$$K_t = K_c f^2 \qquad (8)$$

Introducing the Debye-Hückel expression with suitable constants, including an average value of $a = 5 \times 10^{-8}$, one obtains the expression

$$pK_c = pK_t - \frac{4.48u^{1/2}}{1 + 1.70u^{1/2}} \qquad (9)$$

Therefore, a plot of experimental values of pK_c *vs.* $u^{1/2}/(1 + 1.70\,u^{1/2})$ should yield a straight line of slope -4.48 whose intercept is pK_t (*4*). Figure 1 gives such a plot with a straight line fitted to the experimental points by the least squares method having a slope of -4.45, in excellent agreement with the equation. Extrapolation to infinite dilution yields a value fo $pK_t = 7.9$ or a solubility product at 90° C. of 1.23×10^{-8} which is about one order of magnitude less than the solubility product at 25° C. By combining the above value of the solubility product at 90° C. with the value obtained by Farr (*6*) at 25° C., an average value of ΔH over the range 25° to 90° C. may be obtained. This ΔH value of -9515 calories is the heat given off when one mole of solid $CaHPO_4$ dissolves in a saturated aqueous solution.

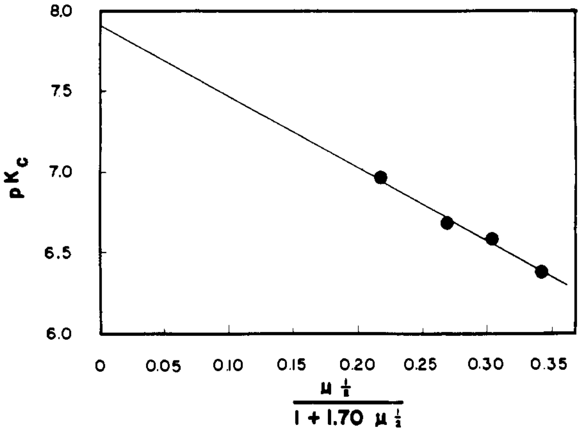

Figure 1. Solubility product as a function of ionic strength

ACKNOWLEDGMENT

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Solubility of Ethylene in Water

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ALTHOUGH BRADBURY and others (*1*) have made a comprehensive study of the solubility of ethylene in water at high pressures, almost no data have been published at pressures below 500 p.s.i.a. This work is a study of the solubility of ethylene in water at pressures below 500 p.s.i.a. and temperatures from 100° to 250° F.

EXPERIMENTAL METHODS

Equilibrium. The apparatus used to attain equilibrium included a rocking autoclave that has been described by Brooks and McKetta (*2*) and Culberson, Horn, and McKetta (*3*). This cell was charged with ethylene and water and rocked for 45 minutes at constant temperature. The cell was kept at rest for 15 minutes to allow complete separation of the phases. The liquid phase was then sampled directly into the analytical train. Culberson, Horn, and McKetta (*3*) showed that these equilibrating and settling times are satisfactory for hydrocarbon-water systems.

Analytical. The method of analysis is absolute and does not depend on predetermined data. The analytical train is shown in Figure 1. A sample of about 50 ml. is removed

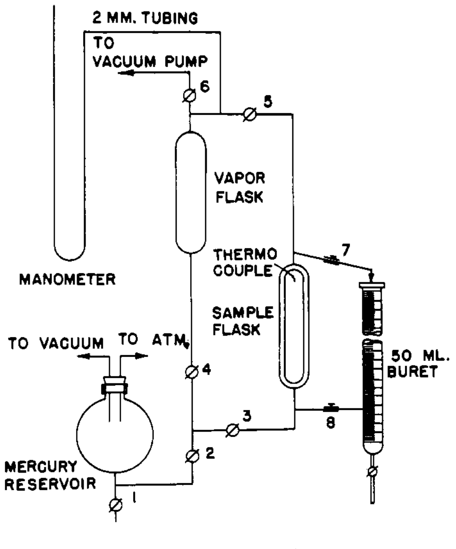

Figure 1. Analytical train

from the water-rich liquid in the equilibrium cell into a jacketed flask, previously evacuated. The low pressure in the flask causes the liquid to be stripped of the dissolved gas. After equilibrium has been established in the sample flask, pressure measurements are taken. The vapor is displaced into another flask using mercury as the displacing fluid. The sample is then isolated and the mercury removed. As the mercury flows out, the pressure is further reduced and the remaining gas is stripped. In the case of ethylene this second stripping removed all the dissolved gas. A third stripping would amount to a determination of the vapor pressure of water. The results by this method had an average deviation of 2 × 10^{-5} mole fraction of ethylene from the true value. A detailed discussion of the analytical procedure is presented by Davis (*4*).

Materials Used. The water was degassed, distilled water. The ethylene was analyzed to be 99.2% ethylene, the main impurity being nitrogen.

DISCUSSION OF RESULTS

The experimental results of this investigation are shown in Table I. A plot of the fugacity of ethylene in the vapor phase *vs.* the mole fraction dissolved ethylene yields a straight line. The smoothed data shown in Table II were were taken from such plots and are plotted on a temperature-composition diagram in Figure 2. This figure shows that ethylene exhibits, at 160° F., the minimum solubility usually expected for a gas dissolved in water.

For the sake of clarity, the experimental data are presented on partial pressure-composition diagrams. Figure 3 shows the region of decreasing solubility, and Figure 4 shows the region of increasing solubility.

Table I. Experimental Data for Concentration of Ethylene in Water-Rich Liquid

Total pressure, p.s.i.a.	Mole fraction ethylene × 10^4	Total pressure, p.s.i.a.	Mole fraction ethylene × 10^4	Total pressure, p.s.i.a.	Mole fraction ethylene × 10^4
100° F.		130° F.		160° F.	
47	2.30	32	0.91	17	0.27
89	4.10	91	2.82	74	1.90
145	6.10	147	4.71	114	2.85
197	7.71	291	9.23	184	5.19
257	10.2	355	11.0	210	5.27
340	13.8	409	12.9	333	8.23
461	17.8	452	14.2	345	9.00
481	18.0	521	15.5	491	12.2
497	18.6			504	12.5
190° F.		220° F.		250° F.	
75	2.0	59	1.28	116	2.68
185	5.29	130	3.61	195	5.14
219	6.30	198	5.41	276	8.10
289	7.94	229	6.47	354	10.3
331	9.06	269	7.49	367	10.3
412	11.4	416	12.0	543	15.6
506	13.7	527	14.9		

Table II. Smoothed Data for Concentration of Ethylene in Water-Rich Liquid Phase in Mole Fraction × 10^4

Pressure, P.S.I.A.	Temperature, ° F.					
	100°	130°	160°	190°	220°	250°
14.7	0.64	0.42	0.37	0.18		
50	2.30	1.65	1.35	1.30	1.10	0.70
100	4.50	3.30	2.70	2.70	2.70	2.30
150	6.60	4.90	4.00	4.20	4.3	3.90
200	8.60	6.50	5.25	5.70	5.90	5.60
250	10.80	8.00	6.50	7.10	7.40	7.30
300	12.40	9.50	7.70	8.50	8.80	8.90
350	14.10	11.10	8.90	9.80	10.30	10.60
400	15.80	12.70	10.10	11.00	11.70	12.00
450	17.40	14.10	11.30	12.30	13.10	13.40
500	18.70	15.50	12.40	13.40	14.30	14.70

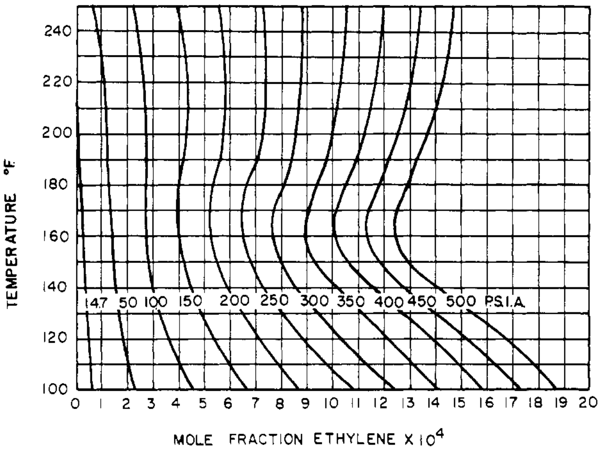

Figure 2. Temperature *vs.* composition of solubility of ethylene in water

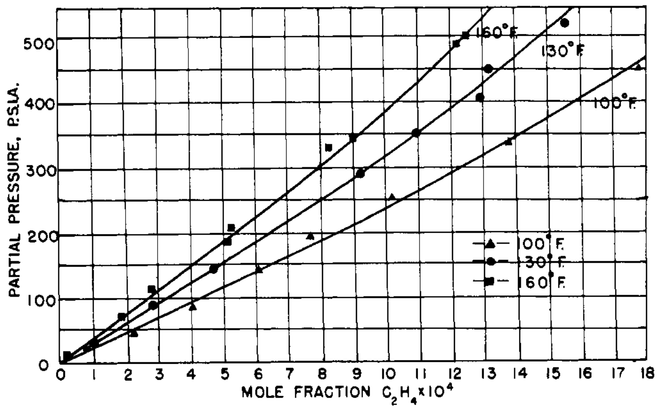

Figure 3. Partial pressure of ethylene *vs.* concentration in region of decreasing solubility

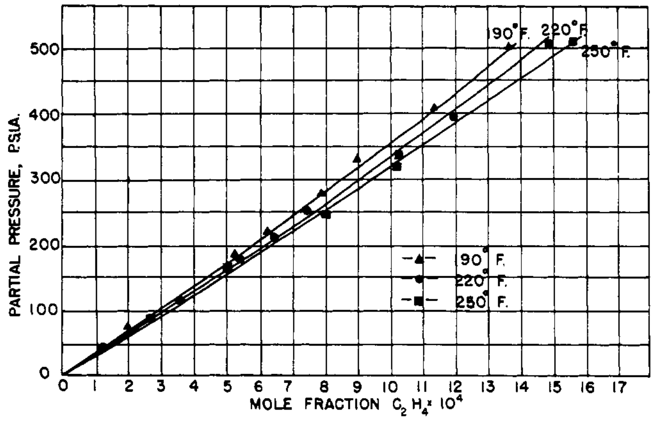

Figure 4. Partial pressure of ethylene *vs.* concentration in region of increasing solubility

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