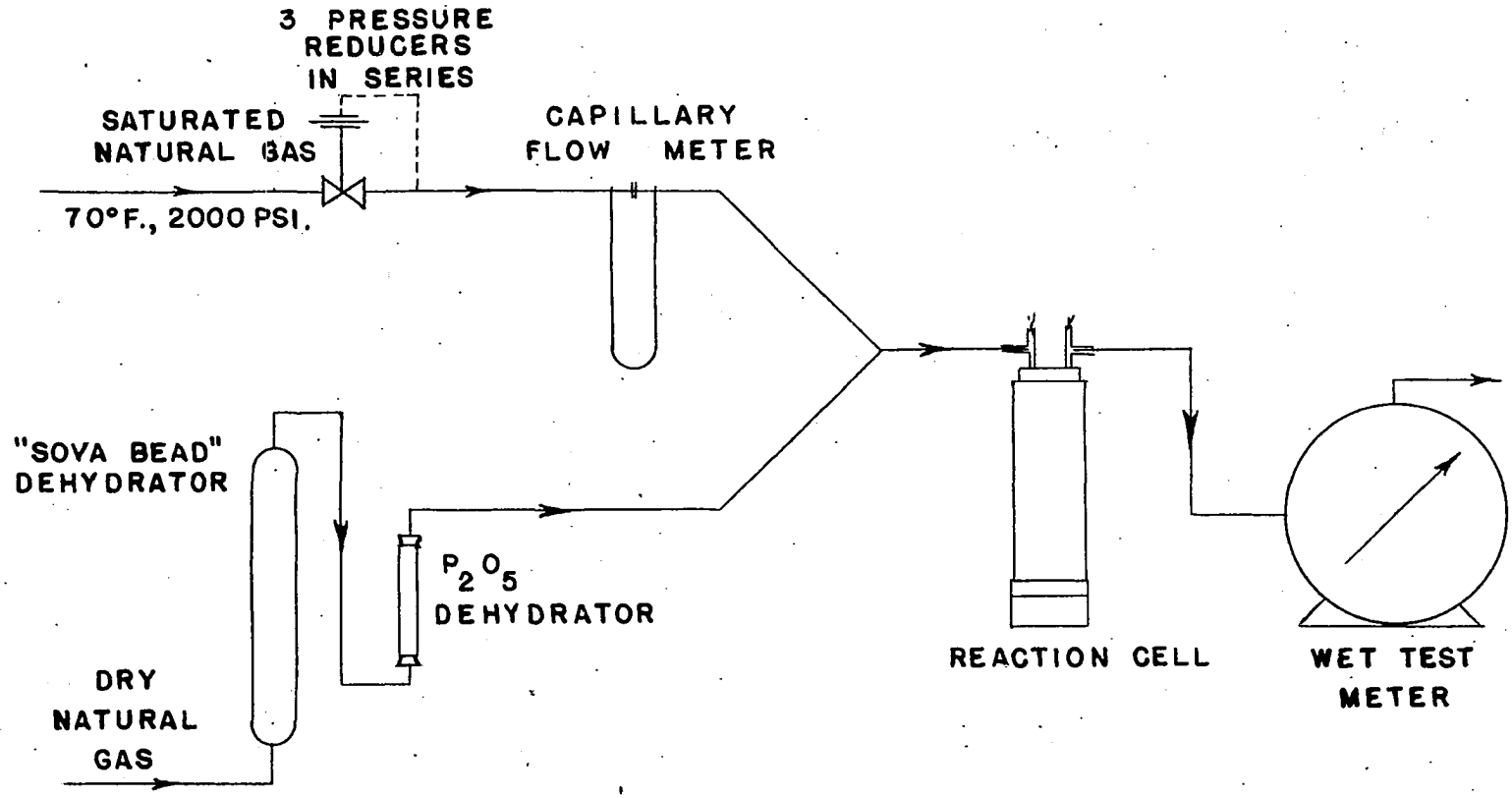


FIGURE 7. FLOW DIAGRAM FOR CALIBRATION OF THERMISTOR BRIDGE CIRCUIT

gas outlet tube, the tip of a 10.00 milliliter buret, and two 3-millimeter electrodes. The buret is sealed from the atmosphere by a 100 milliliter drying tube filled with "Dehydrite", anhydrous magnesium perchlorate. The platinum electrodes are formed by sealing a platinum wire into a Pyrex glass tube, and filling the tube with mercury to form the junction. The gas passes through the gas dispersion tube into the Karl Fischer reagent, and through the outlet tube to a "Sova Bead" dehydrator thence to a Precision wet test meter. The dehydrator is a glass column approximately four inches high, two inches in diameter filled with "Sova Beads".

The end-point of the reaction of water vapor in the natural gas with the Karl Fischer reagent is determined by the electrometric circuit[22] shown in Figure 8, comprising a Leeds and Northrup Precision Portable Potentiometer, Model No. 8662. The platinum electrodes are connected by copper leads to the electromotive force terminals of the potentiometer. The current through the solution is regulated by the millivolt dial of the potentiometer to approximately 20 millivolts.

The water concentration of the glycol-water solutions is determined by titration in a standard Karl Fischer titration assembly. The end-point is determined by an electrometric circuit identical to that described above.

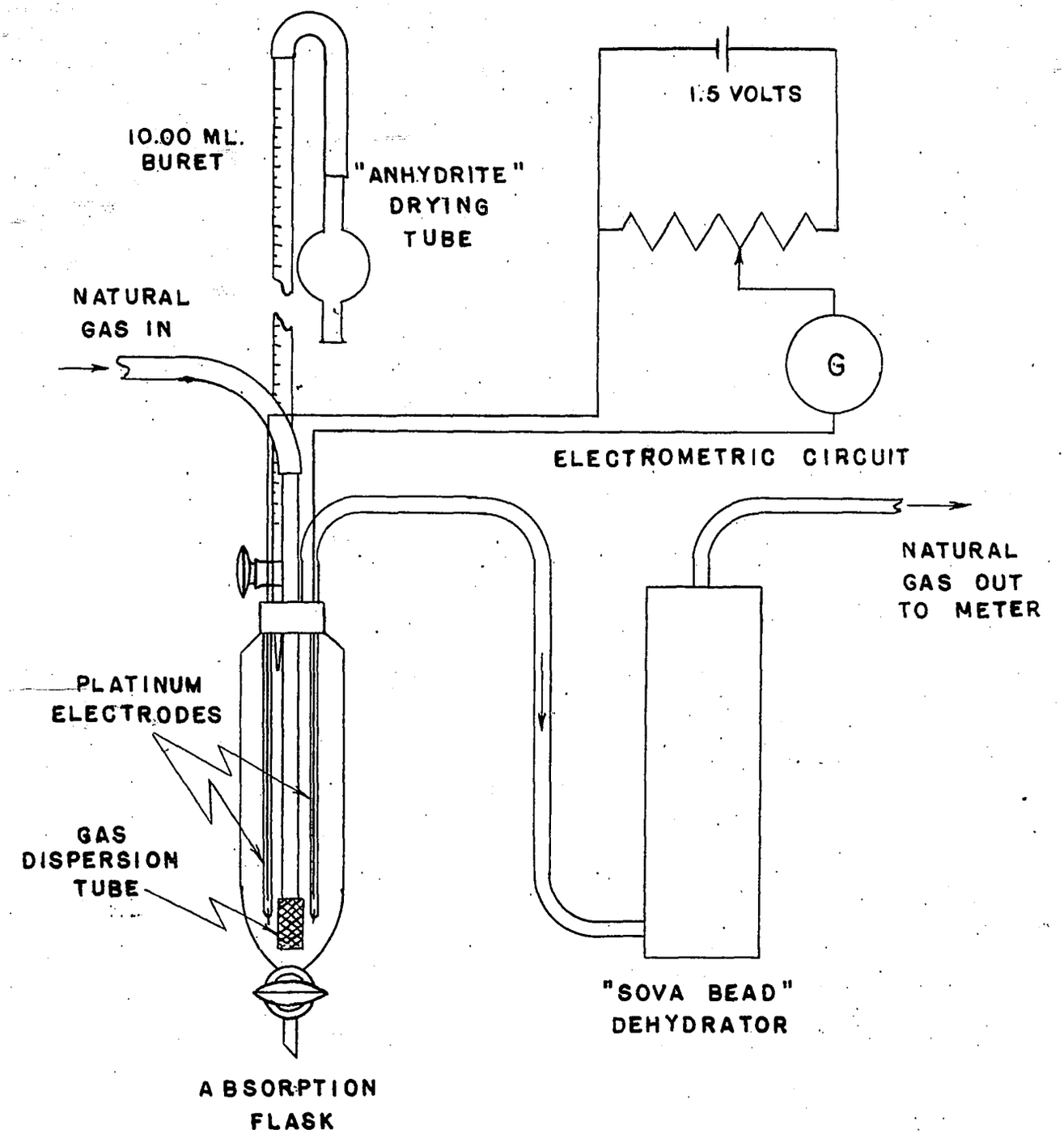


FIGURE 8. FLOW DIAGRAM FOR MEASUREMENT OF THE WATER CONTENT OF NATURAL GAS BY KARL FISCHER REAGENT

Temperature and Pressure Measuring Equipment

The temperature of each of the two constant temperature water baths is determined by a mercury-filled thermometer immersed in each water bath. Temperatures are maintained constant to within $\pm$ 0.5°F. of 70°F. during calibration runs, and to within $\pm$ 1.0°F. of the desired temperature during experimental runs by manually adding ice or steam as necessary to the water in the baths. Uniform temperature in the water baths is maintained by continuous circulation of the water by a centrifugal pump which draws water simultaneously from the bottom of both baths and discharges to the tops of both baths.

The temperature of the dew point of the saturated natural gas is measured by a low-temperature, alcohol-filled thermometer provided with the U.S. Bureau of Mines dew point tester.

Gas pressure during calibration and experimental runs are maintained at the desired pressure within $\pm$ 10 pounds per square inch by a Taylor "Fulscope" pressure controller. Gas pressure is indicated by a 4000 pounds per square inch Bourdon-type gauge graduated in 100 pounds per square inch increments and calibrated to $\pm$ 10 pounds per square inch.

The pressures reported in this investigation corresponding to the equilibrium water contents of the various glycol solutions is that indicated by a 4000 pounds per square inch Bourdon-type gauge which is connected to the equilibrium cylinder after thorough mixing of the contents

in the cylinder. This gauge is graduated in 50 pounds per square inch increments and is also calibrated to ±10 pounds per square inch.

The pressure corresponding to the dew point temperature is measured by a 600 pounds per square inch Bourdon-type gauge graduated in 5 pounds per square inch increments and calibrated to ±2 pounds per square inch. Pressure in the dew point tester is maintained constant within ±5 pounds per square inch by two Meco pressure reducing regulators in series upstream from the dew point tester and by a third pressure-reducing regulator downstream from the tester.

CHAPTER IV

PROCEDURE OF COLLECTING EXPERIMENTAL DATA

Technique in Saturating Natural Gas With Water

A specific operating procedure for preparing saturated natural gas was followed during the investigations. In bringing the apparatus to the desired pressure, the saturator was by-passed to prevent condensation of moisture in the system. After the desired operating pressure was attained, the gas was turned through the saturator and the gas flow through the dew point tester equipment was adjusted to approximately 25 standard cubic feet an hour. The equipment was allowed to operate for an hour or more to reach a state of equilibrium, at which time the gas was tested for saturation in the Bureau of Mines dew point tester. Since the pressure of the gas in the dew point tester was 200 pounds per square inch absolute, it was necessary to convert the dew point at that pressure to a water content by the use of a water content graph.[23] This water content, when converted to a dew point at the system temperature and pressure, was checked to agree within 1°F. with the saturated water content of the gas at the operating temperature and pressure.

Technique Used in Filling and Rotating Equilibrium Cylinder

When it was determined that the gas was saturated, the dew point equipment was completely by-passed and the equilibrium cell was connected directly to the high pressure saturating system.

The equilibrium cell had previously been completely filled with glycol of the desired concentration. The valves leading to the top of the equilibrium cell from the gas saturating system were opened completely, imposing system pressure on the cell. The glycol was slowly displaced from the equilibrium cell through the copper tubing leading from the bottom of the vessel and collected in a calibrated 18 liter bottle. The rate of glycol flow was controlled by the outlet valve on the copper tube at such a rate that the gas flow into the equilibrium cell did not exceed 25 standard cubic feet an hour. Since the capacity of the upper cylinder was 8885 milliliters, 9000 milliliters of glycol were displaced from the cell and collected in the calibrated bottle. This left approximately 2000 milliliters of glycol in the lower cylinder. The equilibrium cell valves on the inlet and outlet lines were closed and the connections to the saturating system broken. Plugs were then screwed in the outlet valves and rotation was begun in the constant temperature bath. Temperature of the bath was maintained within 1°F. of the desired temperature by the manual addition of ice or steam as required.

Rotation rate was controlled at approximately one revolution per minute. The cell was rotated for at least two hours, and many runs

exceeded this by at least one hour. As determined by a series of preliminary runs, this time interval permitted attainment of an equilibrium state sufficiently close to true equilibrium. In fact, there was evidence to indicate that fifteen minutes agitation would be adequate but the longer two-hour interval was adopted as a safe minimum.

On all runs on diethylene and triethylene using essentially 100 per cent glycol concentration, the equilibrium cell was separately filled for each run. However, on the 95 per cent and 98 per cent glycol concentration runs the equilibrium cell was filled initially at 2500 pounds per square inch and rotated for two hours. The water content was then measured by the thermistor circuit. This measurement was usually completed before the pressure in the cell had dropped more than 200 pounds per square inch so, for the next run, gas was bled from the cell until the pressure had dropped to 2000 pounds per square inch. Then the equilibrium cell was sealed and rotated again for two hours at this new pressure. This dropping of pressure to the next lower pressure run was continued to the final run at 500 pounds per square inch. Comparison of the 500 pounds per square inch data obtained by this method with that obtained by Russell[9] and Porter[10] on 95 per cent by weight diethylene and triethylene glycols, respectively, indicates that this method is satisfactory. A separate check was made on 98 per cent by weight diethylene glycol at 500 pounds per square inch and 80°F. by filling the equilibrium cell initially to that pressure, rotating the cell,

and measuring the equilibrium water content of the gas phase. The results were then compared with the data obtained at essentially the same conditions but arrived at by the pressure drop method described. Check Run No. 107 at 515 pounds per square inch, 80°F., showed a water content of 2.50 pounds per million standard cubic feet and compares within experimental error with Run No. 106 at 505 pounds per square inch, 80°F., which showed a water content of 2.05 pounds per million standard cubic feet.

Technique in Measuring the Water Content of the Gas

After the equilibrium cell had rotated for at least two hours, rotation was stopped, the cell was turned to an upright position, and hoisted out of the water bath sufficiently to remove the plug in the inlet valve on top of the cell, and insert a pressure gauge to measure the pressure of the system. This is the pressure recorded in the data at the temperature of the water bath. Pressure was read to the nearest 10 pounds per square inch. The cell was then hoisted completely out of the water to permit closing of the 1/2-inch valves connecting the upper and lower cylinders. This was to prevent any further contact of the glycol solution with the dehydrated natural gas, thus tending to maintain the gaseous phase at constant composition. The drop in gas pressure resulting from the taking of gas samples creates the tendency for the gas to pick up additional water, thus the equilibrium water content will

not decrease during the taking of the sample. Errors in measurement of the water contents should then tend to be in the direction of larger values than the equilibrium values.

The cell was lowered back into the water bath, and the pressure gauge removed. The top valve was then carefully dried with a cloth, and fitted with a 5/16-inch copper tubing connection. To this was attached a 5-foot length of "Tygon" plastic tubing leading to the reaction cell. Gas flow from the equilibrium cell to the reaction cell was regulated by the 1/4-inch needle valve on top of the equilibrium cell at the rate of two cubic feet an hour. This rate was maintained constant within 10 per cent of the desired rate.

Gas was allowed to flow through the reaction cell for at least an hour before thermistor circuit readings were made. Readings to the nearest 0.1 ohm were continued at 15-minute intervals until the resistance ratio was constant in the fourth digit with an average deviation not exceeding 0.0005 in a resistance ratio reading of approximately 0.8250 for at least an hour. This corresponds to a water content average deviation of 0.3 pounds per million standard cubic feet.

Technique of Calibrating the Thermistor Bridge Circuit

The water content was determined from the ratio of the resistance readings of the two thermistors by use of a calibration curve of water content versus resistance ratio previously obtained by calibration

of the reaction cell. This curve was obtained by use of the calibration equipment of Figure 7. The P_2O_5 dehydrated gas only was first passed through the reaction cell at the rate of two cubic feet an hour as indicated by the wet test meter. Thermistor resistance readings were taken until their ratio remained constant within the desired limits for approximately one hour. The average of these readings was taken as the zero water content. During this time natural gas saturated with water at 2000 pounds per square inch and 70°F. was prepared and tested for saturation by the dew point tester. The dry gas rate through the reaction cell was then decreased, and the wet gas allowed to begin flowing at a rate, indicated on the capillary flow meter, such that the total gas flow was two cubic feet an hour. Resistance readings were again taken until their ratio remained constant again for approximately an hour. The actual water content was calculated from the known volume of wet gas in the total gas volume, and recorded as the water content of the gas in pounds per million standard cubic feet at 14.7 pounds per square inch, 60°F., corresponding to the resistance ratio reading. In this way the data of Table 6 were obtained and from these data the calibration curve of Figure 9 was prepared.

Technique in Measuring the Water Content of Natural Gas by Karl Fischer Reagent

Approximately 25 milliliters of Karl Fischer reagent were added to the absorption flask and titrated to an end-point with a standard

methanol solution. Stirring was accomplished by allowing gas from the equilibrium cylinder to bubble through the Karl Fischer reagent. Once the end-point was reached, the flow of gas was stopped, and exactly two milliliters of fresh Fischer reagent was added to the neutral solution. The wet test meter was adjusted to zero reading, and the flow of dehydrated gas through the reagent was started. Flow was regulated at 1/2 to 1 cubic feet an hour. A faster rate caused excessive frothing of the reagent and too much carry-over of entrained liquid. Approximately two cubic feet of gas were required to react with the two milliliters of Fischer reagent. Meter temperature pressure and rate readings were taken at 15 minute intervals and averaged for calculation of the volume of gas passed through the solution. From the water equivalence of the Karl Fischer reagent, and the volume of gas passed through to an end-point, the water content of the gas was calculated.

CHAPTER V

PROPERTIES OF MATERIALS AND EXPERIMENTAL DATA

Properties of Materials

The natural gas used in this investigation was obtained from the mains of the Oklahoma Natural Gas Company, Norman, Oklahoma. A representative analysis, determined by Mr. J. T. Bailey, Norman, Oklahoma, is shown in Table 1. The actual composition of this gas varied widely during the course of the research due to air injection by the distributor to regulate the heating value of the gas.

The diethylene and triethylene glycols used were commercial grades with guaranteed 0.2 per cent maximum water content, contributed by Carbide and Carbon Chemicals Company. The actual water content of these and other glycols used was determined by titration with Karl Fischer reagent using an electrometric circuit to determine the end point. The triethylene and diethylene glycols, as received, were essentially 100 per cent and 99.8 per cent glycol, respectively. For runs requiring essentially 100 per cent glycol the material was used as received. The concentrated commercial glycol was diluted with the proper amount of water to form the 95 per cent and 98 per cent by weight glycol

solutions. The final water concentration was checked by titration with Karl Fischer reagent. All concentrations are believed accurate within 0.5 per cent by weight. Some properties of diethylene and triethylene glycol are presented in Table 2. These properties are those reported by Carbide and Carbon Chemicals Company.[24]

The "Dicol" used was a commercial grade contributed by the Wyandotte Chemicals Corporation, Chicago, Illinois. A representative analysis furnished by the manufacturer is shown in Table 3. The hexylene glycol used was supplied by Shell Chemical Corporation, and the physical properties, as determined by Carbide and Carbon Chemicals Company[24], are shown in Table 4.

Karl Fischer reagent was prepared from absolute methanol, pyridine, iodine, and sulfur dioxide as recommended in the U.O.P. Laboratory Manual.[21] This gave a Fischer reagent with a water equivalence of approximately two milligrams of water per milliliter of reagent. This solution was standardized before use every day by titration against a standard water-methanol solution. Check determinations of the standardization agreed within 0.1 milliliter.

Thermistor Bridge Circuit Calibration Data

Table 5 gives the data for the variation of the thermistor circuit resistance ratio for natural gas dehydrated by phosphorous pentoxide or anhydrous magnesium perchlorate, or by both desiccants in series with

TABLE 1

ANALYSIS OF NATURAL GAS

Sp. Gr., 0.7228

Component	Volume %
O_2	1.88
CO_2	0.00
N_2	10.16
CH_4	72.07
C_2H_6	9.82
C_3H_8	4.25
iC_4H_{10}	0.41
C_4H_{10}	0.88
iC_5H_{12}	0.19
C_5H_{12}	0.17
C_6H_{14}	0.10
C_7H_{16}	0.07
	100.00

Analysis by J. T. Bailey, Norman, Oklahoma

TABLE 2

PHYSICAL PROPERTIES OF DIETHYLENE AND TRIETHYLENE GLYCOL[24]

Diethylene Glycol

Formula: $HOCH_2CH_2OCH_2CH_2OH$

Molecular Weight: 106.12

Specific Gravity: 1.1184 at 20/20°C

Vapor Pressure:

760 mm at 245°C
0.01 mm at 20°C

Solubility in water, 20°C: Miscible all proportions

Triethylene Glycol

Formula: $HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$

Molecular Weight: 150.17

Specific Gravity: 1.1255 at 20/20°C

Vapor Pressure:

760 mm at 291.2°C
0.01 mm at 20°C

Solubility in water, 20°C: Miscible all proportions

TABLE 3

PHYSICAL PROPERTIES OF "DICOL"

Specific gravity: 1.10 - 1.11 at 20°C.

Water content: 0.5% maximum

Composition:

Diethylene glycol: 75% - 82%

Dipropylene glycol: 12% - 19%

Monoglycols: 6% maximum

Boiling range:

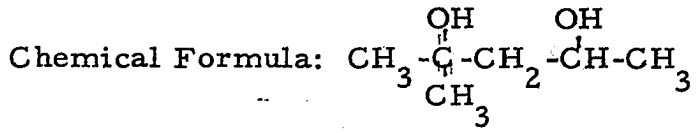
Initial Boiling Point: 226°F.

90% distilled at 248°F.

Material and data supplied by Wyandotte Chemicals Corporation, Chicago, Illinois.

TABLE 4

PHYSICAL PROPERTIES OF HEXYLENE GLYCOL[24]

Chemical Formula: 

Molecular Weight: 118.17

Apparent Specific Gravity at 20/20°C: 0.9234

Boiling Point at 760 mm. Hg: 197.1°C

Vapor Pressure at 20°C: 0.05 mm. Hg.

Freezing Point: Sets to glass below -50°C.

Heat of Vaporization: 208 Btu/lb.

Absolute Viscosity at 20°C: 34.4 cps.

phosphorous pentoxide in last position in the drying train. Also shown is the effect of the amount of calcium hydride in the reaction cell. These data were taken over a period of several weeks, and represent resistance readings taken when the change in room temperature did not exceed approximately 1.0°F. per hour. Variation in the zero water content readings is believed to be due to factors such as sunlight and air drafts in the laboratory which influenced the very sensitive thermistors.

Table 6 gives the data for the variation of the thermistor circuit resistance ratio with the water content of natural gas. After a lapse of several months in use of the thermistor circuit, it was noted that there was an increase in the resistance ratio readings. This required recalibration of the circuit, and the recalibration data is shown at the bottom of Table 6. The shift did not appear to take place during continuous operation for periods exceeding approximately one month. Therefore, recalibration was carried out just before each new series of runs. It was not believed necessary to run a complete set of points for each calibration, but only points for zero water content and one other point of known water content. Experimental data showed that the water content curves were parallel to each other within experimental error.

The capillary flow meter used in metering the wet gas stream was calibrated with a Precision wet test meter by adjusting the gas flow through the capillary flow meter to give a series of different manometer

TABLE 5

VARIATION OF THERMISTOR CIRCUIT RESISTANCE RATIO FOR NATURAL GAS WITH ANHYDROUS MAGNESIUM PERCHLORATE AND WITH PHOSPHOROUS PENTOXIDE

Resistance Ratio	Average Deviation	Room Temp., °F	Desiccant	Calcium Hydride, depth, in.
0.83700	0.00057	74.2	P_2O_5	2
0.83737	0.00020	74.0		
0.83761	0.00004	74.0		
0.83733	0.00024	68.0		
0.83648	0.00109	68.0		
0.83702	0.00055	68.0		
0.83624	0.00133	67.8		
0.83737	0.00020	72.2		
0.83741	0.00016	72.3	Anhy. $Mg(ClO_4)_2$	2
0.83707	0.00050	72.0		
0.83564	0.00193	71.0		
0.83599	0.00158	70.4		
0.83628	0.00129	70.0		
0.83672	0.00085	70.0		
0.83689	0.00069	68.6		3
0.83727	0.00030	69.0		
0.83950	0.00193	70.7		
0.83766	0.00009	70.3		
0.83706	0.00051	70.8		
0.83754	0.00003	71.7		
0.83632	0.00125	69.3	P_2O_5	3
0.83798	0.00041	67.5		
0.83694	0.00063	63.6		
0.83739	0.00018	66.3		
0.83809	0.00052	63.3		
0.83926	0.00169	66.0		
0.83736	0.00021	83.0		
0.83755	0.00002	63.8		
0.83751	0.00006	63.8		
0.83861	0.00104	65.2		

Table 5 - Continued

Resistance Ratio	Average Deviation	Room Temp., °F	Desiccant	Calcium Hydride, depth, in.
0.83881	0.00124	65.8		
0.83812	0.00055	65.5		
0.83705	0.00052	67.5		
0.83655	0.00102	65.2		
0.83790	0.00033	66.3		
0.83927	0.00170	67.8		
0.83931	0.00174	67.8		
0.83905	0.00148	67.0		
0.83998	0.00241	64.4		
0.83681	0.00076	67.0		
0.83655	0.00092	66.8		
0.83992	0.00235	71.7		
0.83744	0.00013	69.0		
0.83691	0.00066	68.0		
0.83643	0.00144	68.2		
0.83615	0.00142	68.0		
0.83663	0.00094	68.1	P_2O_5	3
0.83655	0.00102	67.9		
0.83905	0.00148	69.2		
0.83929	0.00172	68.9		
0.93897	0.00140	68.9		
0.83863	0.00106	69.3		

Average Resistance Ratio: 0.83757

Average Deviation: 0.00087

readings and measuring the different volume rates of gas flow. The volume rate of gas flow was corrected to standard cubic feet of gas per hour measured at 14.7 pounds per square inch absolute and 60°F., and plotted against the following function to obtain a straight line. The function is,

$$\sqrt{\frac{h_{TEG} P_f}{T_f}}$$

where:

h_{TEG} = manometer readings in inches of triethylene glycol

P_f = flowing pressure of gas, inches of Mercury

T_f = flowing temperature, degrees Rankine

This calibration curve permitted the measurement of the quantity of wet gas mixed with the total volume of wet and dry gas measured with the wet test meter. From these data the water content of the gas being passed through the reaction cell could be easily calculated.

Vapor-Liquid Equilibrium Data

Since the Gibbs' Phase Rule required that equilibrium data for the two phase, three component system of water-glycol-natural gas be taken as a function of temperature, pressure and composition, data were taken at temperatures of 70°F., 80°F., and 90°F.; at pressures varying from 500 to 2500 pounds per square inch absolute; at glycol concentrations of 95, 98, and essentially 100 per cent by weight. Tables 7, 8,

TABLE 6

VARIATION OF THERMISTOR CIRCUIT RESISTANCE RATIO WITH WATER CONTENT OF NATURAL GAS+

Gas rate: 2.0 $ft^3/hr.$

First Calibration

Resistance Ratio	Water Content lbs/MMSCF*
0.8343	0
0.8316	1.20
0.8302	2.29
0.8285	3.55
0.8254	4.35
0.8237	5.93
0.8226	7.09
0.8062	15.7

Second Calibration

Resistance Ratio	Water Content lbs/MMSCF*
0.83757	0
0.82872	6.70

+ Plotted in Figure 9.

* Pounds per million standard cubic feet of gas measured at 14.7 lbs. per sq. in. absolute, 60°F.

and 9 show the water contents of natural gas dehydrated by diethylene glycol. Water contents were measured by the thermistor bridge circuit. Tables 10 and 11 show the water content of natural gas dehydrated by essentially 100 per cent triethylene glycol. The water content data in Table 10 were measured by the Karl Fischer method while those of Table 11 were determined by the thermistor bridge circuit. Comparison of these two tables indicates substantial discrepancy. The inconsistency of the Karl Fischer data in this low concentration range led to abandonment of this method for water vapor determinations in the gaseous phase. Tables 12 and 13 show the water contents of natural gas dehydrated with lesser concentrations of triethylene glycol, water contents being measured by the thermistor bridge circuit. Table 14 shows the "check points" of the water contents of natural gas dehydrated with "Dicol" and hexylene glycol. These water contents were also determined by use of the thermistor bridge circuit.

TABLE 7

WATER CONTENTS OF NATURAL GAS DEHYDRATED BY 99.8 PER CENT BY WEIGHT DIETHYLENE GLYCOL+

Water contents measured by thermistor bridge circuit

Run No.	Temperature °F	Pressure, Psia.*	Water Content, lbs/MMSCF*
40	70	2525	1.33
51	70	2035	2.52
41	70	1525	3.33
52	70	1020	0.90
42	70	535	1.83
45	80	2515	1.72
50	80	2015	0
43	80	1590	1.34
49	80	1030	0.63
44	80	550	2.62
48	90	2515	1.05
46	90	1565	0.73
47	90	510	2.08

+ Plotted in Figure 10.

* Pounds per square inch absolute.

* Pounds per million standard cubic feet of gas at 14.7 lbs. per sq. in. absolute, 60°F.

TABLE 8

WATER CONTENTS OF NATURAL GAS DEHYDRATED BY 98 PER CENT BY WEIGHT DIETHYLENE GLYCOL+

Water contents measured by thermistor bridge circuit

Run No.	Temperature °F	Pressure, Psia.*	Water Content, lbs/MMSCF*
73	70	2535	1.00
108	70	2415	0.40
74	70	2065	2.00
109	70	1985	0.80
110	70	1565	0.90
75	70	1525	2.83
76	70	1025	2.15
111	70	1015	1.20
112	70	545	1.00
77	70	510	3.55
102	80	2535	0.20
68	80	2535	2.48
69	80	2065	2.50
103	80	1845	2.60
104	80	1605	1.10
70	80	1565	2.55
105	80	1065	1.40
71	80	990	3.80
107	80	515	2.45
72	80	510	3.33
106	80	505	2.05
78	90	2540	0.20
79	90	2090	2.15
80	90	1565	2.40
81	90	1135	2.43
82	90	515	6.80

+ Plotted in Figure 11.

* Pounds per square inch absolute.

* Pounds per million standard cubic feet of gas at 14.7 lbs. per sq. in., 60°F.

TABLE 9

WATER CONTENTS OF NATURAL GAS DEHYDRATED BY 95 PER CENT BY WEIGHT DIETHYLENE GLYCOL+

Water contents measured by thermistor bridge circuit

Run No.	Temperature, °F	Pressure, Psia.*	Water Content, lbs/MMSCF*
63	80	2505	2.27
64	80	2040	2.85
65	80	1545	4.63
66	80	1015	5.66
67	80	490	9.35

+ Plotted in Figure 12.

* Pounds per square inch absolute.

* Pounds per million standard cubic feet of gas at 14.7 lbs. per sq. in. absolute, 60°F.

TABLE 10

WATER CONTENTS OF NATURAL GAS DEHYDRATED BY ESSENTIALLY 100 PER CENT TRIETHYLENE GLYCOL+

Water contents measured by Karl Fischer reagent

Run No.	Temperature °F	Pressure, Psia.‡	Water Content, lbs/MMSCF*
23	70	535	3.59
24	70	1075	1.79
26	70	1515	1.71
20	80	505	2.76
19	80	515	4.42
18	80	520	2.30
15	80	1020	3.09
21	80	1025	2.12
16	80	1507	1.84
17	80	2055	1.56
22	80	2315	1.88
25	90	545	3.32
28	90	1055	3.96
27	90	1575	1.82

+ These data are not plotted, but are presented only for comparison with the data of Table 11.

‡ Pounds per square inch absolute.

* Pounds per million standard cubic feet of gas at 14.7 lbs. per sq. in. absolute, 60°F.

TABLE 11

WATER CONTENT OF NATURAL GAS DEHYDRATED BY ESSENTIALLY 100 PER CENT TRIETHYLENE GLYCOL+

Water contents measured by thermistor bridge circuit

Run No.	Temperature, °F.	Pressure, Psia.#	Water Content, lbs/MMSCF*
31	70	2545	1.32
30	70	2035	0.32
29	70	1555	0.00
32	70	1090	0.87
33	70	515	0.73
34	80	2515	1.22
35	80	1540	0.93
36	80	540	2.10
37	90	2565	0.60
38	90	1540	1.25
39	90	565	1.05

+ Plotted in Figure 13.

Pounds per square inch absolute.

* Pounds per million standard cubic feet of gas at 14.7 lbs. per sq. in. absolute, 60°F.

TABLE 12

WATER CONTENT OF NATURAL GAS DEHYDRATED BY 98 PER CENT BY WEIGHT TRIETHYLENE GLYCOL+

Water contents measured by thermistor bridge circuit

Run No.	Temperature, °F.	Pressure, Psia.‡	Water Content, lbs/MMSCF*
88	70	2545	1.05
89	70	2085	1.00
90	70	1420	2.75
91	70	1015	2.50
92	70	505	2.70
53	80	2515	0.87
54	80	2015	1.20
55	80	1535	0.90
56	80	990	1.73
57	80	455	4.35
83	90	2536	2.27
84	90	2055	3.33
85	90	1565	2.00
86	90	1005	2.05
87	90	515	4.17

+ Plotted in Figure 14.

‡ Pounds per square inch absolute.

* Pounds per million standard cubic feet of gas at 14.7 lbs. per sq. in. absolute, 60°F.

TABLE 13

WATER CONTENT OF NATURAL GAS DEHYDRATED BY 95 PER CENT BY WEIGHT TRIETHYLENE GLYCOL+

Water contents measured by thermistor bridge circuit

Run No.	Temperature, °F.	Pressure, Psia.‡	Water Content, lbs/MMSCF*
93	70	2535	2.35
94	70	2040	3.10
95	70	1600	2.17
96	70	1015	3.60
97	70	435	6.45
58	80	2525	1.85
59	80	2095	2.80
60	80	1515	3.50
61	80	1015	4.12
62	80	485	7.85

+ Plotted in Figure 15.

‡ Pounds per square inch absolute.

* Pounds per million standard cubic feet of gas at 14.7 lbs. per sq. in. absolute, 60°F.

TABLE 14

WATER CONTENT OF NATURAL GAS DEHYDRATED BY "DICOL" AND HEXYLENE GLYCOL+

Water contents measured by thermistor bridge circuit

Run No.	Glycol	Glycol Concentration weight %	Temperature °F.	Pressure Psia.*	Water Content, lbs/MMSCF*
100	"Dicol"	95	80	1006	3.27
99	"Dicol"	100	70	555	2.00
98	"Dicol"	100	70	1040	2.31
101	Hexylene	100	70	2415	2.08

+ These data are not plotted.

* Pounds per square inch absolute.

* Pounds per million standard cubic feet of gas at 14.7 lbs. per sq. in. absolute, 60°F.

CHAPTER VI

ANALYSIS OF DATA

It is the purpose of this section to show graphically the results of this investigation, to discuss the accuracy of the results, to describe in detail the method used in correlating the data, and to compare the experimental data with that of other investigators.

Accuracy of Data

The accuracy of the data presented will be discussed separately for the three distinct phases of this investigation. They are as follows: (1) determination of the zero water content point of the water measuring instrument; (2) calibration of the water measuring instrument; and (3) measurements of the equilibrium water contents of gases dehydrated by aqueous glycol solutions.

To determine the zero water content reading of the water measuring instrument a dry gas was prepared by passing the gas through a phosphorous pentoxide or an anhydrous magnesium perchlorate drying tube or through the tubes connected in series with the phosphorous pentoxide tube in final position in the drying train. Since the residual water content of gases dehydrated by either anhydrous magnesium

perchlorate[25] or phosphorous pentoxide[26] is less than 0.1 pound per million standard cubic feet, a gas of essentially zero water content was so prepared and used in the determination of the resistance readings corresponding to zero water content.

In observing the resistance readings corresponding to zero water content, resistances were read to the nearest 0.1 ohm. If an error of $\pm$ 0.1 ohm is permissible in the measurements of the two resistances, then the error in water content measurement would be less than 0.2 pounds per million standard cubic feet.

The resistance ratios corresponding to zero water content given in Table 5 were taken over a period of several weeks and at times during which the variation in room temperature did not exceed 1°F. per hour. These values were then averaged to give a value of the resistance ratio of 0.83757 with an average deviation of 0.00087. Inspection of the data presented in Figure 9 reveals that the average deviation represents an error of approximately $\pm$ 0.66 pounds per million standard cubic feet in the water content measurement.

The ratio of the resistances of the two thermistors used in the water measuring instrument was not affected by temperature changes over a wide range so long as both thermistors were at the same temperature. However, a very slight difference in the temperatures of the two thermistors at any instant caused a great variation in the resistance ratio reading. It is believed that direct sunlight and air drafts in the labora-

tory caused sufficient variation of the temperatures of the two thermistors to account for the error of ± 0.66 pounds per million standard cubic feet cited above.

Harris and Nash[20] report the effect of variable gas composition on water content measurements to be negligible at the low water contents employed in this investigation. Harris and Nash also report that varying gas flow through the water measuring apparatus has negligible effect when rates are held constant within ± 10 per cent.

Since the wet test meter used with this apparatus had an error of less than one per cent, as determined by calibration at the rates involved, the accuracy of the water content measurements is not affected by the gas volume measurements.

In preparing the calibration curve presented in Figure 9, it was necessary to mix a definite volume of wet gas with dry gas to give a total flow rate of the mixture of two cubic feet per hour through the water measurement apparatus. Possible errors in the preparation of the wet gas were, (1) errors in measuring the temperature and pressure in the saturator, and (2) errors in measuring the temperature and pressure in the dew point tester. Since the temperature was maintained within $\pm 0.5°F.$ and the pressure within ± 10 pounds per square inch of the desired values in the saturator, the maximum error in the water content of the gas would not exceed ± 0.4 pounds per million standard

cubic feet. The temperature of the dew point of the wet gas was determined within ± 1.0°F. at 200 pounds per square inch absolute within a pressure error of ± 5 pounds per square inch. This corresponds to a maximum error of ± 0.5 pounds per million standard cubic feet in the determination of the water content by use of the Bureau of Mines dew point tester.

In mixing the wet and dry gases, two possible sources of error are (1) errors in measurement of the wet gas through the capillary flow meter, and (2) errors in measurement of the total gas volume by the wet test meter. The maximum error obtained from compounding these with the maximum error in the water content of the wet gas, gave a total error in the water content of ± 0.40 pounds per million standard cubic feet. From this it is evident that the error of ± 0.66 pounds per million standard cubic feet in the zero water content determination is still the maximum of all errors discussed to this point.

In the measuring the equilibrium water contents of gases dehydrated by aqueous glycol solutions, the possible errors are (1) errors in measuring the temperature and pressure of the equilibrium mixture, (2) errors in determination of the concentration of the glycol solutions, and (3) errors due to faulty technique in analysis of the water content of gases.

Inspection of the experimental data presented in Figures 10 to 15 inclusive, shows that temperature and pressure errors would have little effect over a relatively wide range of both temperature and pressure.

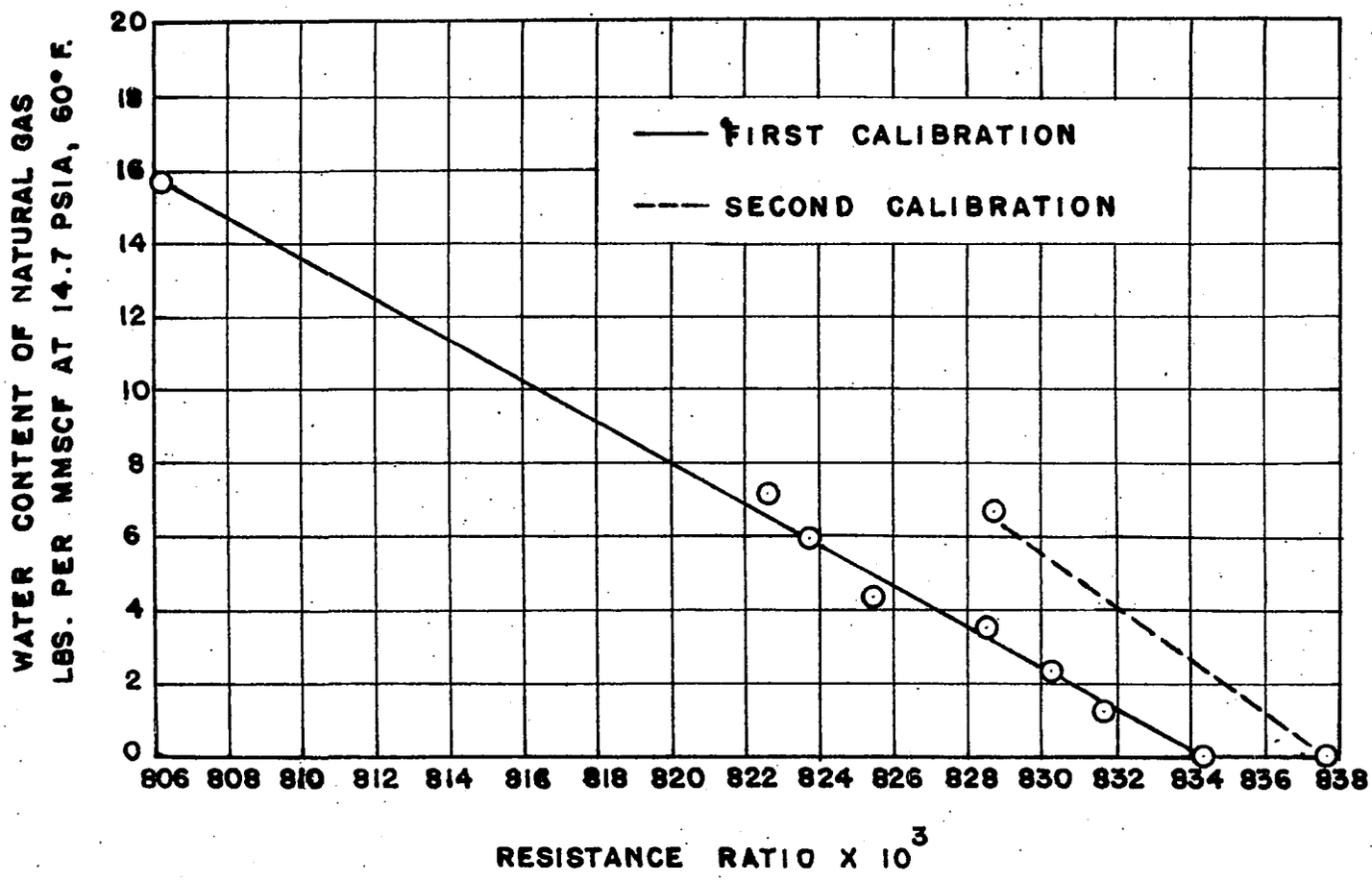


FIGURE 9. GRAPH OF CALIBRATION DATA FOR THERMISTOR BRIDGE CIRCUIT

Inspection of Figures 16 and 17 shows that an error of ± 0.5 weight per cent in the concentration of the aqueous glycol, solutions is, with one exception, within the experimental error of ± 0.66 pounds per million standard cubic feet. An error of ± 0.5 weight per cent in the concentration of 95 per cent diethylene glycol at 500 pounds per square inch absolute causes an error of approximately ± 0.9 pounds per million standard cubic feet in the water content of natural gas in contact with the solution.

All errors discussed up to this point, with the single exception noted above, should fall within the instrument error of ± 0.66 pounds per million standard cubic feet. If there were no other sources of error, then the average error in experimental data should fall within the limits of accuracy of the instrument. However, there is one other source of error which sometimes caused the error in experimental data to exceed that of the instrument. This was caused by dehydration of droplets of glycol solution sprayed into the sampling line connecting the equilibrium cylinder and the water measuring instrument. Natural gas in the equilibrium cylinder at pressures exceeding 500 pounds per square inch was dropped to atmospheric pressure in the sampling line by expansion across a needle valve. This large pressure drop sometimes caused droplets of glycol solution to be sprayed from within the valve to the walls of the sampling line. The very dry, low-pressure natural gas then stripped the water from the glycol droplets causing a substantially larger water content to be indicated. This effect was especially pronounced for the 95 per cent

and 98 per cent glycol solutions.

The error caused by the droplets of glycol solution was minimized by first opening the valve on the equilibrium cylinder and discharging the glycol spray to the atmosphere. The valve outlet was then thoroughly dried with a clean cloth and, finally, the sampling line was attached. In this manner the amount of glycol sprayed into the sample line was very small, causing negligible errors that did not exceed the instrument error of ± 0.66 pounds per million standard cubic feet.

Correlation of Data

One of the principal objectives of this investigation was to develop a broad, relatively simple and generally applicable correlation of the experimental data presented in Tables 7 to 13, inclusive, based on the thermodynamic approach outlined in Chapter II. It is conceded that there may well be other methods for correlation of this phase of the problem, and other methods were investigated. Some of these indicated some merit. In general, they were more complex, required more data than were available and promised rather limited usage. The discussion that follows will point out some of the difficulties encountered in obtaining a satisfactory empirical correlation.

Attempts were made using Equation (24), written for water as component 2, thus:

$$\frac{y_2}{x_2} = B_2 \gamma_2 K_2 \qquad (24)$$

to correlate the experimental data. Experimental values[10, 12] of y_2 and x_2, mole fractions water in the vapor and liquid phases, respectively, obtained at constant temperature and glycol concentration but at varying pressures, were substituted into Equation (24) together with values of K_2 calculated from Equation (18). It was thought that the values of $B_2\gamma_2$ obtained could be constant at all pressures under the conditions of constant temperature and glycol concentration. Results indicated that $B_2\gamma_2$ calculated in this manner was primarily a function of pressure, and relatively independent of temperature and glycol concentration. The variation of the $B_2\gamma_2$ values with pressure was as great as the variation in the water content determinations, so values of $B_2\gamma_2$ obtained in this manner were of no use in correlating the data.

In an attempt to devise a correlation method that would work, a study was made on the methane-water system in equilibrium at various temperatures and pressures. Good experimental data[23, 27] were available on this system, and it was hoped that a method could be developed from this study which could be extended to the methane-water-glycol system.

Application of Thermodynamic Equations to the Methane-Water System

Equation (24) can be written for methane as component 1,

$$\frac{y_1}{x_1} = \frac{B_1\gamma_1 P_1 (\nu_1)_{P_1}^{\,e^{\frac{V_m(\pi - P_1)}{RT}}}}{\pi (\nu_1)_\pi} = B_1\gamma_1 K_1 \qquad (25)$$

At equilibrium the following are true:

$$x_1 + x_2 = 1.0 \tag{26}$$

$$y_1 + y_2 = 1.0 \tag{27}$$

In addition, let it be required without explanation until later that the following is true:

$$\gamma_1 + \gamma_2 = 1.0 \tag{28}$$

Equations (24), (25), (26), (27) and (28) are five independent equations with six unknowns in x, y, and γ; so a solution for any single unknown is impossible. However, values of y_2 in terms of x_1 and x_2 can be obtained by eliminating y_1, γ_1, and γ_2 to give:

$$y_2 = B_2 x_2 K_2 \left[\frac{B_1 x_1 K_1 - 1}{B_1 x_1 K_1 - B_2 x_2 K_2} \right] \tag{29}$$

If the temperature and pressure of the methane-water system are fixed, then values of K_1 and K_2 can be determined from Equation (18). By means of Equation (18), values of the vaporization constants K_1 and K_2 were calculated for both methane and water at various temperatures and pressures. The use of Equation (18) for methane systems at room temperatures required the vapor pressure and molal volume of liquid methane above its critical temperature. Equation (20) was used in the following form to estimate the vapor pressure of the methane:

$$\log_{10} p = -\frac{2.3383}{T_r} + 6.8800 - e^{-20(T_r)^2} \tag{30}$$

where:

p = vapor pressure in millimeters of Mercury

T_r = reduced temperature

The vapor pressure of water was taken from experimental data.[28]

The molal volumes of pure liquid methane and pure water were obtained from Equation (19) where the value of $(V\omega)$, which is a characteristic constant for each component, was established from a single molal volume measurement, V, and the corresponding value of ω, an expansion factor, which is expressed by Watson[29] as a function of reduced temperature and pressure.

It was found by trial and error that if values of y_2, K_1 and K_2 obtained at any temperature and pressure were substituted into Equation (29), and B_2x_2 was arbitrarily assigned a value of 1.0, then the calculated values of B_1x_1 were constant, and approximately equal to the reciprocal of the fugacity coefficient of liquid methane, $(\nu_1)_{P_1}$ determined at the temperature of the system. Use was made of the information thus obtained to calculate values of y_2 at any other temperature and pressure. For example, values of K_1 and K_2 are determined for methane and water at any temperature and pressure. These values of K_1 and K_2, together with the values $B_2x_2 = 1$ and $B_1x_1 = \frac{1}{(\nu_1)_{P_1}}$ are substituted into Equation (29), and the value of y_2 is calculated. This term is simply converted into water contents in pounds per million standard cubic feet.

Using the method described above, the water contents of methane gas at saturation at various temperatures and pressures were calculated.

Table 15 shows a comparison of calculated water contents with experimental values. Column 3 of this table shows the experimental values,[23] and column 4 shows the calculated values based on the assumption that $B_2x_2 = 1.0$ and $B_1x_1 = \frac{1}{(\nu_1)_{P_1}}$. It is seen by comparing the values in these two columns that the agreement is reasonably good over the temperature and pressure range involved.

The requirement of Equation (28) that the sum of γ_1 and γ_2 equals unity is an unusual requirement for activity coefficients. It is probable that $\gamma_1 + \gamma_2$ are equal to a constant which is near unity in value. Any difference from unity is absorbed into B_1x_1 which in reality is an empirical factor.

The importance of the term γ_2 for calculating the mole fraction water in the vapor phase can be seen from an inspection of Table 16 in which the value of each term of Equation (24) $y_2 = B_2x_2K_2\gamma_2$, is shown for the methane-water system at 80°F. at pressures from 14.7 to 3000 pounds per square inch absolute.

The values of y_2 in Table 16 were calculated from experimental data.[23] The values of K_2, vaporization constant for water, were calculated at 80°F. and the appropriate pressure by means of Equation (18). The value of B_2x_2 was assumed equal to 1.0, and the value of $B_1x_1 = \frac{1}{(\nu_1)_{P_1}}$. The values of γ_2 were then calculated by simultaneous solution of Equations (24), (25), (27) and (28).

TABLE 15

COMPARISON OF CALCULATED WATER CONTENTS OF METHANE GAS AT SATURATION WITH EXPERIMENTAL WATER CONTENTS[23]

Pressure Psia.*	Temperature, °F.	Experimental Water Content, lbs/MMSCF*	Calculated Water Content; $B_1 x_1 = \frac{1}{(v_1)_{P_1}}$ lbs/MMSCF*
14.7	70	1190	1193
100	70	178	177
300	70	65	62.7
500	70	42.5	40.0
1000	70	24.7	24.8
1500	70	19.0	19.6
2000	70	15.8	16.8
2500	70	14.3	14.7
3000	70	13.0	13.2
14.7	80	1670	1680
100	80	242	248
300	80	89.0	87.6
500	80	58.0	55.6
1000	80	34.0	34.3
1500	80	26.0	26.9
2000	80	21.4	22.9
2500	80	19.8	20.0
3000	80	18.0	18.0
14.7	90	2330	2355
100	90	335	343
300	90	122	120
500	90	79.0	76.4
1000	90	46.0	46.9
1500	90	35.0	36.4
2000	90	29.0	30.9
2500	90	26.5	27.1
3000	90	24.3	24.4

* Pounds per square inch absolute.

* Pounds per million standard cubic feet of gas at 14.7 lbs. per sq. in. absolute, 60°F.

It is evident from an inspection of Column 5 of Table 16 that the variation of γ_2 is an important factor to be considered in Equation (24). If the value of γ_2 did not decrease with increasing pressure, the value of B_2x_2 would not be a constant, but would have to decrease with increasing pressure. It is evident, therefore, that γ_1 and γ_2 are relating activities to mole fractions, and so are activity coefficients. The requirement that $\gamma_1 + \gamma_2 = 1.0$ is a special solution for this particular system, and is not to be considered a general requirement for activity coefficients.

Application of Thermodynamic Equations to the Methane-Water-Glycol System

A strict application of this approach to the methane-water-glycol system requires the addition of terms to indicate the presence of glycol in the system. An equation similar to Equation (24) can be written for glycol as component 3:

$$\frac{y_3}{x_3} = B_3\gamma_3K_3 \tag{31}$$

where the terms have the same significance for glycol as the corresponding terms in Equation (24) have for water.

At equilibrium the following are true,

$$x_1 + x_2 + x_3 = 1 \tag{32}$$

$$y_1 + y_2 + y_3 = 1 \tag{33}$$

In addition, again let it be required that the following is also true,

TABLE 16

VARIATIONS IN THE TERMS OF EQUATION (24), $y_2 = B_2 x_2 K_2 \gamma_2$, FOR THE METHANE-WATER SYSTEM WITH PRESSURE AT 80°F.

Pressure, Psia.*	Mole Fraction, $y_2 \times 10^3$	Empirical Factor, $B_2 x_2$	Vaporization Constant, $K_2 \times 10^3$	Activity Coefficient, γ_2
14.7	3.52	1.00	34.45	1.02
500	1.22	1.00	1.410	0.865
1000	0.716	1.00	1.035	0.692
1500	0.547	1.00	0.9575	0.571
2000	0.451	1.00	0.933	0.483
2500	0.417	1.00	0.930	0.449
3000	0.379	1.00	0.9425	0.402

* Pounds per square inch absolute.

$$\gamma_1 + \gamma_2 + \gamma_3 = 1 \qquad (34)$$

Equations (24), (25), (31), (32), (33) and (34) are six equations with nine unknowns, excluding B_1, B_2, and B_3, so that a simultaneous solution for any single unknown is impossible. The three-component, two-phase, methane-water-glycol system can be thermodynamically fixed at equilibrium by setting the temperature, pressure and composition of the system. Then the values of K_1, K_2, and K_3 can be calculated; and values of x_1, x_2, x_3, and y_1 are approximately known. This reduces the number of equations and number of unknowns, but a simultaneous solution for y_2, mole fraction water in the vapor phase, is still impossible. Therefore, certain simplifying assumptions are necessary before the method of calculation of equilibrium water contents for the methane-water system can be used for the methane-water-glycol system.

Experimental data[12] indicate that the mole fraction of triethylene glycol in the vapor phase is of the order of 1×10^{-6}. The mole fraction water vapor in most cases is greater than 20×10^{-6}, which corresponds to 1.0 pounds per million standard cubic feet. No experimental data are available for diethylene glycol in the vapor phase, but the mole fraction should be of the same order of magnitude as that of triethylene glycol. Because of the small amount of glycol present in the vapor phase relative to the amount of water in the vapor phase the mole fraction, y_3, of glycol in the vapor phase can be considered negligible. Then Equation

(33) would read,

$$y_1 + y_2 = 1.0 \qquad (35)$$

In Equation (22) γ_2 was defined to be an activity coefficient which took into account deviations from the laws of ideal solutions resulting from differences in molecular sizes or volatilities. The value of γ_2 should then be proportional to the partial pressure of component 2 in the mixtures. Then the values γ_2 and γ_3 in Equation (34) should be proportional to the respective partial pressures of water and glycol in the equilibrium mixture. In other words, γ_2 and γ_3 should bear a definite ratio to each other depending on the relative amounts of water and glycol and their relative pressures. If this can be assumed true, then γ_2 and γ_3 could be replaced by γ_2' in Equation (34) which would then read,

$$\gamma_1 + \gamma_2' = 1.0 \qquad (36)$$

The solubility of methane in aqueous glycol solutions is comparable to that of methane in water[10, 12], so that the values of B_1x_1 for methane should not differ greatly in water and glycol solutions. Hence values of $B_1x_1 = \frac{1}{(\nu_1)_{P_1}}$ used for the methane-water system should be applicable to the methane-water-glycol system.

Applying the considerations given above, which are equivalent to assuming that the ternary system is a binary one, the following equations remain:

$$y_1 = B_1 x_1 K_1 \gamma_1 \quad (25)$$

$$y_2 = B_2 x_2 K_2 \gamma_2' \quad (24)$$

$$y_1 + y_2 = 1 \quad (35)$$

$$\gamma_1 + \gamma_2' = 1 \quad (36)$$

$$x_1 + x_2 + x_3 = 1 \quad (32)$$

These equations can be solved simultaneously, eliminating y_1, γ_1, and γ_2', to give:

$$y_2 = B_2 x_2 K_2 \left[\frac{1 - B_1 x_1 K_1}{B_2 x_2 K_2 - B_1 x_1 K_1} \right] \quad (37)$$

This is the same as Equation (29) for the methane-water system. Fixing the temperature, pressure, and composition of the methane-water-glycol system will determine the values of y_2, K_1, and K_2, and if $B_1 x_1$ is taken to be $\frac{1}{(\nu_1)_{P_1}}$ for the methane-water system, then only $B_2 x_2$ is unknown.

Water content measurements were made on natural gas dehydrated by 95, 98 and essentially 100 per cent by weight solutions of diethylene and triethylene glycols at temperatures of 70°F., 80°F., and 90°F., at pressures varying from 500 to 2500 pounds per square inch absolute. These water contents were converted into mole fractions to give the values of y_2 required in Equation (37). Values of K_1 and K_2 were calculated for methane and water at the temperature and pressure of the system. The value of $B_1 x_1$ was arbitrarily taken to be the same as that determined for the methane-water system at the same temperature; i.e.,

$B_1x_1 = \frac{1}{(v_1)_{P_1}}$. Values of B_2x_2 were then calculated. It was found that, for the methane-water-glycol system, B_2x_2 behaved just as it did for the methane-water system; that is, independent of pressure and primarily a function of glycol concentration and system temperature.

The calculated values of B_2x_2 for 99.8 per cent diethylene and 100 per cent triethylene glycols are shown in Tables 17 and 18, together with values of B_2x_2 obtained for the other glycols. Inspection of the calculated values of B_2x_2 for 99.8 per cent diethylene and essentially 100 per cent triethylene glycol reveals quite a great variation in the terms. But an average value obtained for essentially 100 per cent glycols, from a summation of all the terms except those specifically listed, had an average deviation of only 50 per cent. This large error is not unexpected, however, because of the extremely low water contents measured, and because of the accuracy limits of the instrument. It must be remembered that the water contents in these cases were of the order of 1.0 pounds per million standard cubic feet, and that the accuracy of the measuring instrument is no greater than $\pm$0.66 pounds per million standard cubic feet. Also, it should be noted that the average value of B_2x_2 was obtained by including all data obtained at the three temperatures of 70°F., 80°F., and 90°F.

The average value of B_2x_2 obtained for each glycol was used, together with values of K_1 and K_2 determined at 80°F. and at pressures

varying from 500 to 3000 pounds per square inch absolute, in Equation (37) to calculate values of y_2 which were then converted into equivalent water contents in pounds per million standard cubic feet. The water contents were then plotted on Figures 10 and 13 for diethylene and triethylene glycols, respectively. These water contents are represented by the solid black lines. Inspection reveals that this curve does represent the majority of the data points. It is evident also that the effect of temperature is not exhibited. It should be noted that the radii of the plotted data points correspond to the instrument error of ± 0.66 pounds per million standard cubic feet of gas.

The procedure given above was repeated for the 98 per cent by weight glycol solutions. In this case it is plainly seen that the values of B_2x_2 are more nearly constant with an average deviation of less than 32 per cent in the case of triethylene glycol, and less than 45 per cent in the case of diethylene glycol. Water content measurements are still low, and the accuracy limits of the instrument is still a large fraction of the amount of water measured. Again the average value of B_2x_2 obtained by averaging all 98 per cent glycol data at all temperatures for each glycol was substituted into Equation (37) together with values of K_1 and K_2 determined at 80°F, and pressures varying from 500 to 3000 pounds per square inch absolute. The calculated values of y_2 were converted into their equivalent water contents in pounds per million standard

TABLE 17

CALCULATED VALUES OF B_2x_2, EMPIRICAL FACTOR, FOR AQUEOUS SOLUTIONS OF DIETHYLENE GLYCOL AT HIGH PRESSURES

99.8 per cent by weight Diethylene Glycol

Run No.	Temperature, °F.	Pressure, Psia.#	W ter Content lbs/MMSCF*	B_2x_2	Average deviation
40	70	2525	1.33	0.0905	0.0478
51+	70	2035	2.52	0.1540	-
41+	70	1525	3.33	0.1726	-
52	70	1020	0.90	0.0369	0.0058
42	70	535	1.83	0.0487	0.0050
45	80	2515	1.72	0.0861	0.0434
50	80	2015	0	0	0.0427
43	80	1590	1.34	0.0514	0.0087
49	80	1030	0.63	0.0188	0.0239
44	80	550	2.62	0.0508	0.0081
48	90	2515	1.05	0.0390	0.0037
46	90	1565	0.73	0.0204	0.0223
47	90	510	2.08	0.0274	0.0153
			Average	0.0427	0.0206

Pounds per square inch absolute.

* Pounds per million standard cubic feet of gas at 14.7 lbs. per sq. in. absolute, and 60°F.

\+ Runs No. 51 and 41 were omitted in calculating the average value of B_2x_2.

Table 17 - Continued

98 per cent by weight Diethylene Glycol

Run No.	Temperature, °F.	Pressure, Psia.	Water Content lbs/MMSCF	B_2x_2	Average deviation
73	70	2535	1.00	0.0687	0.0008
108	70	2415	0.40	0.0267	0.0412
74	70	2065	2.00	0.1233	0.0554
109	70	1985	0.80	0.0482	0.0197
110	70	1565	0.90	0.0472	0.0207
75	70	1525	2.83	0.1462	0.0783
76	70	1025	2.15	0.0883	0.0204
111	70	1015	1.20	0.0492	0.0187
112	70	545	1.00	0.0269	0.0410
77	70	510	3.55	0.0916	0.0237
102	80	2535	0.20	0.0136	0.0543
68	80	2535	2.48	0.1243	0.0564
69	80	2065	2.50	0.1126	0.0447
104	80	1605	1.10	0.0424	0.0255
70	80	1565	2.55	0.0966	0.0287
105	80	1065	1.40	0.0424	0.0255
71	80	990	3.80	0.1110	0.0431
107	80	515	2.45	0.0454	0.0225
72	80	510	3.33	0.0610	0.0069
106	80	505	2.05	0.0372	0.0307
78	90	2540	0.20	0.0072	0.0607
79	90	2090	2.15	0.0719	0.0040
80	90	1565	2.40	0.0673	0.0006
81	90	1135	2.43	0.0564	0.0115
82	90	515	6.80	0.0912	0.0233
			Average	0.0679	0.0303

Table 17 - Continued

95 per cent by weight Diethylene Glycol

Run No.	Temperature, °F.	Pressure, Psia.	Water Content lbs/MMSCF	B_2x_2	Average deviation
63	80	2505	2.27	0.1133	0.0363
64	80	2040	2.85	0.1272	0.0224
65	80	1545	4.63	0.1750	0.0254
66	80	1015	5.66	0.1673	0.0177
67	80	490	9.35	0.1652	0.0156
			Average	0.1496	0.0235

TABLE 18

CALCULATED VALUES OF B_2x_2, EMPIRICAL FACTOR, FOR AQUEOUS SOLUTIONS OF TRIETHYLENE GLYCOL AT HIGH PRESSURES

100 per cent Triethylene Glycol

Run No.	Temperature, °F.	Pressure, Psia.*	Water Content lbs/MMSCF*	B_2x_2	Average deviation
31	70	2545	1.32	0.0903	0.0564
30	70	2035	0.32	0.0195	0.0144
29	70	1555	0	0	0.0339
32	70	1090	0.87	0.0357	0.0018
33	70	515	0.73	0.0190	0.0149
34	80	2515	1.22	0.0613	0.0274
35	80	1540	0.93	0.0350	0.0011
36	80	540	2.10	0.0403	0.0064
37	90	2565	0.60	0.0224	0.0115
38	90	1540	1.25	0.0346	0.0007
39	90	565	1.05	0.0151	0.0188
			Average	0.0339	0.0170

98 per cent by weight Triethylene Glycol

Run No.	Temperature, °F.	Pressure, Psia.*	Water Content lbs/MMSCF	B_2x_2	Average deviation
88	70	2545	1.05	0.0722	0.0107
89	70	2085	1.00	0.0618	0.0003
90	70	1555	2.75	0.0144	0.0471
91	70	1015	2.50	0.1022	0.0407
92	70	505	2.70	0.0681	0.0066

* Pounds per square inch absolute.

* Pounds per million standard cubic feet of gas at 14.7 lbs. per square inch absolute, 60°F.

Table 18 - Continued

98 per cent by weight Triethylene Glycol - Continued

Run No.	Temperature, °F.	Pressure Psia.	Water Content lbs/MMSCF	B_2x_2	Average deviation
53	80	2515	0.87	0.0437	0.0178
54	80	2015	1.20	0.0529	0.0086
55	80	1535	0.90	0.0337	0.0278
56	80	990	1.73	0.0505	0.0110
57	80	455	4.35	0.0722	0.0107
83	90	2536	2.27	0.0849	0.0234
84	90	2055	3.33	0.1102	0.0487
85	90	1565	2.00	0.0563	0.0052
86	90	1005	2.05	0.0441	0.0174
87	90	515	4.17	0.0558	0.0057
			Average	0.0615	0.0188

95 per cent by weight Triethylene Glycol

Run No.	Temperature, °F.	Pressure, Psia.	Water Content lbs/MMSCF	B_2x_2	Average deviation
93	70	2535	2.35	0.1617	0.0094
94	70	2040	3.10	0.1900	0.0377
95	70	1600	2.17	0.1158	0.0365
96	70	1015	3.60	0.1472	0.0051
97	70	435	6.45	0.1470	0.0053
			Average	0.1523	0.0188
58	80	2525	1.85	0.0927	0.0296
59	80	2095	2.80	0.1273	0.0050
60	80	1515	3.50	0.1310	0.0087
61	80	1015	4.12	0.1223	0.0000
62	80	485	7.85	0.1380	0.0157
			Average	0.1223	0.0118

cubic feet and plotted in Figures 11 and 14 for diethylene and triethylene glycols, respectively. The solid curves obtained by joining these calculated points does properly represent the majority of the data points within the accuracy of the instrument. Again the effect of temperature is not evident.

The procedure was repeated for the 95 per cent by weight glycols, and best results were obtained from these data. The average deviation in B_2x_2 for diethylene glycol is less than 16 per cent, and for triethylene glycol it is less than 12 per cent. This is due primarily to the larger water contents being measured. This reduces the effect of the limits of accuracy of the measuring instrument. The effect of temperature first definitely appears in the data obtained on 95 per cent by weight triethylene glycol solutions. An average value of B_2x_2, obtained by averaging the 70°F. and 80°F. data, when used with values of K_1 and K_2 determined at 70°F. and 80°F., did not give a satisfactory curve for either temperature data points. Hence it was necessary to determine an average value of B_2x_2 for each temperature, and use it with K_1 and K_2 determined at the same temperature. As is expected, the 80°F. curve is slightly higher than the 70°F. curve.

The water contents calculated by the above procedure at 80°F. for 100 per cent, 98 per cent, and 95 per cent by weight diethylene and triethylene glycol solutions at pressures varying from 500 to 3000 pounds

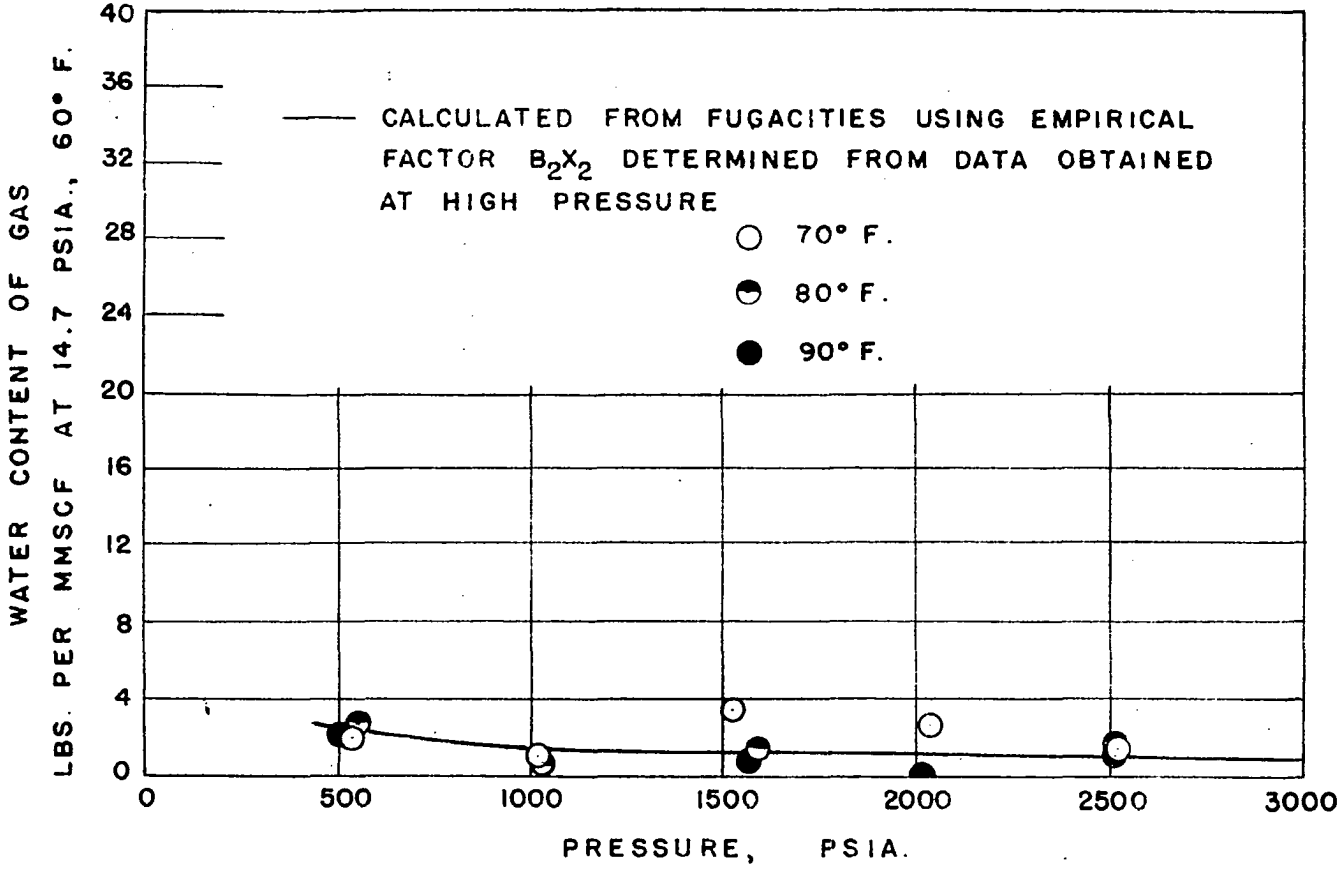


FIGURE 10. WATER CONTENT OF NATURAL GAS DEHYDRATED WITH 99.8 % BY WEIGHT DIETHYLENE GLYCOL

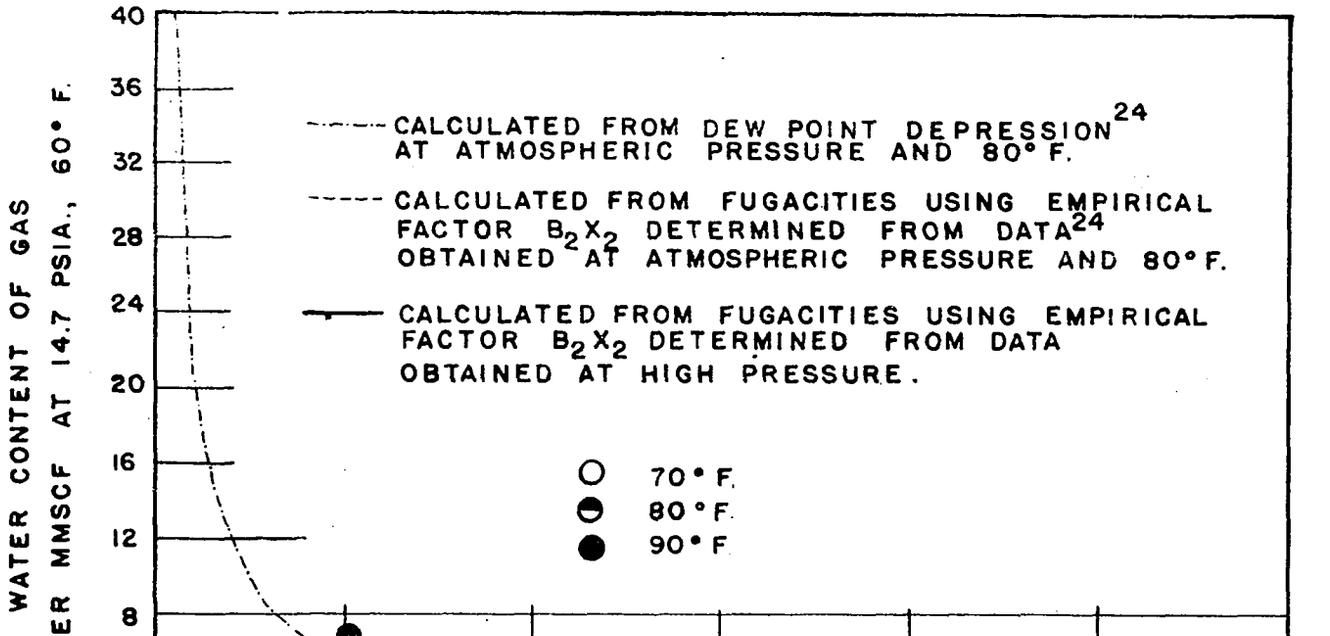


FIGURE 11. WATER CONTENT OF NATURAL GAS DEHYDRATED WITH 98% BY WEIGHT DIETHYLENE GLYCOL

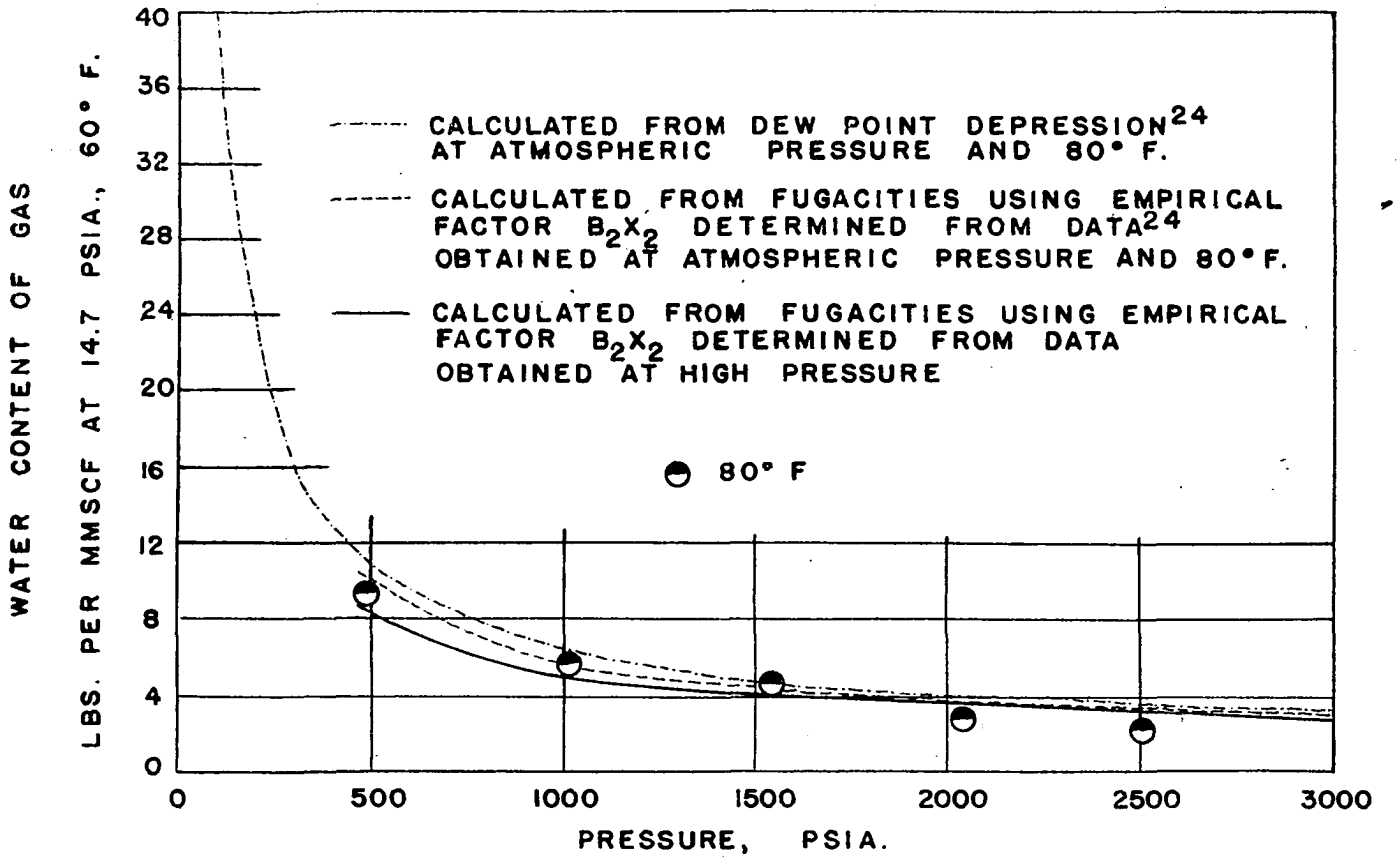


FIGURE 12. WATER CONTENT OF NATURAL GAS DEHYDRATED WITH 95 % BY WEIGHT DIETHYLENE GLYCOL

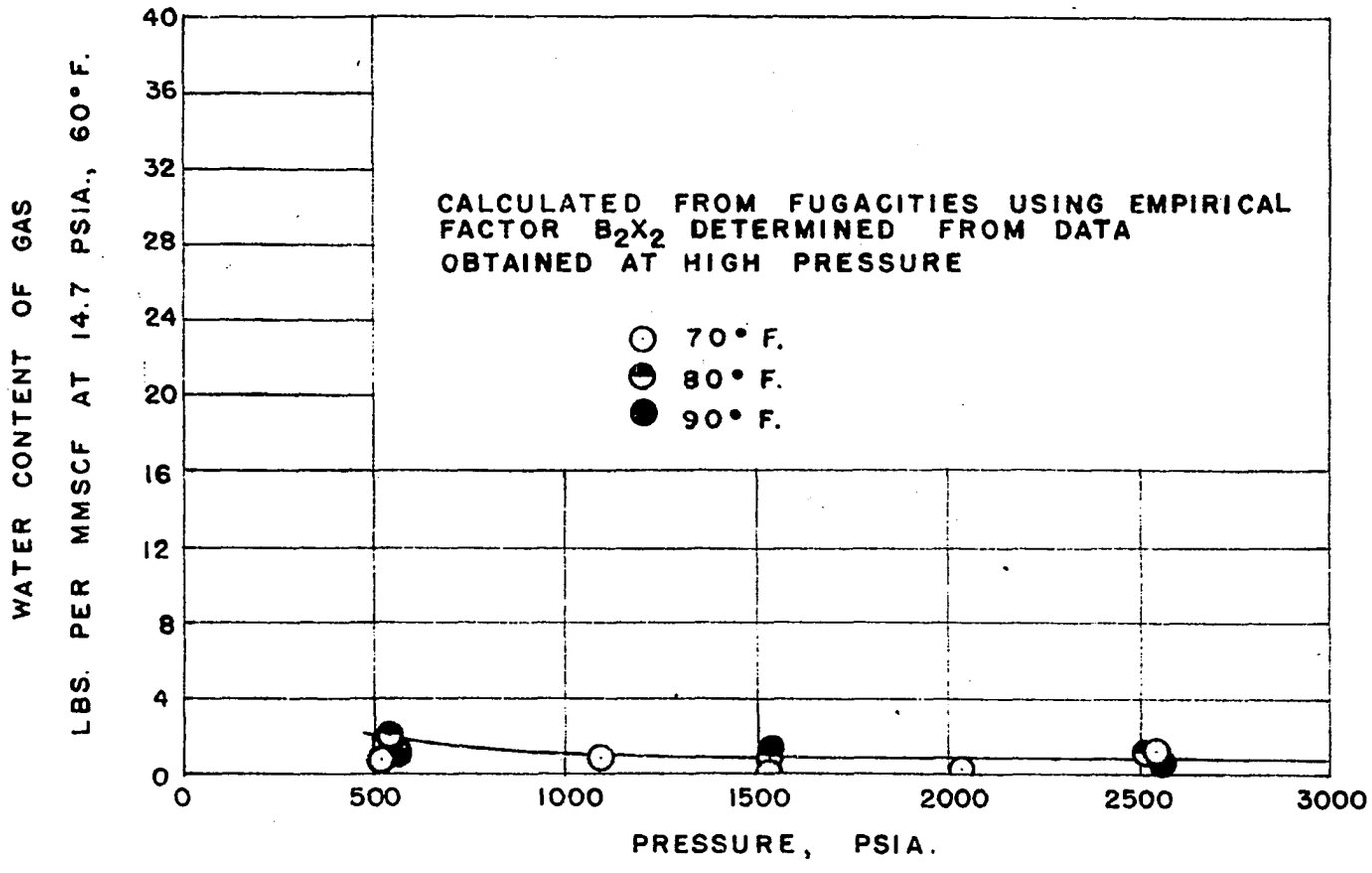


FIGURE 13. WATER CONTENT OF NATURAL GAS DEHYDRATED WITH 100% TRIETHYLENE GLYCOL

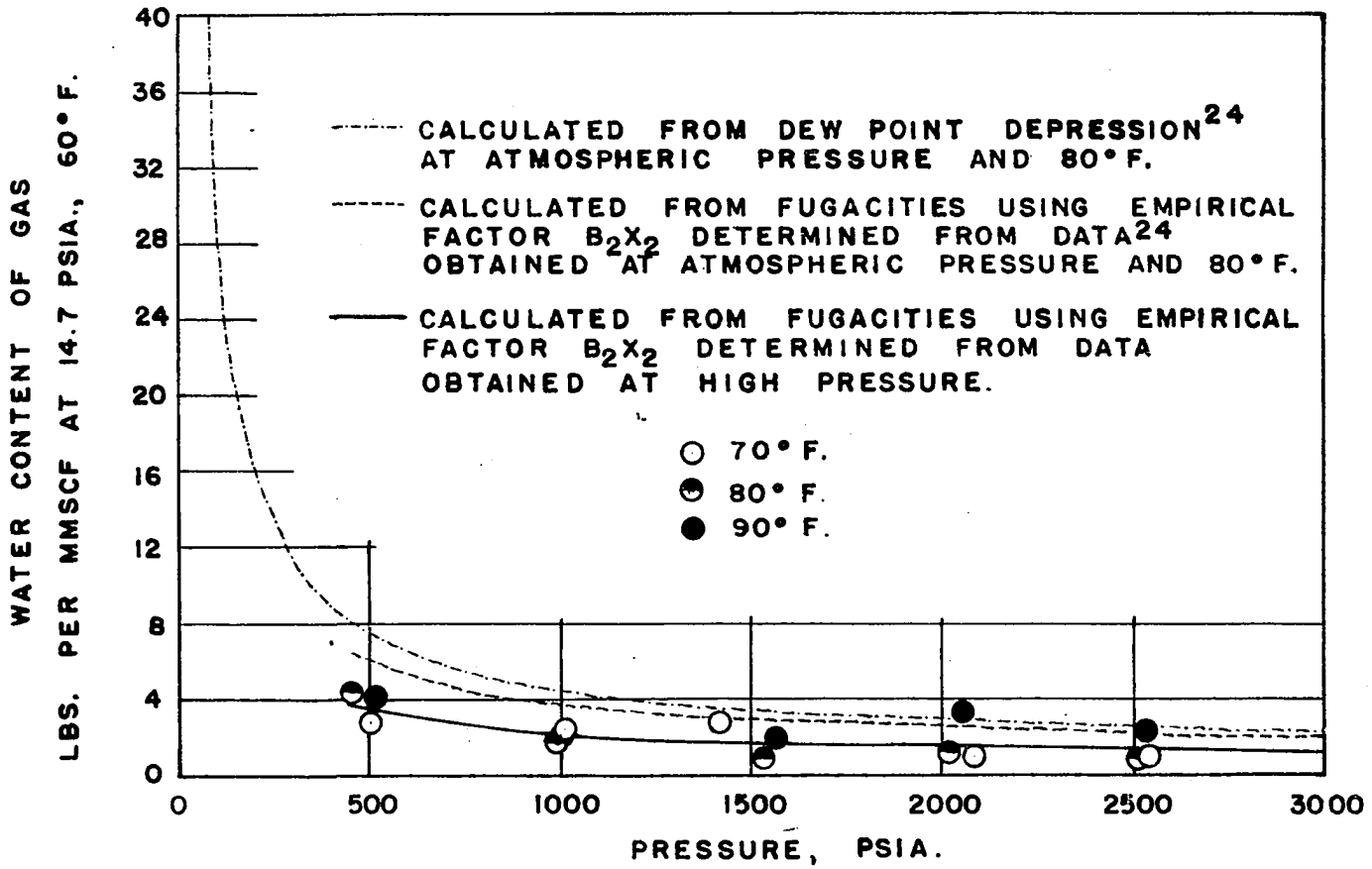


FIGURE 14. WATER CONTENT OF NATURAL GAS DEHYDRATED WITH 98% BY WEIGHT TRIETHYLENE GLYCOL

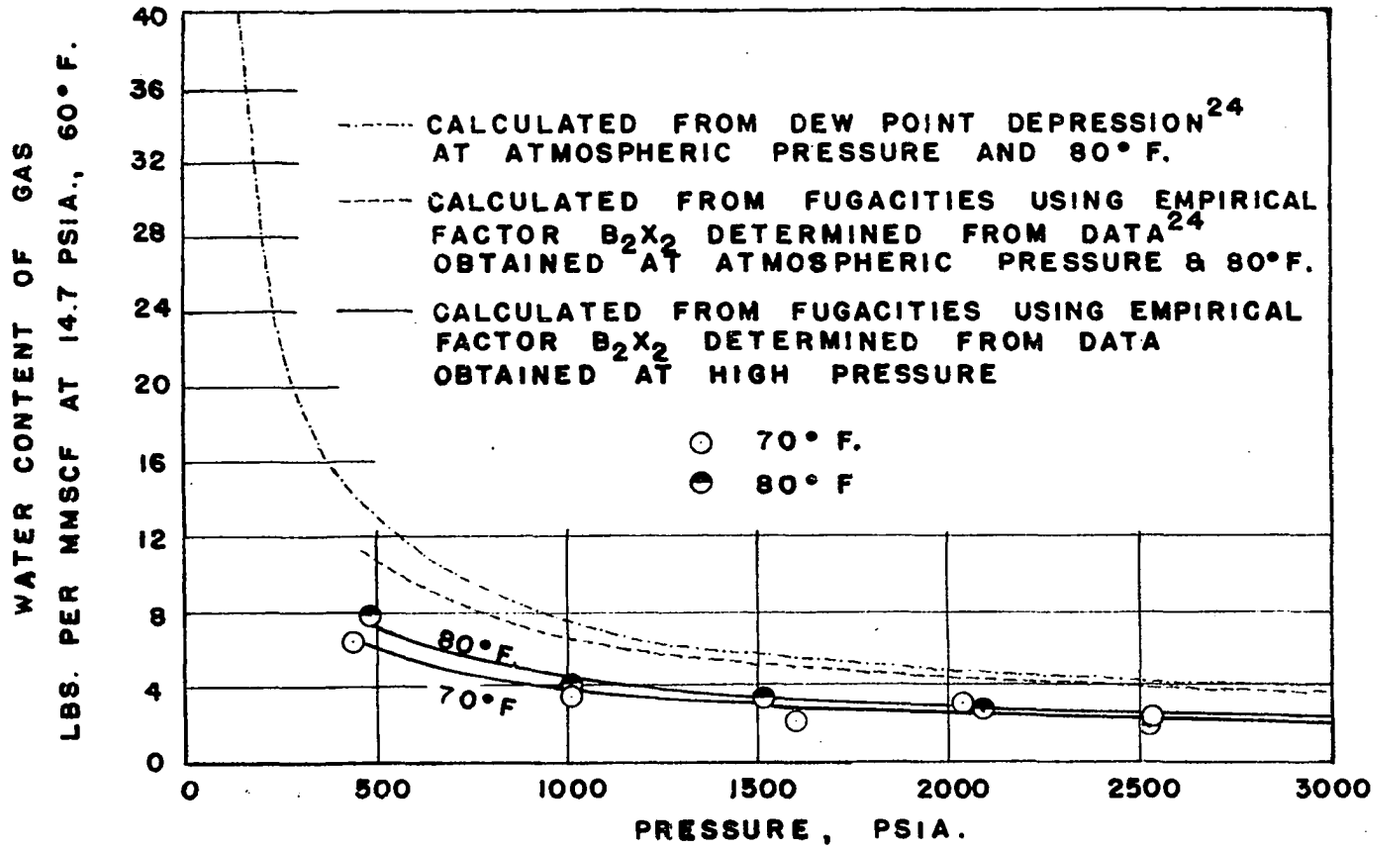


FIGURE 15. WATER CONTENT OF NATURAL GAS DEHYDRATED WITH 95%
BY WEIGHT TRIETHYLENE GLYCOL

per square inch absolute are presented in Table 19. It is believed that these values do best represent the experimental data, and are recommended for gases of similar composition to that used in this investigation. Gases greatly different in composition would require more experimental data. While these values are for 80°F., they are satisfactory for use over the temperature range of 70°F. to 90°F.

Figures 16 and 17 are cross plots of the experimental data presented in Figures 10 to 15, inclusive. These figures make it possible to predict water contents at intermediate glycol concentrations. The term 100 per cent glycol is used to represent commercial glycol of 0.2 per cent maximum water content.

Figure 18 is a comparison of the 80°F. data obtained in this investigation with the data of Russell[7] and Porter[8]. These data compare reasonably well up to 1000 pounds per square inch absolute, but the inefficiency of the dynamic apparatus used by these investigators becomes evident at higher pressures. Fortunately there has been little need for these data in the higher pressure levels thus far, but the new data presented here offer potentially attractive applications in this range. Indications are that the water contents will approach zero concentration at the higher pressures using the more concentrated glycol solutions.

Investigation of "Dicol" and hexylene glycol revealed that, while they showed dehydrating potentialities, there are other considerations such as vapor pressure and resultant vapor losses which should determine

TABLE 19

SMOOTHED VALUES OF THE WATER CONTENTS OF NATURAL GAS DEHYDRATED WITH DIETHYLENE AND TRIETHYLENE GLYCOL SOLUTIONS AT 80°F.

Diethylene Glycol		Triethylene Glycol	
99.8 per cent by Weight		100 per cent by Weight	
Pressure, Psia.*	Water Content, lbs/MMSCF*	Pressure, Psia.*	Water Content, lbs/MMSCF*
500	2.37	500	1.88
1000	1.46	1000	1.16
1500	1.15	1500	0.91
2000	0.97	2000	0.77
2500	0.85	2500	0.68
3000	0.77	3000	0.61
98 per cent by Weight		98 per cent by Weight	
500	3.76	500	3.41
1000	2.32	1000	2.10
1500	1.83	1500	1.66
2000	1.55	2000	1.40
2500	1.36	2500	1.23
3000	1.22	3000	1.10
95 per cent by Weight		95 per cent by Weight	
500	8.30	500	6.79
1000	5.12	1000	4.18
1500	4.03	1500	3.29
2000	3.42	2000	2.79
2500	2.99	2500	2.45
3000	2.68	3000	2.20

* Pounds per square inch absolute.

* Pounds per million standard cubic feet of gas at 14.7 lbs. per sq. in. absolute, 60°F.

their economic feasibility as commercial dehydrating agents. Since the vapor pressures of these materials are much higher than those of diethylene and triethylene glycol, little use is expected except where low cost sources make their use economically feasible.

Prediction of the Extent of Dehydration at High Pressure from Low Pressure Data

Data[24] are available giving the effect of glycol concentration on the dew points of natural gas dehydrated at atmospheric pressure with diethylene and triethylene glycol solutions. These data, shown in Table 20, can be used to predict the extent of dehydration of natural gas at high pressures. The method used can be described as follows: The dew points from the above data can be converted into an equivalent water content in pounds per million standard cubic feet by means of a water content graph[23]. The water content can then be converted into a mole fraction y_2 of water in the vapor phase. This mole fraction, together with values of K_1 and K_2, vaporization constants for methane and water, can be substituted into Equation (37) leaving only values of B_1x_1 and B_2x_2 unknown. If the values of B_1x_1 are assumed to be the same as those determined for the methane-water system, then values of B_2x_2 can be calculated. These values of B_2x_2 can be used with Equation (37) to calculate the water content of the vapor phase at any other pressure at the same temperature and glycol concentration.

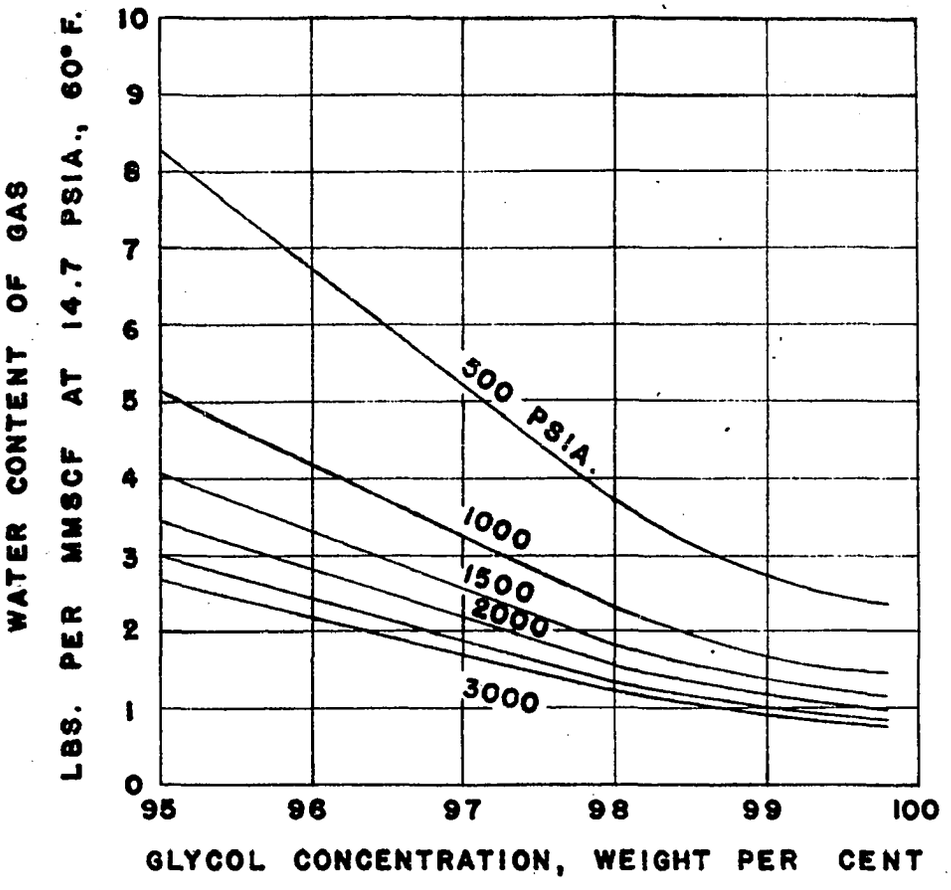


FIGURE 16. EFFECT OF GLYCOL CONCENTRATION ON THE WATER CONTENT OF NATURAL GAS DEHYDRATED WITH DIETHYLENE GLYCOL AT 80° F.

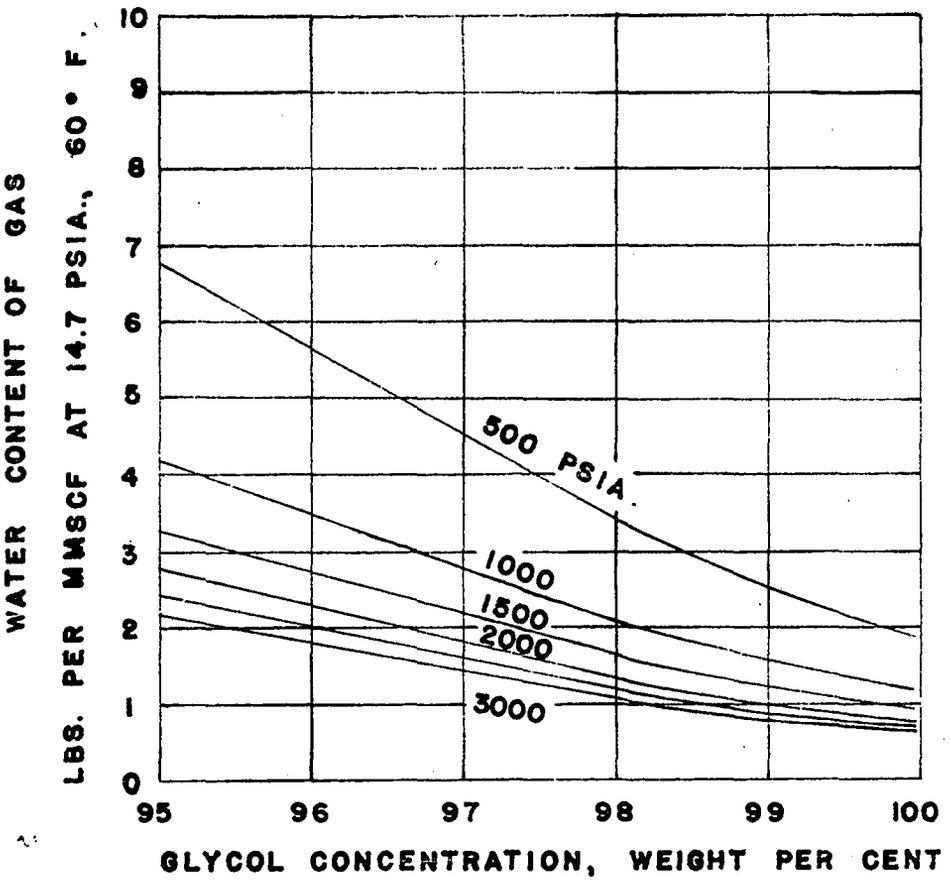


FIGURE 17. EFFECT OF GLYCOL CONCENTRATION ON THE WATER CONTENT OF NATURAL GAS DEHYDRATED WITH TRIETHYLENE GLYCOL AT 80° F.

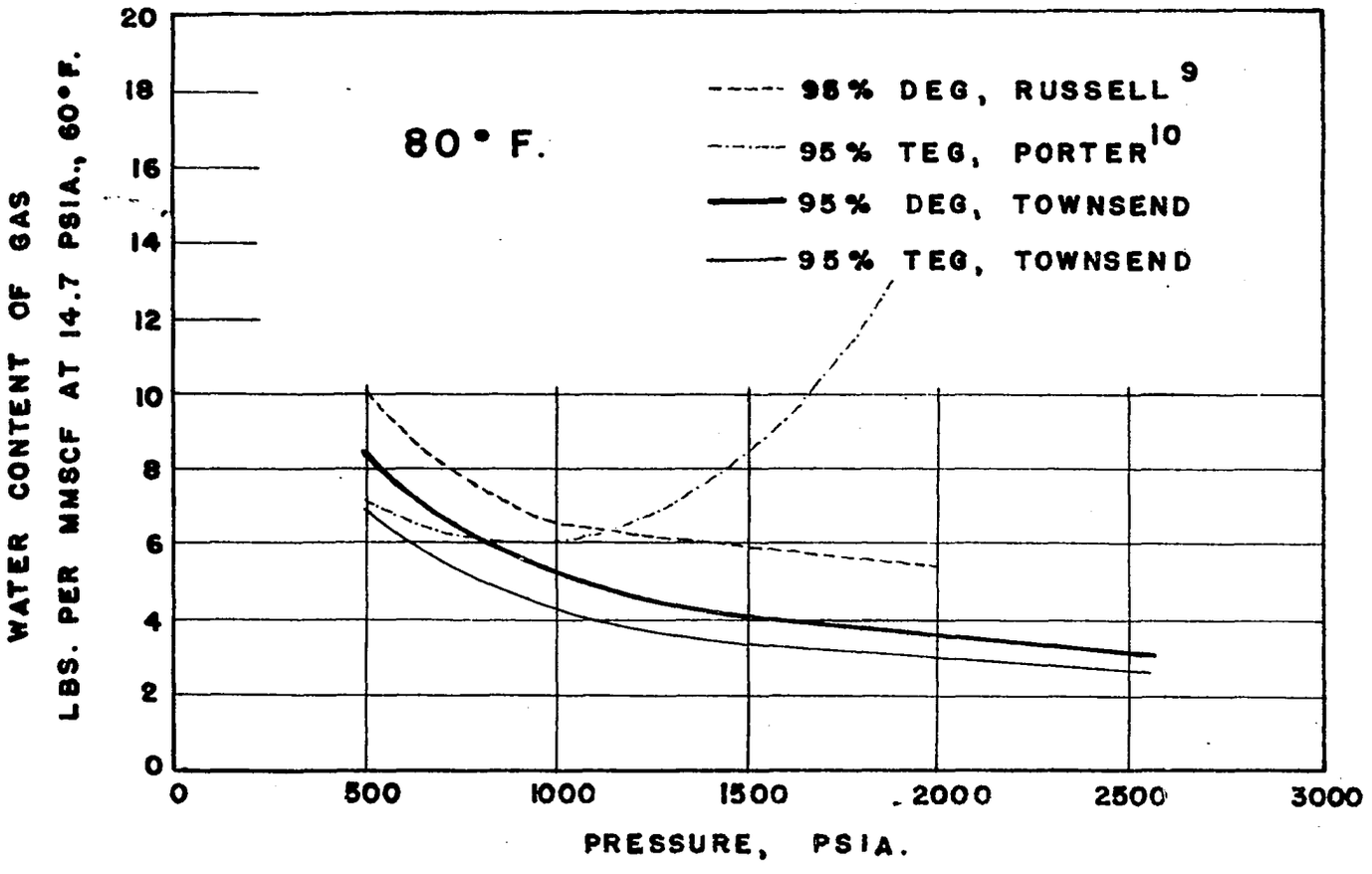


FIGURE 18. COMPARISON OF WATER CONTENTS OF DEHYDRATED NATURAL GAS DETERMINED BY VARIOUS INVESTIGATORS.

Using the method just described, values of B_2x_2 were calculated at atmospheric pressure and temperatures of 70, 80 and 90°F. for glycol concentrations of 0, 50, 60, 70, 80, 90, 95, and 98 per cent by weight diethylene and triethylene glycol. The results are shown in Table 21. It should be noted that B_2x_2 is primarily a function of glycol concentration and only slightly influenced by temperature over the temperature range investigated.

The values of B_2x_2 obtained for 95 per cent and 98 per cent diethylene and triethylene glycol solutions at 80°F. were used to calculate the equilibrium water contents of methane gas dehydrated by these glycol solutions at 80°F. at pressures ranging up to 3000 pounds per square inch absolute. The calculated water contents are shown by the dotted lines of Figures 10 to 15, inclusive. It should be noted that there is reasonably good agreement of calculated water contents with experimental water contents for diethylene glycol solutions of all concentrations. The agreement of calculated and experimental values is good for the 98 per cent triethylene glycol solutions, but there is poor agreement for the 95 per cent triethylene glycol solution. Two different sets of data are available on the triethylene glycols, and these are not consistent with each other. The more recent data have been used in predicting values of B_2x_2 for the triethylene glycols, but the earlier data give much better agreement.

TABLE 20

THE EFFECT OF AQUEOUS SOLUTIONS OF DIETHYLENE AND TRIETHYLENE GLYCOL ON DEW POINTS OF NATURAL GAS AT VARIOUS CONTACT TEMPERATURES [24] AND ATMOSPHERIC PRESSURE

Diethylene Glycol

	70°F Contact Temp.		80°F Contact Temp.		90°F Contact Temp.	
Glycol, weight %	Dew Point °F.	Water Content, lbs/MMSCF [23]	Dew Point °F.	Water Content, lbs/MMSCF	Dew Point °F.	Water Content, lbs/MMSCF
0	70.0	1190	80.0	1670	90.0	2320
50	63.5	930	73.4	1330	83.3	1850
60	60.6	850	70.5	1210	80.3	1700
70	56.8	730	66.5	1020	76.3	1450
80	50.0	580	59.6	820	69.4	1160
90	37.7	365	47.0	520	56.2	730
95	21.8	187	30.0	265	38.3	370
98	5.0	90	13.3	126	21.5	180

Triethylene Glycol

	70°F Contact Temp.		80°F Contact Temp.		90°F Contact Temp.	
Glycol, weight %	Dew Point °F.	Water Content, lbs/MMSCF [23]	Dew Point °F.	Water Content, lbs/MMSCF	Dew Point °F.	Water Content, lbs/MMSCF
0	70.0	1190	80.0	1670	90.0	2320
50	64.4	970	74.5	1380	84.3	1900
60	62.2	890	72.1	1250	82.0	1780
70	58.5	790	68.3	1140	78.2	1580
80	52.1	620	62.0	890	71.7	1260
90	38.0	370	47.9	540	57.5	770
95	25.5	215	34.5	315	44.2	460
98	12.5	125	21.0	178	29.3	252

TABLE 21

CALCULATED VALUES OF B_2x_2, EMPIRICAL FACTOR, FOR AQUEOUS SOLUTIONS OF DIETHYLENE AND TRIETHYLENE GLYCOLS AT ATMOSPHERIC PRESSURE

Diethylene Glycol

Glycol weight %	B_2x_2 at 70°F.	B_2x_2 at 80°F.	B_2x_2 at 90°F.
0	1.017	1.017	1.035
50	0.797	0.816	0.825
60	0.728	0.743	0.758
70	0.626	0.626	0.646
80	0.497	0.503	0.517
90	0.313	0.319	0.325
95	0.160	0.163	0.165
98	0.0772	0.0773	0.0803

Triethylene Glycol

Glycol weight %	B_2x_2 at 70°F.	B_2x_2 at 80°F.	B_2x_2 at 90°F.
0	1.022	1.026	1.037
50	0.831	0.848	0.847
60	0.763	0.767	0.795
70	0.678	0.700	0.705
80	0.532	0.546	0.562
90	0.317	0.331	0.343
95	0.184	0.194	0.205
98	0.107	0.109	0.112

It should be realized, however, that in the absence of high-pressure data, low pressure data can be used to predict the equilibrium water content at any pressure with some degree of assurance.

The Dew Point Method of Predicting the Water Contents of Gases Dehydrated at Various Pressures

It has been the general practice of engineers who design gas dehydration equipment to assume that the dew point depression obtained on water-saturated gas by the glycols is independent of pressure. Hence the dew point depression obtained at one pressure would be the same obtained at any other pressure when using the same concentration of glycol at the same contact temperature. The validity of this assumption can be tested by using the dew point depression data[24] obtained at atmospheric pressure to calculate the equilibrium water contents of natural gas dehydrated by the same glycol concentrations at the same temperature but at higher pressures. For example, as shown in Table 20, when water-saturated natural gas is contacted at atmospheric pressure and 70°F. by a 98 per cent by weight diethylene glycol solution, the dew point of the gas is lowered to 5°F. from the initial dew point of 70°F. Thus a 65°F. dew point depression is obtained. This same 65°F. dew point depression should be obtained at all pressures when using a 98 per cent by weight glycol solution at 70°F. to dehydrate water-saturated natural gas having an inlet dew point of 70°F.

Stating this another way, when water-saturated natural gas at 70°F. is contacted by a 98 per cent by weight diethylene glycol solution at 70°F., the outlet dew point will be 5°F. at any pressure. It is then a simple matter to determine the equilibrium water content of the outlet gas at any pressure by laying a straight-edge along the 5°F. temperature line on the water content graph[23] and reading the equilibrium water content corresponding to any desired pressure directly from the graph.

Values of the water contents determined by use of the dew point method are also shown by separate dotted lines on Figures 10 to 15, inclusive. It is seen that, in each case, the values of the dew point method are higher than experimental values, but it should also be noted that the dew point values closely parallel the experimental values and follow the same family curves.

CHAPTER VII

DISCUSSION

Apparatus Used for Water Content Measurement

In the initial planning of the research program for the determination of the water contents of natural gas dehydrated by various glycols, it was decided that water contents were to be measured by adsorption of the water vapor of natural gas on a solid desiccant and determination of the weight increase per volume of gas passed through the adsorbing tube. Preliminary calculations indicated that approximately 10 to 30 standard cubic feet of gas would be required to furnish the weight of water vapor necessary for accuracy in weighing the desiccant tube. Accordingly, the equilibrium cell was designed to contain approximately 50 cubic feet of gas measured at 80°F. and 14.7 pounds per square inch. The excess volume of the equilibrium cell would prevent excessive pressure drops during the taking of samples from the cell.

During the initial runs attempts were made to adsorb water vapor on "Dehydrite", anhydrous magnesium perchlorate, but in using 100 per cent glycols the water content of the dehydrated gas was so low that there was no detectable weight increase of the desiccant mass. A

more accurate method of measuring water content was sought, and use of Karl Fischer reagent seemed promising. Attempts to use the Karl Fischer reagent did not prove satisfactory for gases containing less than 10 pounds of water vapor per million standard cubic feet so the method was discarded, and the thermistor bridge circuit adopted.

The thermistor bridge circuit was first built according to the description given by Harris and Nash[20], in which only one Wheatstone Bridge circuit was used and both thermistors were in the circuit. This arrangement, however, was so sensitive that it was impossible to calibrate the circuit with sufficient accuracy. It is believed that the wide deviations were due to relatively small changes in room temperature caused by changes in atmospheric conditions, and air drafts in the laboratory. Attempts were made to change the wiring circuit, but these were not satisfactory until two Wheatstone Bridge Circuits were built, with only one thermistor in each circuit.

A reaction cell similar to that described by Harris and Nash[20] was first used. A tube of 1/2-inch inside diameter was recommended for the calcium hydride chamber, but only one of 3/16-inch diameter was available. Gas velocities through the hydride mass were considered to be too great for dependable results, so the vacuum bottle arrangement shown in Figure 5 was used. The larger volume of the vacuum bottle served as a mixing chamber to dampen the effects of changes in atmospheric conditions, and from the calibration curve of Figure 9 is apparent-

ly satisfactory for use. It also possesses the advantage of being readily constructed from materials easily obtained from most laboratory stock rooms.

Harris and Nash recommended a calcium hydride mass of approximately one gram. This amount was too small for the equipment used in this investigation, so a two-inch layer of 4/18 mesh particles was used instead. The increased amount of calcium hydride used only requires a longer time to reach temperature equilibrium.

Using the same gas sample, attempts were made to study the effects of varying amounts of calcium hydride used. After thermistor resistance-ratio readings were constant, more hydride was added or the whole mass removed, screened and replaced. After closing the reaction cell the resistance-ratio soon returned to its previous constant reading.

Saturation of Natural Gas

This investigation is a study of equilibrium conditions existing among the components natural gas, water, and glycol in a mixture. Therefore, equilibrium should be attained by an approach from either direction, that is, by using either a bone-dry or a water-saturated gas in contact with an aqueous glycol solution. However, in using glycols of essentially 100 per cent concentration the water content of the glycols was so low that water-saturated natural gas was used to insure the

presence of sufficient water for measurement of the water content of the vapor phase when equilibrium was attained. In all other runs, except one, the initial filling of the equilibrium cylinder was made with water-saturated natural gas for the run at 2500 pounds per square inch, thus approaching equilibrium from the "wet" side. Runs at lower pressures were obtained by successively dropping the pressure to the desired value from the higher pressure, thus approaching equilibrium from the "dry" side.

The single run excepted above was Run No. 107 at 515 pounds per square inch absolute in which the gas was introduced into the equilibrium cylinder water-saturated at 80°F. and 515 pounds per square inch absolute. This run was to determine whether or not the same equilibrium value would be obtained as was obtained by the pressure drop method. Since the values obtained by both methods of approach to equilibrium agreed within the accuracy of the instrument, it is evident that either method of approach to equilibrium is satisfactory.

Technique of Obtaining Gas Samples from the Equilibrium Cylinder

In taking samples of vapor and liquid phases in equilibrium it is generally essential that the system temperature and pressure remain constant while sampling. This is often accomplished by mercury displacement of the same. The large volume of gas samples required in

this investigation made the use of mercury displacement impractical. Two equilibrium cylinders, connected by two pipes with valves, were decided upon to overcome this difficulty. Only the lower cylinder would contain glycol, and this could be sealed off from the dehydrated gas in the upper cylinder by the valves in the connecting pipes. Gas samples could then be taken from the upper cylinder without effecting the contents of the lower cylinder. Since gas tends to pick up more water as its pressure declines, it was decided that even though the drop of pressure in the upper cylinder would tend to give a higher water content than the equilibrium value, the actual water content would be so low that the increase would be negligible. Experiment proved this to be true at high pressures for pressure drops of about 200 pounds per square inch. The only difficulty was encountered with 95 per cent and 98 per cent glycol solutions at 500 pounds per square inch. The drop in pressure of 200 pounds per square inch necessary to obtain the resistance reading caused the water content curve to pass through a minimum value during the run. This minimum value was chosen as the water content.

The insertion of the pressure gauge into the equilibrium cylinder to obtain the pressure of the system did introduce some possibility of error by changing the volume of the system, and by introducing some air and also some water. However, since the outlet into which the gauge was inserted was also the gas sample outlet any entrapped air and

water would be immediately dispelled in taking the gas sample. The change in volume of the system was negligible.

CHAPTER VIII

CONCLUSIONS

The results of this investigation may be summarized as follows:

1. Smoothed data are presented on the equilibrium water vapor contents of natural gas dehydrated by diethylene and triethylene glycols of 95, 98 and essentially 100 per cent by weight concentrations at 80°F. and at pressures ranging from 500 to 2500 pounds per square inch.

2. The water vapor content of gases dehydrated with diethylene and triethylene glycols decreases with increasing glycol concentration and increasing pressure within the limits of the investigation cited in (1) above.

3. Variation in system temperature from 70°F. to 90°F. has a negligible effect on water vapor content of the dehydrated gases throughout the ranges of glycol concentration and pressure investigated.

4. A method is presented whereby the equilibrium water vapor content of natural gas dehydrated, at constant temperature and at any pressure, by glycols of known concentration may be estimated from data obtained at atmospheric pressure.

5. The commonly used but unconfirmed premise that dew point depression of gases dehydrated by diethylene or triethylene glycols of known concentration, at a specified temperature, is independent of system pressure is substantially valid for quick estimating purposes, though it is probably not sufficiently accurate for precise design of dehydration facilities.

6. For precise design purposes, the experimental data, and the method for estimating equilibrium water vapor contents of natural gases of similar composition dehydrated by diethylene or triethylene glycols at intermediate concentrations, pressures and temperatures, as presented here, are recommended.

7. Hexylene glycol and a poly-glycol mixture known commercially as "Dicol" show promise as gas dehydrating media and might be investigated in greater detail if other economic factors involved in their use should warrant it.

APPENDIX

SAMPLE CALCULATIONS

Prediction of Dehydration at High Pressures from Data Obtained at Low Pressures

The sample calculation presented below illustrates the determination of B_2x_2 from atmospheric pressure data, and the use of the value of B_2x_2 obtained to calculate the water content at a higher pressure. While the example uses atmospheric pressure data, the same procedure could be used to calculate B_2x_2 from data obtained at any pressure.

Problem: The dew point[24] of natural gas dehydrated by 95 per cent by weight diethylene glycol at 80°F., 14.7 pounds per square inch absolute, is 30°F. This corresponds to a water content[23] of 265 pounds per million standard cubic feet at 14.7 pounds per square inch absolute, 60°F. Assuming that $B_1x_1 = \frac{1}{(\nu_1)_{P_1}}$, determine the value of B_2x_2, and use the value to calculate the equilibrium water content of natural gas dehydrated by 95 per cent diethylene glycol at 80°F. and 2000 pounds per square inch absolute.

Solution: Assume natural gas to be methane. Then at 14.7 pounds per square inch absolute, and 80°F., by Equations (18), (30),

and (19),

$$K_1 = \frac{4730\,(0.740)\; e^{\frac{0.726\,(14.7 - 4730)}{(10.71)\,(540)}}}{(14.7)\,(1.0)} = 132.0 \qquad (38)$$

Equations (18) and (19) together with the vapor pressure of water at 80°F. can be combined to give the following:

$$K_2 = \frac{0.5067\,(1.0)\; e^{\frac{0.289\,(14.7 - 0.5)}{(10.72)\,(540)}}}{(14.7)\,(1.0)} = 0.0345 \qquad (39)$$

Substituting these values of K_1 and K_2 together with $B_1x_1 = \frac{1}{0.740}$ into Equation (29):

$$y_2 = B_2x_2K_2 \left[\frac{B_1x_1K_1 - 1}{B_1x_1K_1 - B_2x_2K_2}\right] \qquad (29)$$

$$y_2 = B_2x_2(0.0345) \left[\frac{\frac{1}{0.740}(132.0) - 1}{\frac{1}{0.740}(132.0) - B_2x_2(0.03445)}\right]$$

Converting the water content into y_2:

$$y_2 = \frac{W_2 \times 379}{18.01 \times 10^6} = \frac{265 \times 379}{18.01 \times 10^6} = 0.00558$$

Equating this value of y_2 in Equation (29) and solving for B_2x_2:

$$B_2x_2 = 0.1628$$

This value of B_2x_2 can now be used at the same temperature and glycol concentration to calculate the value of y_2 at any other pressure by use of Equation (29) and the appropriate values of K_1 and K_2. For example, at 2000 pounds per square inch absolute, and 80°F:

$$K_1 = \frac{4730\,(0.740)\,e^{\frac{0.726\,(2000 - 4730)}{(10.72)\,(540)}}}{(2000)\,(0.812)} = 1.530$$

$$K_2 = \frac{0.5067\,(1.0)\,e^{\frac{0.289\,(2000 - 0.5)}{(10.72)\,(540)}}}{(2000)\,(0.30)} = 0.000933$$

$$B_1x_1 = \frac{1}{0.740}$$

$$B_2x_2 = 0.1628$$

Substituting these values into Equation (29):

$$y_2 = 0.1628\,(0.000932)\left[\frac{\frac{1}{0.740}\,(1.530) - 1}{\frac{1}{0.740}(1.530) - 0.1628\,(0.000933)}\right]$$

$$y_2 = 78.5 \times 10^{-6}$$

Converting y_2 into an equivalent water content:

$$W_2 = \frac{y_2 \times 18.01 \times 10^6}{379} = \frac{78.3 \times 18.01}{379} = 3.73 \text{ lbs. per MMSCF}$$

This compares with an experimental value of 3.42 pounds per million standard cubic feet.

The Dew Point Method of Predicting the Water Contents of Gases Dehydrated at Various Pressures

Problem: In Table 20 the dew point of natural gas dehydrated by an aqueous 98 per cent by weight diethylene glycol solution at a contact temperature of 70°F. and atmospheric pressure is 5°F. Using the dew point method determine the equilibrium water content of this

gas in contact with the same glycol solution at 70°F. and 2000 pounds per square inch absolute.

Solution: According to the water content graph[23], the saturated water content of natural gas at 5°F. and 2000 pounds per square inch absolute is 1.5 pounds per million standard cubic feet at 14.7 pounds per square inch absolute, 60°F. This compares with an experimental water content of approximately 1.0 pounds per million standard cubic feet.

Calculation of the Variation in the Water Content of Glycol Solution Used for Natural Gas Dehydration

Problem: Natural gas saturated with water at 2500 pounds per square inch gauge and 90°F. is contained in a cylinder of 8885 milliliter capacity. It is dehydrated by 2232 milliliters of 98 per cent by weight solution of diethylene glycol. Calculate the change in the composition of the glycol solution due to water absorbed from the natural gas.

Solution: Assume natural gas to be methane. The volume of gas measured at 14.7 pounds per square in absolute and 60°F. can be calculated as follows:

Critical Pressure, $P_c = 673.1$ psia.

Critical Temperature, $t_c = -116.5°F.$

Reduced Pressure, $P_r = \frac{2515}{673} = 3.74$

Reduced Temperature, $T_r = \frac{460 + 90}{460 - 116.5} = 1.60$

Then from a compressibility factor chart,

$$z_1 = 0.84$$

Using these values the volume of the gas is,

$$v_2 = v_1 \frac{P_1 T_2 z_2}{P_2 T_1 z_1} = \frac{8885}{28,320} \times \frac{2515}{14.7} \times \frac{520}{550} \times \frac{1}{0.84} = 60.4 \text{ cu. ft.}$$

The saturated water content of natural gas at 2515 pounds per square inch absolute and 90°F. is 26.0 pounds per million standard cubic feet.[23] Therefore, the water content of the gas sample in the cylinder is,

$$26.0 \times \frac{60.4}{10^6} \times 453.6 = 0.713 \text{ gms.}$$

The equilibrium water content of natural gas dehydrated by 98 per cent diethylene glycol at 2500 pounds per square inch gauge and 90°F. is approximately 1.36 pounds per million standard cubic feet. Then the water content of the dehydrated gas sample is,

$$1.36 \times \frac{60.4}{10^6} \times 453.6 = 0.0373 \text{ gms.}$$

The water absorbed by the glycol is then,

$$0.713 - 0.0373 = 0.6757 \text{ gms.}$$

This quantity of water is absorbed in 2232 milliliters of 98 per cent glycol having a density of 1.1075 grams per milliliter. So the weight of the glycol sample is,

$$2232 \times 1.1075 = 2470 \text{ gms.}$$

The water content of the 98 per cent glycol solution is,

$$0.02 \times 2470 = 49.4 \text{ grams}$$

To this is added the 0.6757 grams of water absorbed from the natural gas, making the final water content of the glycol,

$$\frac{(49.4 + 0.6757) \times 100}{2470 + 0.6757} = 2.024 \text{ per cent by weight}$$

This increase in the water content is less than the accuracy of the method used for the water content determination, so the change can be considered to be negligible.

BIBLIOGRAPHY

1. Casper, J. C., "Natural-Gas Consumption Increasing," Oil and Gas Journal, 51, 94 (1952)

2. Buchan, R. C., R. J. Sullivan, Milton Williams, and H. H. Spain, "Dehydration of Natural Gas," World Oil, 130, No. 6, 148 (1950).

3. Huntington, R. L., Natural Gas and Natural Gasoline, McGraw-Hill Book Company, Inc., New York (1950).

4. Morris, J. I., "Basic Problems in Gas Dehydration," World Oil, 128, No. 8, 194 (1948).

5. Katz, D. L., "Prediction of Conditions for Hydrate Formation in Natural Gases," Am. Inst. Mining Met. Engr., Tech. Pub. No. 1748, 10 pp. (1944).

6. Amero, R. C., J. W. Moore, and R. C. Coppell, Chem. Engr. Prog., 43, 349 (1947).

7. Records, L. R., and D. H. Seely, Jr., "Low Temperature Dehydration of Natural Gas," Paper presented at New Orleans, Louisiana, Meeting of Petroleum Branch, American Institute of Mining and Metallurgical Engineers, October (1950).

8. Laurence, L. L., and L. S. Reid, "Low-Temperature Separation - A Means for Dehydrating High Pressure Natural Gas and Increasing Hydrocarbon Recovery," Proceedings A.P.I. Los Angeles meeting, November (1950).

9. Russell, G. L., L. S. Reid and R. L. Huntington, "Experimental Determination of the Vapor-Liquid Equilibria Between Natural Gas and 95 per cent Diethylene Glycol up to a Pressure of 2000 P.S.I.," Trans. Am. Inst. Chem. Engr., 41, 315 (1945).

10. Porter, J. A., "Dehydration of Natural Gas with Triethylene Glycol,"

M. Chem. Engr. Thesis, University of Oklahoma, Norman, Okla., (1949).

11. Boyd, W. L., "Vapor-Liquid Equilibria of the System Glycol Polyformal-Water-Natural Gas," M. Chem. Engr. Thesis, University of Oklahoma, Norman, Oklahoma (1950).

12. Townsend, F. M., "The Effect of Solution Concentration on the Vapor-Liquid Equilibria of the System Triethylene Glycol-Water-Nitrogen," M. Chem. Engr. Thesis, University of Oklahoma, Norman, Oklahoma (1951).

13. Campbell, J. M., Personal communication.

14. Gibbs, J. W., Trans. Conn. Acad., 3, 152 (1876).

15. Hougen, O. A., and K. M. Watson, Chemical Process Principles, John Wiley and Sons Inc., New York (1947).

16. Gamson, B. W., and K. M. Watson, Nat'l. Petroleum News, Tech. Sec. 36, R623, (Sept. 6, 1944).

17. Lewis, G. N., and M. Randall, Thermodynamics and the Free Energy of Chemical Substances, McGraw-Hill Book Co., (1923).

18. Souders, M. Jr., C. W. Selheimer and G. G. Brown, Ind. Eng. Chem., 24, 517 (1932).

19. Gamson, B. W., and K. M. Watson, presented before Petroleum Div., Am. Chem. Soc., Pittsburg meeting, Sept., 1943.

20. Harris, F. E., and L. K. Nash, "Determination of Traces of Water Vapor in Gases," Analytical Chemistry, 23, 736 (1951).

21. U. O. P. Laboratory Test Methods for Petroleum and Its Products, G-107, Universal Oil Products Company, Chicago, Ill., (1940).

22. Mitchell, John Jr., and D. M. Smith, Aquametry, Interscience Pubs., New York (1948).

23. McCarthy, E. L., W. L. Boyd and L. S. Reid, "The Water Vapor Content of Essentially Nitrogen-Free Natural Gas Saturated at Various Conditions of Temperature and Pressure," A.I.M.E. Trans., 189, 241 (1950).

24. Carbide and Carbon's Glycols, Carbide and Carbon Chemicals Company, Union Carbide and Carbon Corporation, New York (1955).

25. Bower, John H., J. Research Natl. Bur. Standards, 33, 199-200 (1944).

26. Yoe, John H., Chem. News, 130, 343 (1925).

27. Frolich, Per K., E. J. Tauch, J. J. Hogan and A. A. Peer, Ind. Eng. Chem., 23, 548 (1931).

28. Keenan, J. H., and F. G. Keyes, Thermodynamic Properties of Steam, John Wiley and Sons, Inc., New York (1936).

29. Watson, K. M., Ind. Eng. Chem., 35, 398 (1943).