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Use of Water Vapor Desorption Data in the Determination of Capillary Pressures

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ABSTRACT

The equilibrium conditions applicable to a single liquid phase held by capillary forces within the pore space of a reservoir rock sample are reviewed. It is shown that, if the conditions for both chemical and capillary equilibrium are satisfied, an extended form of the classical Kelvin relationship is obtained. Using available thermodynamic data, it is also shown that the classical form of the Kelvin relationship can be used to compute air/brine capillary pressures for core plug samples. Experimentally, it is only necessary to allow such samples to reach equilibrium in a constant vapor pressure environment. Thus, the conventional methods for determining capillary pressures can be usefully supplemented by vapor phase desorption experiments. Although such experiments require relatively long equilibration times, they are simple to perform and are free from the difficulties common to other methods. A convenient way to establish a constant vapor pressure environment is to use saturated solutions of such salts as $BaCl_2$, KNO_3, and K_2SO_4. The available vapor pressure data for these solutions are reviewed and tabulated. Using these data Kelvin capillary pressures are calculated for a range of NaCl brine compositions and a range of temperatures. Some preliminary data using this technique are reported for a pair of matched Berea core plugs of approximately 10 cm^3 pore volume.

INTRODUCTION

It has long been known that a relationship exists between the curvature of a gas/liquid interface and the vapor pressure of the liquid phase.[1] Since interface curvature is directly related to capillary pressure, it follows that a measurement of the reduction in vapor pressure over a concavely curved interface can be used to determine the capillary pressure applicable to that interface. A rigorous thermodynamic analysis of this approach to the measurement of capillary pressure is given elsewhere.[2,3] Capillary pressures determined by vapor pressure reduction are called Kelvin capillary pressures.

In this paper previous work on the measurement of Kelvin capillary pressures is briefly reviewed. It is then shown that the corrections to the classical form of the Kelvin equation are of negligible magnitude for values of the air/brine capillary pressure which are less than about 100 bar (1450 psi). Next, a simple experimental method for controlling the water vapor pressure for a partially desaturated core plug sample is described. The corresponding Kelvin capillary pressures are presented in both tabular and graphical form. Some preliminary data for a pair of Berea core plug samples are given. The measured saturations for these samples ranged from 3.3 to 6.8 pore volume percent.

PREVIOUS WORK

Scientific studies on the retention of liquids in porous solids by capillary forces have been carried out for over 250 years. However, the first application of the Kelvin equation to the interpretation of such data appears to be due to Zsigmondy[4] in 1911. The literature relating to this use of the Kelvin equation is now very extensive. The earlier work is reviewed by McBain[5] and by Brunauer.[6] Some of the more recent work is cited in reference 3.

Although the method was first applied to the study of core plug samples by Calhoun and co-workers[7] in 1949, it has seldom been used in this field. Recently, Hsieh and Ramey[8] have reported some high temperature water vapor adsorption/desorption data on Berea samples. However, Hsieh and Ramey suggest that for these data adsorption is dominant and the Kelvin equation is not applicable. On the other hand, the equivalent or Kelvin pore radii calculated from the

References and illustrations at end of paper.

Hsieh and Ramey data at the highest relative vapor pressure range from 1.9 to 3.1 nm. Uncertainties in the liquid phase specific volume and surface tension are such that these Kelvin radii may actually be too small by a significant amount. Consequently, it seems possible that the saturations may include at least a small contribution from capillary-held liquid.

Other recent studies in which the Kelvin equation has been employed are those of Morrow and co-workers.[9-10] In this work room temperature desorption isotherms were reported for water vapor in contact with a set of low permeability gas sand samples. Kelvin capillary pressures ranged from about 700 bar down to about 14 bar. At pressures below about 55 bar approximate agreement was found with independent high-speed centrifuge data. Thus, in the range of air/brine capillary pressures from about 55 bar (800 psi) to 14 bar (200 psi), it appears to be clearly established that the Kelvin equation can be used to determine valid capillary pressures.

The experimental technique used by Morrow and co-workers[9-10] is extremely simple. Samples are equilibrated in a series of controlled humidity chambers. Saturation is then determined gravimetrically. This method is actually widely used in fields other than core analysis. Descriptions of the method are given by Burns[11], Martin[12], Porter et al[13] and in the literature dealing with standard test methods.[14] A variation of the method utilizes saturated solutions of various salts for humidity control. In Figure 1 a schematic illustration of a controlled humidity chamber is shown.

In the work of Morrow and co-workers[9-10] equilibration times of up to 3 weeks were required. The solutions used to control the humidity were sulfuric acid solutions of varying concentration.

A somewhat more complex version of the method is that described by Weatherwax.[15] In this work the vapor phase was circulated through the sample, while NaCl solutions of varying concentration were used to control the water vapor pressure. Equilibration never required more than 8 days, but runs were carried out for as long as 44 days. The highest relative pressure used corresponded to a Kelvin capillary pressure of only 6 psi (0.4 bar).

In the present work saturated solutions of $BaCl_2$, KNO_3, and K_2SO_4 were used to control the water vapor pressure to which the samples were exposed. Two advantages of this variation of the method should be mentioned. First, since an excess amount of the solid salt was always present, the water vapor depends only on the temperature. No independent determination of the amount of salt in solution is required. Secondly, any possible complication due to the adsorption of SO_3 on the sample is avoided. Such complications have been reported by some workers.[16-17]

NEGATIVE PRESSURES AND THE KELVIN EQUATION

As indicated previously, the relationship between the curvature of a gas/liquid interface and the vapor pressure of the liquid can be subjected to an exact thermodynamic analysis.[2-3] This analysis utilizes the Gibbs condition for chemical equilibrium between the phases, a condition unknown to Thomson (Lord Kelvin) in 1871. Thomson's treatment also assumes ideality for the vapor phase and incompressibility for this liquid phase. Thus the classical Kelvin equation is actually an approximation. The exact treatment shows, however, that the corrections for liquid compressibility and vapor non-ideality are often of negligible importance. At the same time, the analysis shows that the classical expression is not in conflict with the conclusion that a relatively large negative pressure may exist in the liquid phase.

A further consequence of the rigorous analysis is the prediction of a definite limit for the application of even the corrected form of the Kelvin equation. This limit arises because the liquid compressibility increases as the vapor pressure and liquid density are reduced. Eventually, the compressibility increases very sharply, and the liquid becomes thermodynamically unstable. However, an extrapolation[18] of available PVT data for water suggests that this limit corresponds to an enormous negative pressure in the liquid. At room temperature this extrapolated pressure is about -2100 bar, or -30,000 psi. This implies a Kelvin capillary pressure of 2100 bar, a relative vapor pressure of 0.22, and a Kelvin pore radius equivalent to 2.5 molecular diameters.

Such an estimate for the limiting negative pressure is, of course, highly speculative. It is therefore of interest to consider the available experimental evidence. In 1950 Briggs[19] reported a negative pressure for liquid water as large as -275 bar (about -4000 psi). This corresponds to a relative vapor pressure of 0.82 and a Kelvin pore radius equivalent to 19 molecular diameters. More recently, liquid stretching measurements[20-21] on cyclohexane have indicated that a relative vapor pressure of 0.76 is still compatible with thermodynamic stability. This corresponds to a liquid phase negative pressure of around -60 bar (-870 psi) and a Kelvin pore radius of roughly 16 molecular diameters. These results provide direct evidence for the applicability of the thermodynamic analysis referred to above.

CORRECTIONS TO THE KELVIN EQUATION

We now turn to the question of the various corrections which are identified by the rigorous treatment of the problem. It should be noted in this connection that the case to be analyzed here is somewhat different than the one-component case treated previously.[2-3] This is because we now have four components associated with three fluid phases. These phases are the saturated salt solution used to control the water vapor pressure, the gas phase itself, and the aqueous NaCl solution within the sample (see Figure 1). The four components, which will be denoted by numeral subscripts, are H_2O (1), NaCl (2), inert gas (3), and the salt (4) used in the external equilibrating phase.

Component 3, the inert gas, is of course a pseudo-component, since in the present case it is the air in the humidity chamber. Thus, it is assumed that the total gas phase pressure, P_G, is always 1.0 bar (14.504 psi). The independent intensive variables are then the temperature, T, and the NaCl concentration in the aqueous phase retained in the sample. This concentration is expressed either as weight percent or as m, the mols of NaCl per kg of water.

We can now write the following expressions for the various changes in chemical potential, $\Delta\mu$, defined as in the previous treatment[2-3]:

$$(\Delta\mu_1)_G^{id} = RT\ln(\alpha_2/\alpha_4) \quad (1)$$

$$(\Delta\mu_1)_G^{*} = -(\alpha_2-\alpha_4)\, BP_G \quad (2)$$

$$(\Delta\mu_1)_L = \nabla_1 P_C + (\Delta\mu_1)_L^{*} \quad (3)$$

In eq. (1) R is the gas constant, 83.144 cm^3 mol^{-1} bar K^{-1}, while α_2 and α_4 are, respectively, the relative water vapor pressures for the brine phase within the sample and for the equilibrating salt solution. The parameter denoted as B in eq. (2) is the mixed second virial coefficient for the gas phase. In eq. (3) ∇_1 is the partial molal volume of H_2O in the brine within the sample and P_C is the capillary pressure. The chemical potential changes denoted as $(\Delta\mu_1)_G^{*}$ and $(\Delta\mu_1)_L^{*}$ represent, respectively, the effects of gas phase non-ideality and liquid phase compressibility. Thus, the total change in chemical potential for the liquid is $(\Delta\mu_1)_L$, while that for the gas is

$$(\Delta\mu_1)_G = (\Delta\mu_1)_G^{id} - (\Delta\mu_1)_G^{*} \quad (4)$$

According to the Gibbs condition for chemical equilibrium, the total changes in chemical potential for the two phases must be equal. Eqs. (1) - (4) can therefore be combined to give the following expression for the capillary pressure:

$$P_C = (\nabla_1)^{-1}\{RT\ln(\alpha_2/\alpha_4) - (\Delta\mu_1)_G^{*} - (\Delta\mu_1)_L^{*}\} \quad (5)$$

This expression differs from the one-component expression obtained previously.[2-3] First, the correction representing the change in the gas phase pressure, ΔP_G, does not appear, since P_G is now held constant. Secondly, the quantity represented by ∇_1 differs slightly from the molar volume for pure liquid H_2O. This, in principle, requires a correction which does not arise in the one-component case.

As for the magnitudes of the various corrections, that given by eq. (2) may be considered first. Values for the pure gas second virial coefficients, B_{11} and B_{33}, and for the interaction coefficient, B_{13}, are reported by Harrison[22]. Of these three coefficients B_{11} is much the largest in magnitude[23]. However, since the mol fraction of H_2O in the gas phase is only about 0.03, the inert gas (air) second virial coefficient, B_{33}, makes the dominant contribution to B. Thus, it is found that the mixed virial coefficient, B, is about -10.8 cm^3mol^{-1}. A more rigorous analysis of the effect of gas phase non-ideality, following that given by Guggenheim[24], indicates that the parameter B in eq. (2) is even smaller in magnitude, about -6.0 cm^3mol^{-1}. In either case, it is found from eqs. (1) and (2) that the ratio, $(\Delta\mu_1)_G^{*}/(\Delta\mu_1)_G^{id}$, is less than 0.0005 for capillary pressure values less than 100 bar. The gas phase non-ideality correction may therefore be considered as negligible in comparison with the usual experimental errors.

The liquid phase compressibility correction, as defined by eq. (3), can be shown to have the following form,

$$(\Delta\mu_1)_L^{*} = \tfrac{1}{2}\beta_T(\nabla_1)^{-1}(\Delta\mu_1)_L^2 \quad (6)$$

Here, β_T is the isothermal compressibility of the brine phase. An equation analogous to eq. (6) has been derived by Keyes.[25] Compressibility data for aqueous NaCl solutions are given by Rogers and Pitzer.[26] For a capillary pressure of 100 bar eq. (6) indicates that the ratio $(\Delta\mu_1)_L^{*}/(\Delta\mu_1)_L$ would be about 0.002. For smaller capillary pressures, this ratio would be proportionally smaller. Again, it is seen that the correction represented by $(\Delta\mu_1)_L^{*}$ may be neglected.

The final correction to be considered is that arising from the use of $M_1v_1^0$ for ∇_1, the partial molar volume of H_2O in the brine phase. Here, M_1 is the molecular weight of H_2O and v_1^0 is the specific volume of pure water. The treatment given by Harned and Owen[27] shows that ∇_1 can be written as

$$\nabla_1 = M_1v_1^0\{1 + Dm^{3/2}\}^{-1} \quad (7)$$

In eq. (7) the parameter D is approximately 0.001 for NaCl solutions at 25°C. Thus, if the molal concentration does not exceed unity, the fractional correction will not be greater then 0.001. Further, it is seen that this correction will tend to cancel that due to the liquid compressibility.

We may conclude from eqs. (5), (6), and (7) that all of the corrections to the classical form of the Kelvin equation are of negligible magnitude. Thus, for the type of three-phase, four-component system considered here, eq. (4) can be written as follows,

$$P_C = \frac{RT}{M_1v_1^0}\ln\left(\frac{\alpha_2}{\alpha_4}\right) \quad (8)$$

CALCULATED CAPILLARY PRESSURES

The relative water vapor pressure represented in eq. (8) by α_2 is a function of both temperature and NaCl concentration, while α_4 is a function of both temperature and type of salt. It will therefore be useful to compute values of the capillary pressure, P_C, for various temperatures, brine concentrations, and types of equilibrating salt.

The vapor pressure data for the three different equilibrating salts mentioned above, K_2SO_4, KNO_3 and $BaCl_2$, are given in Table 1. The corresponding vapor pressure data for NaCl solutions are given in Table 2. Both tables include references to the sources of the data on which the tables are based. The relative vapor pressures for the NaCl solutions given in Table 2 are in good agreement with those tabulated by Robinson and Stokes.[35] It should be emphasized that the vapor pressure data for various types of electrolyte solutions are generally very accurate and have usually been verified by a number of independent studies.

Capillary pressures calculated from the data given in Tables 1 and 2, using eq. (8), are recorded in Tables 3, 4, and 5. These tables correspond to the three different salts used in the form of saturated aqueous solutions to provide a controlled vapor pressure condition. These results are shown in graphical form in Figures 2, 3, and 4. It is seen that in each case both temperature and NaCl concentration have a significant effect on the Kelvin capillary pressure. The trends with temperature and brine concentration are, however, nearly linear. Consequently, linear interpolation in Tables 3-5 or in Figures 2-4 will usually be sufficient to evaluate the Kelvin capillary

pressure corresponding to given values of temperature and NaCl concentration.

EXPERIMENTAL METHOD AND RESULTS

Vapor desorption measurements were carried out on a pair of matched Berea core plug samples. The experiment initially involved three samples which were desaturated to a top end-face capillary pressure of about 40 bar (580 psi) in a Beckman L5-50P rock core ultracentrifuge. It was observed that one of the centrifuge cells did not seal properly, so that the data for the sample originally in this cell were disregarded. The dry core data for the two remaining samples are given in Table 6. Temperatures during sample cleaning did not exceed 120°C.

The samples were nominally two inches in length and one and a half inches in diameter. Samples of these dimensions are suitable for use with the Beckman PIR-16.5 rotor. It is seen from Table 6 that pore volumes were in excess of 10 cm^3 and dry weights in excess of 110 g. The samples were initially saturated with a 2.0 weight percent NaCl solution.

After centrifugation the average saturation, S_w, in both samples was approximately 8.5 percent. Most of the sample length, however, was in each case at a significantly lower saturation, since the top end-face saturation was about 4.7 percent. Both samples were next placed in a controlled humidity chamber containing a saturated solution of K_2SO_4. Changes in saturation were followed by weight loss measurements. These measurements indicated that the samples were either at or near equilibrium after 96 days.

It should be noted that this first desorption step involved different mechanisms than the subsequent desorption steps. At the beginning of the desorption process the effective capillary pressure imposed by the humidity chamber was about 23 to 24 bar. At the end of the process, since the NaCl concentration within the sample increased to about 2.6 percent, the capillary pressure had dropped to 18 to 19 bar. At the same time the saturation dropped from the initial value of about 8.5 percent to around 6.5 percent. However, the initial saturation and capillary pressure distributions were highly non-uniform. As indicated above, the top end-face was initially at a capillary pressure of about 40 bar and the corresponding saturation was only 4.7 percent. At the bottom end-face the saturation was presumably at 100 percent and the capillary pressure was zero.[36] Thus, during the process of desorption there also there also occurred a drastic redistribution of the aqueous phase within each sample. Over most of the length of both samples the saturation actually increased from roughly 5 percent to about 6.5 percent. Near the bottom end-face, on the other hand, on the saturation dropped from 100 percent to 6.5 percent. It follows that the first nominal desorption step must have involved imbibition and adsorption over most of the sample length, with drainage and desorption occurring only near the bottom end-face.

The samples were next placed in a humidity chamber in which the water vapor pressure was controlled by a saturated KNO_3 solution. In this case the first weight loss measurements were not made until about 60 days had elapsed. It appeared from subsequent measurements that equilibrium had already been reached. The samples were kept at the saturated KNO_3 vapor pressure for an additional 100 days. Over this period of time no further weight changes of significance were observed.

Finally the samples were placed in a chamber containing a saturated $BaCl_2$ solution. Again, equilibrium appeared to have been reached at the time of the first weight loss measurements (63 days). Over the next 61 days no significant further weight loss was observed. Tables 7 and 8 record the final values of the fluid weights, as well as the total elapsed time at each of the constant humidity conditions. Temperatures were held at 23 ∓ 0.5°C over the entire equilibration period.

The fluid weight data permit the calculation of the resulting brine concentrations within the samples at each humidity condition. It was assumed that all of the NaCl originally present in a sample at the end of the centrifugation step remained in the aqueous phase during the subsequent equilibrations. These calculated NaCl concentrations are given in Table 7. From these concentrations values of the aqueous phase densities were interpolated from literature data.[26] Any change in liquid density due to the negative pressure in the liquid phase was neglected. Saturations were then calculated from the fluid weights and densities. These saturations are recorded in Table 8.

The brine concentrations were also used to calculate values of the Kelvin capillary pressure from eq. (8). These calculations used graphical interpolation from large-scale plots of the results given in Tables 3-5. Very minor corrections for the effect of brine concentration on surface tension were then made. These corrections were based on literature data.[37-38] Thus, the P_c values given in Table 8 all refer to the initial brine concentration of 2.0 weight percent NaCl. The surface tension of this reference solution is taken to be 72.88 mNm^{-1} at 23.0°C.

In Figure 5 the capillary pressure and saturation data from Table 8 are plotted using a logarithmic scale for both variables. It is seen that on these scales the pressure versus saturation relationship appears to be linear. The data for the two samples are very similar. At the same capillary pressure slightly lower saturations are observed for the sample with the slightly higher porosity, as would be expected. Thus, the water vapor desorption data do appear to be satisfactory with respect to reproducibility.

DISCUSSION

It is obviously of interest to compare the capillary pressure data presented above with similar data for Berea obtained by the more traditional techniques. Two such techniques are the porous plate method and the ultracentrifuge method. Although the properties of Berea sandstone samples have been studied for many years, it appears that no data suitable for this comparison have yet been published.

The only data which might appear to be suitable are those recently reported by Dullien and co-workers.[39] Using a Berea sample with a permeability range similar to that used in the present work, the lowest brine saturation observed was about 10 percent at a capillary pressure of about 1 bar. Rescaling the pressure to account for an expected factor of two in interfacial tension, this highest

pressure value would be about 2 bar. A comparison with the present data indicates an expected capillary pressure of 7 to 8 bar (see Figure 5) at a saturation of 10 percent.

This rather marked disagreement can, however, be attributed to actual differences in the pore structure of the samples used. Those used in the present work were never subjected to a temperature higher than about 120°C. On the other hand, the sample studied by Dullien and co-workers[39] had been calcined for two days at 600°C. It is quite possible that calcination altered the size and shape of the microporosity associated with the clay component of the Berea sandstone sample. It is known, for example, that the surface area of similar Berea samples is sensitive to the nature of the fluid phase which is involved in the measurement.[40] Whereas the area measured by low temperature gas adsorption is about 1.4 m^2g^{-1}, the area which is observed when the pore space is saturated with brine is about 2.5 m^2g^{-1}.

Until experimental evidence to the contrary becomes available, it would appear that the water vapor desorption method does provide a valid technique for obtaining capillary pressure data. Although the method has rarely been used in core analysis, it is experimentally both extremely simple and highly reliable. Thus it is free from many of the difficulties encountered with more traditional methods.

A disadvantage of the simple version of the method used in the present work is of course the relatively long equilibration time which is required at each capillary pressure level. On the other hand, these equilibration times could probably be shortened by providing for some circulation of the vapor phase through the sample.

The method, as used in the present work, is clearly restricted to the low saturation, high pressure region of the capillary pressure curve. Other methods no doubt require shorter equilibration times in this region. However, these times are still sufficiently long that experimental difficulties frequently arise. These difficulties may require that an experiment be terminated before equilibrium is reached. Thus, the long equilibration time of the more reliable water vapor desorption method may not prove to be as disadvantageous as would appear.

CONCLUSIONS

1. Water vapor desorption is a valid technique for obtaining capillary pressure data. It is particularly suitable for the low saturation, high pressure region of the capillary pressure curve.

2. The interpretation of water vapor desorption data requires the use of either the classical or the corrected form of the Kelvin equation. It is known that this equation is valid for air/brine capillary pressures as high as 275 bar (about 4000 psi).

3. Corrections to the classical form of the equation are negligible for air/brine capillary pressures of less than 100 bar (1450 psi).

4. A simple technique for obtaining water vapor desorption data involves equilibrating a partially saturated core plug sample in a constant humidity environment. Such environments are provided by saturated solutions of such salts as K_2SO_4, KNO_3, and $BaCl_2$.

5. Water vapor desorption data for a pair of Berea core plug samples indicate a saturation of about 3 percent at an air/brine capillary pressure of 100 bar.

NOMENCLATURE

Physical Variables

B = vapor phase second virial coefficient
D = coefficient for effect of NaCl concentration on partial molar volume of H_2O
m = NaCl concentration in mols per kg of H_2O
M = molecular weight
P = pressure
R = gas constant, 83.144 cm^3mol^{-1} bar K^{-1}
S = phase saturation
T = temperature
v = specific volume
V = volume
α = relative vapor pressure
β = liquid phase compressibility
$\Delta\mu$ = chemical potential change

Subscripts

1 = component 1 (H_2O)
2 = component 2 (NaCl)
3 = component 3 (air)
4 = component 4 (K_2SO_4, KNO_3, or $BaCl_2$)
c = capillary property
G = vapor phase property
L = liquid phase property
T = isothermal property
w = brine phase

Superscripts

^{0} = pure component property
$^-$ = partial molar property
id = ideal gas property
* = correction term

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TABLE 1

RELATIVE VAPOR PRESSURES FOR SATURATED SALT SOLUTIONS

Temp., °C	20	25	30
Salt	Relative Vapor Pressure, α		
K_2SO_4 [a]	0.9735	0.9708	0.9682
KNO_3 [b]	0.9373	0.9248	0.9119
$BaCl_2$ [c]	0.9067	0.9027	0.8987

a Leopold and Johnston, ref.(28).

b Stokes and Robinson, ref.(29), for 25°; Wexler and Hasegawa, ref.(30), for temperature dependence.

c Acheson, ref.(31), for 20° and 25°; Collins and Menzies, ref. (32), for 30 °.

TABLE 2

RELATIVE VAPOR PRESSURES FOR AQUEOUS NaCl SOLUTIONS

Temp., °C	20	25	30
m, mol kg^{-1}	Relative Vapor Pressure, α		
0.10	.99664	0.99664	.99664
0.25	.99172	0.99172	.99171
0.50	.9835	0.9835	.9835
0.75	.9753	0.9752	.9752
1.00	.9669	0.9668	.9667

a Computed from osmotic coefficient data of Pitzer et al, ref. (33), using vapor phase non-ideality correction of Gibbard et al, ref. (34).

TABLE 3

CAPILLARY PRESSURES FOR AQUEOUS NaCl SOLUTIONS IN EQUILIBRIUM WITH A SATURATED K_2SO_4 SOLUTION[a]

Temp., °C	20	25	30
m, mol kg^{-1}	Capillary Pressure, P_c, bar		
0.00	36.27	40.66	45.02
0.10	31.73	36.04	40.33
0.25	25.04	29.25	33.42
0.50	13.80	17.83	21.84
0.75	2.49	6.20	10.04
1.00	-	-	-

a Computed from vapor pressure data, Tables 1 and 2, using the Kelvin approximation and specific volume data of Rogers and Pitzer, ref.(26).

TABLE 4

CAPILLARY PRESSURES FOR AQUEOUS NaCl SOLUTIONS IN EQUILIBRIUM WITH A SATURATED KNO_3 SOLUTION[a]

Temp., °C	20	25	30
m, mol kg^{-1}	Capillary Pressure, P_c, bar		
0.00	87.45	107.26	128.62
0.10	82.90	102.64	123.93
0.25	76.22	95.85	117.03
0.50	64.98	84.43	105.45
0.75	53.67	72.80	93.64
1.00	41.99	60.93	81.45

a Computed from vapor pressure data, Tables 1 and 2, using the Kelvin approximation and specific volume data of Rogers and Pitzer, ref.(26).

TABLE 5

CAPILLARY PRESSURES FOR AQUEOUS NaCl SOLUTIONS IN EQUILIBRIUM WITH A SATURATED $BaCl_2$ SOLUTION[a]

Temp., °C	20	25	30
m, mol kg^{-1}	Capillary Pressure, P_c, bar		
0.00	132.28	140.44	148.78
0.10	127.73	135.82	144.09
0.25	121.05	129.03	137.19
0.50	109.81	117.62	125.61
0.75	98.50	105.99	113.80
1.00	86.82	94.12	101.60

a Computed from vapor pressure data, Tables 1 and 2, using the Kelvin approximation and specific volume data of Rogers and Pitzer, ref.(26).

TABLE 6

BASIC CORE DATA FOR NOMINAL TWO-INCH BEREA PLUGS[a]

Sample No.	Dry Wt., g	Pore Vol., cm^3	Porosity, percent
B-22-6	113.0518	10.789	20.22
B-323-1	121.8337	11.343	19.82

a Grain density = 2.655 g cm^{-3}; gas permeability approx. 250 md.

TABLE 7

SAMPLE WEIGHTS AND CALCULATED NaCl CONCENTRATIONS FOR BEREA PLUGS AT VARIOUS EQUILIBRATION CONDITIONS[a]

Sample No.	Equilibr. Condition	Fluid Wt., g	NaCl Conc., wt. percent
B-22-6	Centrifug.	0.9268	2.00
B-22-6	K_2SO_4	0.7132	2.60
B-22-6	KNO_3	0.4156	4.46
B-22-6	$BaCl_2$	0.3563	5.20
B-323-1	Centrifug.	0.9829	2.00
B-323-1	K_2SO_4	0.7849	2.51
B-323-1	KNO_3	0.4740	4.15
B-323-1	$BaCl_2$	0.3900	5.04

a Calculation assumes all NaCl remains in aqueous phase.

TABLE 8

CAPILLARY PRESSURES DETERMINED BY EQUILIBRATION OVER SATURATED SALT SOLUTIONS[a]

Sample No.	Equilibr. Condition	Time, days	S_w, percent	P_c, bar
B-22-6	K_2SO_4	96	6.51	18.0
B-22-6	KNO_3	162	3.74	62.3
B-22-6	$BaCl_2$	124	3.19	92.8
B-323-1	K_2SO_4	96	6.82	18.7
B-323-1	KNO_3	162	4.07	65.1
B-323-1	$BaCl_2$	124	3.33	94.4

a All results calculated assuming T = 23°C.

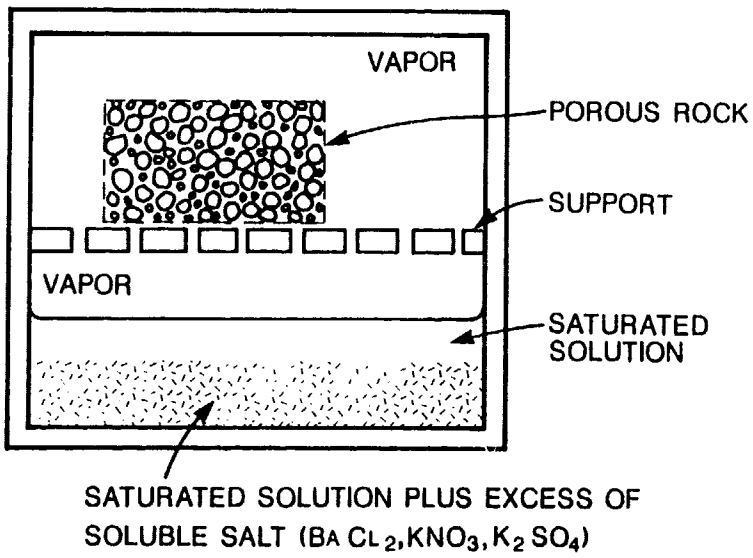

Fig. 1—Schematic diagram for water vapor desorption experiment

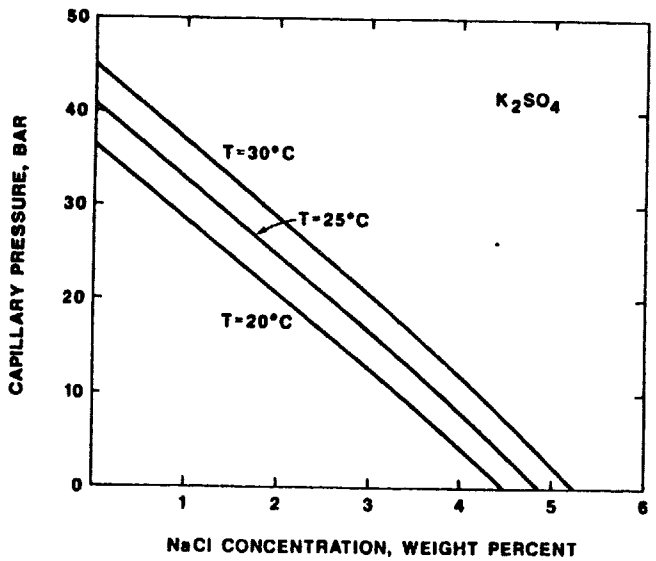

Fig. 2—Kelvin capillary pressure for brine in equilibrium with saturated K_2SO_4 solution

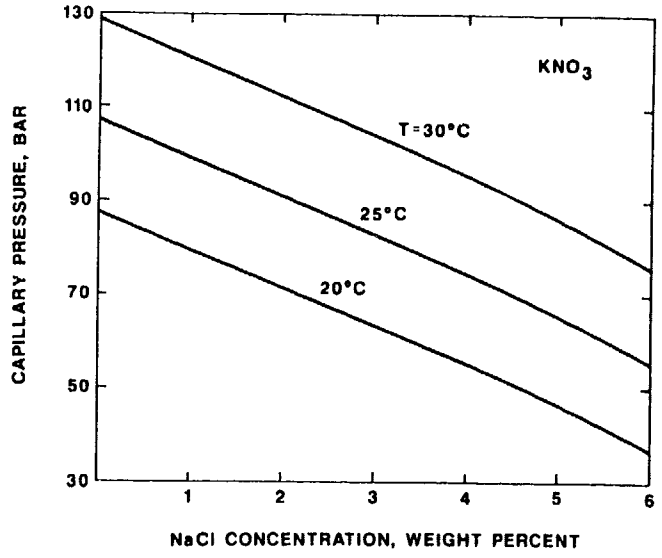

Fig 3--Kelvin capillary pressure for brine in equilibrium with saturated KNO solution

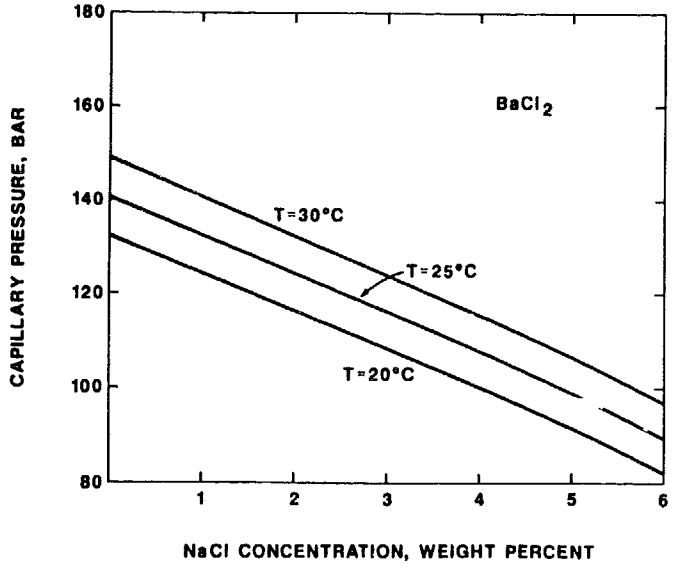

Fig 4—Kelvin capillary pressure for brine in equilibrium with saturated $BaCl_2$ solution

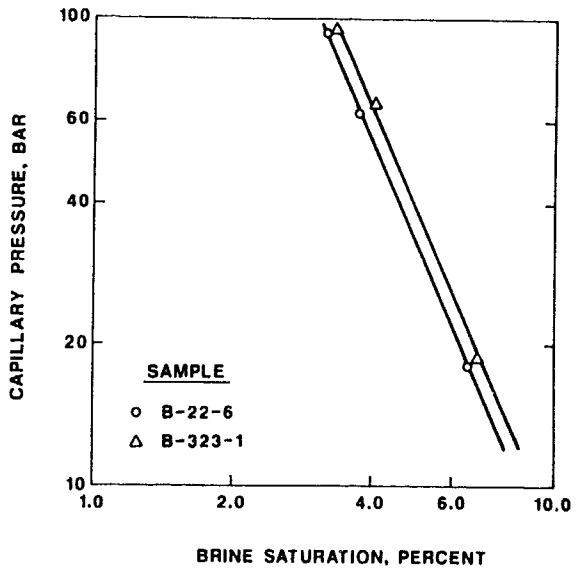

Fig 5- Kelvin capillary pressures vs brine phase saturation Berea sandstone