Phase Equilibrium in the Ethylene-Ethane-Water System

RAYFORD G. ANTHONY[1] and JOHN J. McKETTA
The University of Texas, Austin, Tex.

The mutual solubilities of hydrocarbons and water for the ternary system, ethane-ethylene-water, in the two-phase region were studied. Data were taken at temperatures of 100°, 160°, 220°, and 280° F. for the pressure range of 500 to 5000 p.s.i.a. This study was conducted to extend the available knowledge on the behavior of systems involving mixtures of light hydrocarbons and water. This information is of considerable value in the chemical and refining industries.

THERE is a limited amount of data available on systems involving water and mixtures of pure hydrocarbons at elevated temperatures and pressures. Mcketta and Katz (*13*) report data on the methane–*n*-butane–water system at temperatures from 100° to 280° F. and at pressures from 200 to 3000 p.s.i.a. Wehe and McKetta (*19*) report data on the 1-butene–*n*-butane–water system at temperatures to 280° F. and pressures to 500 p.s.i.a. Dew point water contents for the system, methane–ethane–water ternary, are reported by Villarreal, Bissey, and Nielsen (*17*) at temperatures to 140° F. and pressures to 3000 p.s.i.a. The system studied here differs from these earlier systems because the ethane–ethylene–water system involves a paraffin and an olefin of approximately the same molecular weight, making this a study in which the effects of hydrocarbon molecular weights are minimized; and both hydrocarbon components in the ethane–ethylene–water system are noncondensable, as is the case for the methane–ethane–water system, at the temperatures under consideration. For the methane–*n*-butane–water system, the temperatures investigated are below the critical temperature of one of the components, and only methane is noncondensable. For the *n*-butane–1-butene–water system, both hydrocarbon components are condensable at the temperatures studied. The latter differences in the ternary systems have a major effect on the phase diagram.

The equipment used in this investigation has been described by Wehe and McKetta (*18*, *19*), Li and McKetta (*11*, *12*), and Anthony (*1*). Ethylene (minimum purity 99.3%), ethane (minimum purity 99.1%), and distilled water were the chemicals used.

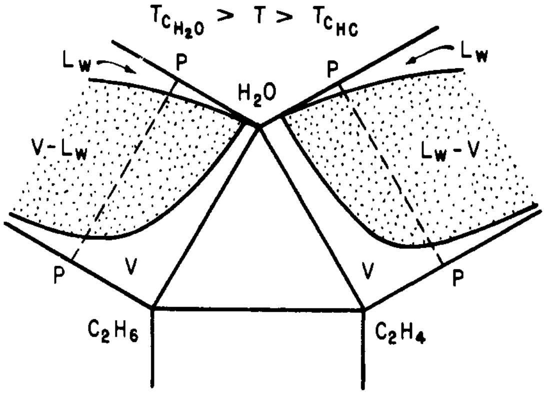
According to the Gibbs phase rule three variables must be specified in order to determine a three-component system completely in the two-phase region at equilibrium. In this work, pressure, temperature, and composition of ethane (ethylene) in the vapor are specified. The binary and ternary diagrams applicable to this work are illustrated in Figure 1. The experimental data for the mutual solubilities for the ethane-ethylene-water ternary are presented in Table I. The smoothed data are in Table II.

The estimated accuracies of the measured variables are summarized below.

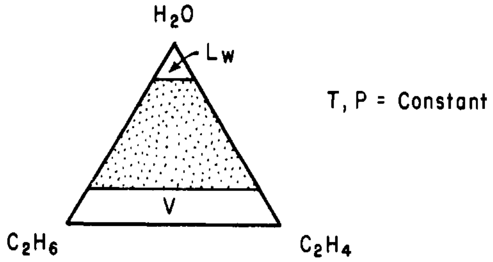
Measured Variable	Estimated Accuracy
Pressure	± 2 parts per 1000 parts (0.2%) or ± 0.5 p.s.i.a., whichever is greater
Temperature	± 0.1° F. at 100° and 160° F. ± 0.2° F. at 220° and 280° F.
Mole fraction total hydrocarbon in water-rich liquid	± 5.0% of value
Mole fraction water in vapor	± 4.6% of value
Chromatographic analysis	± 0.5 mole per cent

The experimental techniques used in determining the water in the hydrocarbon vapor phase and the hydrocarbon in the water phase were tested by comparing data for the propylene-water, *n*-butane–water, and ethane-water throughout the anticipated temperature range of this work with the data of Li and McKetta (*12*), Wehe and McKetta (*19*), Bradbury *et al.* (*4*), and Reamer *et al.* (*14*, *15*). Agreement is believed to be within the accuracy of the literature values in all cases. This comparison was reported by Anthony and McKetta (*2*).

The data at 100° and 160° F. on the ternary, ethane-ethylene-water, indicated a lower water content in the vapor for the ethane-water binary than were given by the data of Reamer *et al.* (*14*). Therefore, data were taken on the ethane-water binary at these two temperatures from 300 p.s.i.a., a point of agreement, to 5000 p.s.i.a., and also at 220° F., a point of agreement (Table III and Figure 2). These new data for the



(a) BINARY



(b) TERNARY

Figure 1. Binary and ternary systems

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[1] Present address: Texas A&M University, College Station, Tex.

Table I. Experimental Data for Ethane-Ethylene-Water System

		Analysis Mole Fraction, Dry Basis			Analysis Mole Fraction, Wet Basis		
		HC Vapor		Water in HC vapor $\times 10^3$	HC in Water $\times 10^3$		
Temp., ° F.	Pressure, P.S.I.A.	Ethane	Ethylene		Ethane	Ethylene	Total
100.1	503.2	0.2741	0.7251	2.320	0.1993	1.2756	1.475
100.0	503.2	0.4033	0.5967	2.139	0.2520	1.0820	1.334
99.9	504.2	0.4517	0.5483	2.159	0.2905	0.9493	1.240
100.1	503.7	0.8154	0.1845	1.817	0.5616	0.3692	0.9308
100.0	995.7	0.7308	0.2692	0.7846	0.589	0.8083	1.398
100.0	1000.7	0.9208	0.0792	0.6778	0.761	0.2007	0.9614
100.0	1000.7	0.2387	0.7613	1.264	0.238	2.162	2.401
99.9	539.6	1.00	—0—	1.796	No liquid sample taken		
100.1	1017.2	—0—	1.00	1.519	No liquid sample taken		
219.8	503.9	0.2201	0.7799	39.19	0.9797	0.9790	1.077
219.7	503.2	0.2115	0.7885	37.75	0.9219	0.9090	1.001
219.9	500.7	0.3284	0.6716	40.58	0.1289	0.7982	0.9272
219.9	501.7	0.5122	0.4878	38.89	0.2194	0.5666	0.7860
219.7	504.7	0.8921	0.1079	37.59	0.3723	0.1269	0.4992
219.8	1002.2	0.6066	0.3934	20.49	0.425	0.9597	1.385
220.0	1005.2	0.8357	0.1643	20.32	0.5783	0.3698	0.9481
220.2	1499.2	0.4925	0.5075	15.15	0.4396	1.4684	1.908
220.1	1004.2	0.6068	0.3932	20.17	0.3593	0.9107	1.270
220.0	1491.2	0.6525	0.3475	14.77	0.5653	0.9977	1.563
220.0	1008.7	0.1481	0.8519	22.07	0.1122	1.852	1.964
220.1	1499.2	0.1943	0.8057	16.44	0.1901	2.3379	2.528
100.1	1080.2	0.9906	0.0094	0.7017	0.8810	0.0030	0.8889
99.9	1499.2	0.9906	0.0094	0.6713	No liquid sample taken		
99.9	1503.2	0.9460	0.0540	0.6809	0.7531	0.2452	0.9983
99.9	1486.2	0.8676	0.2324	0.7886	0.7663	0.4087	1.175
99.9	1521.2	0.6560	0.3440	0.9710	0.5472	1.1368	1.711
99.9	1505.2	0.2423	0.7577	1.383	0.2517	2.417	2.669
99.9	1994.2	0.2570	0.7430	1.201	0.2550	2.4870	2.742
100.0	1513.2	0.2701	0.7299	1.215	0.2463	2.417	2.663
100.0	1992.2	0.2639	0.7361	1.154	0.2932	2.5018	2.795
100.0	1999.2	0.4227	0.5773	0.8641	0.4275	1.9589	2.384
99.9	1975.2	0.8491	0.1509	0.6238	0.7694	0.5006	1.270
100.0	3001.7	0.8324	0.1676	0.644	1.099	0.6561	1.461
159.8	2010.2	0.7958	0.2042	3.171	0.676	0.6556	1.332
159.9	1519.2	0.7860	0.2140	3.429	0.651	0.6098	1.261
160.0	2010.2	0.7830	0.2170	5.108	0.5644	0.4624	1.027
160.1	502.2	0.7740	0.2260	10.24	0.3508	0.2671	0.6181
160.1	2015.2	0.5472	0.4528	3.820	0.468	1.4237	1.892
160.1	1504.2	0.5268	0.4732	4.393	0.437	1.2906	1.728
160.1	997.7	0.5350	0.4650	5.727	0.3645	1.105	1.475
160.1	502.2	0.5281	0.4719	0.916	0.2386	0.6212	0.8598
159.7	1999.2	0.2975	0.7025	3.832	0.271	2.1715	2.443
160.1	1514.2	0.3103	0.6897	4.937	0.474	2.3429	2.817
160.1	995.7	0.3011	0.6989	6.050	0.2353	1.5887	1.824
160.1	504.8	0.6917	0.3083	10.55	0.1494	0.9686	1.118
160.2	1494.2	0.6781	0.3219	3.992	0.547	0.8966	1.444
160.1	1990.2	0.8950	0.1050	2.641	0.788	0.2930	1.066
160.1	1514.2	0.8996	0.1004	3.390	0.710	0.2809	0.9904
160.1	995.7	0.8933	0.1067	4.709	0.698	0.2252	0.9229
160.1	298.2	0.8851	0.1149	10.13	0.332	0.1144	0.446
99.9	2013.2	0.9809	0.0191	0.6005	No liquid sample taken		
99.9	1010.2	0.9846	0.0154	0.6505	No liquid sample taken		
100.1	1013.2	0.3166	0.6834	1.196	No liquid sample taken		
100.1	1000.2	0.8001	0.1999	0.7747	No liquid sample taken		
99.9	1007.2	0.4773	0.5227	1.0110	No liquid sample taken		
99.9	507.2	0.4812	0.5188	2.006	No liquid sample taken		
99.9	501.1	0.2647	0.7353	1.988	No liquid sample taken		
99.9	500.5	0.2637	0.7363	2.137	No liquid sample taken		
99.8	495.7	0.8210	0.1790	1.858	No liquid sample taken		
279.9	1009.2	0.7560	0.2440	57.76	0.6166	0.6304	1.247
279.9	503.7	0.7370	0.2630	108.01	0.3485	0.3275	0.676
280.0	1500.2	0.5447	0.4553	43.44	0.6923	1.4217	2.114
279.9	1002.2	0.5617	0.4383	58.66	0.4530	1.0230	1.476
280.0	512.2	0.5490	0.4510	105.50	0.2718	0.5422	0.814
280.0	1496.2	0.2732	0.7268	38.19	0.2889	2.3140	2.603
279.9	1009.2	0.2651	0.7349	61.45	0.2405	1.7225	1.963
279.5	504.7	0.2830	0.7170	109.4	0.1274	0.9286	1.057
280.0	1494.2	0.7540	0.2460	40.75	0.8060	0.8261	1.537
280.0	1996.2	0.7496	0.2504	33.14	0.8862	0.9168	1.803
100.1	5019.7	0.5488	0.4512	1.131	0.6492	1.9548	2.604
100.1	4004.7	0.5588	0.4412	1.180	0.5823	1.7366	2.319

(Continued on page 23)

Table I. *(Continued)*

Temp., ° F.	Pressure p.s.i.a.	Analysis Mole Fraction, Dry Basis			Analysis Mole Fraction, Wet Basis		
		HC Vapor		Water in HC vapor $\times 10^3$	HC in Water $\times 10^3$		
		Ethane	Ethylene		Ethane	Ethylene	Total
100.1	3007.7	0.5655	0.4345	1.175	0.5748	1.5942	2.169
100.0	5004.7	0.7414	0.2586	0.778	0.8257	1.0773	1.903
100.1	4004.7	0.7485	0.2515	0.7180	0.7635	1.0084	1.772
100.0	3001.5	0.7441	0.2559	0.8490	0.7061	0.9739	1.680
100.0	5022.7	0.3731	0.6269	1.141	0.4198	2.6492	3.069
100.0	4002.2	0.3653	0.6347	1.162	0.4133	2.4916	2.933
100.0	3014.7	0.3636	0.6364	1.293	0.3804	2.3585	2.739
100.0	5004.7	0.2696	0.7304	1.312	0.3236	3.0824	3.406
100.1	3999.7	0.2687	0.7313	1.383	0.2927	3.0453	3.338
100.1	3007.2	0.2729	0.7261	1.299	0.2588	2.7411	2.999
160.1	5008.7	0.2711	0.7289	3.976	0.3126	2.981	3.294
160.0	4010.7	0.2658	0.7342	4.079	0.2900	2.7889	3.079
160.0	3014.7	0.2697	0.7303	4.174	0.2781	2.5599	2.838
160.2	5000.7	0.6779	0.3221	2.752	0.7477	1.155	1.903
160.1	4004.7	0.6922	0.3078	2.736	0.7003	1.1637	1.864
160.2	3008.7	0.7011	0.2989	3.004	0.6413	1.0637	1.705
159.9	4998.7	0.8162	0.1838	2.643	0.8778	0.6710	1.549
159.9	4002.7	0.8144	0.1856	2.580	0.8188	0.6822	1.501
159.9	3007.7	0.8185	0.1815	2.623	0.7336	0.6163	1.380
160.0	5000.0	0.9169	0.0831	2.442	0.9484	0.2627	1.286
160.0	4009.7	0.9186	0.0814	2.325	0.9120	0.3120	1.224
160.0	3004.7	0.9225	0.0775	2.518	0.8529	0.2771	1.130
160.1	2010.2	0.9152	0.0848	2.742	No liquid sample taken		
220.0	4015.7	0.7270	0.2730	6.937	0.9076	1.2314	2.139
219.9	3004.7	0.7247	0.2753	10.16	0.8025	1.0655	1.868
220.0	2012.2	0.7245	0.2755	12.90	0.7052	0.8968	1.602
219.9	4009.7	0.4401	0.5599	9.377	0.5425	2.4124	1.955
219.9	3012.7	0.4392	0.5608	11.65	0.5067	2.1783	2.685
220.0	2010.2	0.4374	0.5626	13.28	0.4499	1.856	2.306
220.0	3997.7	0.2637	0.7363	11.22	0.3586	3.1954	3.554
220.0	3008.7	0.2608	0.7392	12.44	0.3384	2.9466	3.285
219.9	2012.2	0.2587	0.9413	14.10	0.2545	2.4448	2.699
219.9	4014.7	0.9053	0.0947	7.568	1.093	0.3900	1.483
219.8	3010.7	0.9112	0.0888	9.297	1.012	0.3680	1.380
219.8	2011.2	0.9040	0.0960	11.10	0.9072	0.2998	1.207
279.9	3009.7	0.8325	0.1675	22.29	1.237	0.7372	1.974
279.9	2009.2	0.8477	0.1523	27.31	1.0313	0.5967	1.628
280.0	1503.2	0.8336	0.1664	34.88	0.8897	0.4923	1.382
280.0	2993.7	0.5762	0.4238	27.17	0.8337	2.0783	2.912
279.9	2000.2	0.5628	0.4372	32.11	0.7022	1.6548	2.357
279.9	1506.7	0.5608	0.4392	41.20	0.5970	1.3830	1.980
279.9	3002.2	0.3753	0.6247	29.43	0.5504	2.9936	3.544
280.0	1999.2	0.3662	0.6338	35.84	0.4523	2.3747	2.827
280.0	1504.7	0.3606	0.6393	44.13	0.3820	1.9190	2.301
279.7	503.7	0.3612	0.6388	10.64	No liquid sample taken		

ethane-water binary at 100° and 160° F. work in well with the ternary data. Apparently the disagreement with the literature cited above arose from the fact that Reamer *et al.* (*14*) extrapolated the data for the ethane-water vapor phase with the aid of a theoretical correlation. This extrapolation is apparently good at 220°, 280° F., and higher temperatures, but in the critical region of ethane and as the three-phase critical of the binary is approached, is apparently not so good.

The ternary data for the hydrocarbon dissolved in the water phase agree satisfactorily with the ethane-water and ethylene-water binary data of Culberson (*6*) and Bradbury *et al.* (*4*).

A typical composition plot which was obtained for all temperatures studied, on the water content of the hydrocarbon vapors (supercritical fluid), is illustrated in Figure 3 for 220° F. The literature points presented are smoothed values of Reamer *et al.* (*14*). These diagrams indicate a linear change of water concentration with a change in the ethane and ethylene compositions on a dry basis. The effect of pressure on the water content is illustrated in Figure 4 for 220° F. This figure indicates that the effect of pressure on the water content of the ternary vapor is similar to its effect on the respective binaries.

The data on the solubility of the individual hydrocarbons in the water-rich liquid phase were taken at constant pressure and temperature while varying the hydrocarbon composition of the vapor. A plot of partial pressure of the hydrocarbon $[(Y_h)_{WB}P]$ *vs.* the mole fraction of the hydrocarbons in the water permits a test of the validity of Henry's law. Wehe and McKetta (*19*) discuss this procedure. The primary assumption required for this technique is that the presence of the second solute has no effect on the solubility of the solute under consideration. The partial pressures of the hydrocarbon *vs.* mole fraction of the hydrocarbon for the temperature of 220° F. are shown in Figures 5 and 6. Straight lines were obtained for all pressures and temperatures for ethylene, but for ethane a slight

Table II. Graphically Smoothed Values for Mutual Solubilities of Ethane-Ethylene-Water in the Vapor-Liquid Region

	I. VAPOR PHASE				II. LIQUID PHASE							
	% Ethane in Vapor on Dry Basis				% Ethane in Vapor on Dry Basis				% Ethane in Vapor on Dry Basis			
	20	40	60	80	20	40	60	80	20	40	60	80
Pressure p.s.i.a.	$Y_{H_2O} \times 10^3$[a]				$X_{C_2H_4} \times 10^3$[b]				$X_{C_2H_4} \times 10^3$			
	Temperature 100° F.				Temperature 100° F.				Temperature 220° F.			
					0.599	0.443	0.297	0.146	0.377	0.284	0.185	0.099
200					1.180	0.883	0.585	0.299	0.759	0.571	0.375	0.196
400					1.459	1.100	0.730	0.375	0.948	0.714	0.472	0.244
500	2.291	2.170	2.050	1.958	1.725	1.291	0.842	0.425	1.130	0.850	0.563	0.285
600	2.043	1.880	1.640	1.500	2.083	1.538	1.015	0.506	1.477	1.125	0.733	0.366
800	1.644	1.419	1.080	0.958	2.349	1.721	1.129	0.567	1.769	1.332	0.882	0.439
1000	1.408	1.183	0.922	0.803	2.479	1.848	1.226	0.619	2.070	1.544	1.031	0.516
1250	1.372	1.151	0.973	0.770	2.651	1.964	1.299	0.661	2.306	1.718	1.150	0.573
1500	1.345	1.146	0.967	0.761	2.808	2.096	1.414	0.725	2.631	1.979	1.329	0.657
2000	1.335	1.138	0.958	0.745	2.957	2.201	1.498	0.768	2.878	2.178	1.466	0.724
2500	1.328	1.128	0.948	0.728	3.073	2.285	1.557	0.796	3.099	2.335	1.570	0.780
3000	1.320	1.122	0.939	0.713	3.162	2.354	1.600	0.812	3.300	2.470	1.655	0.827
3500	1.317	1.119	0.931	0.700	3.249	2.413	1.631	0.815	3.492	2.593	1.728	0.866
4000	1.312	1.118	0.930	0.690	3.297	2.465	1.655	0.815	3.678	2.705	1.787	0.904
5000	1.315	1.120	0.932	0.700	3.350	2.510	1.671	0.813	3.855	2.806	1.840	0.938
	Temperature 160° F.				$X_{C_2H_6} \times 10^4$[c]				$X_{C_2H_6} \times 10^4$			
200									0.350	0.780	1.120	1.350
400					0.650	1.340	1.900	2.460	0.666	1.440	2.030	2.650
500	10.800	10.510	10.320	10.010	1.135	2.160	3.230	4.230	0.810	1.745	2.460	3.231
600	9.400	9.000	8.805	8.580	1.252	2.525	3.769	5.000	0.943	2.091	2.850	3.719
800	7.651	7.295	7.050	6.609	1.352	2.725	4.065	5.598	1.200	2.539	3.570	4.645
1000	6.295	5.898	5.551	5.068	1.521	3.051	4.451	6.065	1.419	2.910	4.196	5.410
1250	5.395	5.050	4.620	4.122	1.655	3.205	4.755	6.355	1.631	3.259	4.831	6.221
1500	4.999	4.551	4.088	3.605	1.788	3.410	5.049	6.645	1.795	3.561	5.320	6.891
2000	4.575	4.044	3.585	3.095	1.899	3.578	5.275	6.892	2.042	4.039	5.990	7.895
2500	4.423	3.888	3.392	2.909	2.075	3.838	5.645	7.295	2.210	4.375	6.485	8.621
3000	4.425	3.858	3.321	2.799	2.238	4.031	5.935	7.610	2.320	4.621	6.859	9.165
3500	4.413	3.849	3.293	2.749	2.315	4.158	6.165	7.875	2.392	4.780	7.150	9.580
4000	4.410	3.840	3.270	2.699	2.370	4.278	6.365	8.110	2.410	4.905	7.395	9.915
4500	4.410	3.840	3.250	2.647	2.400	4.360	6.541	8.325	2.410	4.980	7.590	10.185
5000	4.410	3.840	3.235	2.610	2.400	4.481	6.850	8.720	2.410	5.039	7.750	10.420
	Temperature 220° F.				Temperature 160° F. $X_{C_2H_4} \times 10^3$				Temperature 280° F. $X_{C_2H_4} \times 10^3$			
200					0.438	0.284	0.217	0.111	0.410	0.315	0.206	0.101
400					0.880	0.573	0.437	0.223	0.821	0.622	0.415	0.201
500	38.890	38.600	38.300	38.010	1.105	0.715	0.555	0.277	1.035	0.778	0.515	0.255
600	33.430	32.860	32.499	31.930	1.128	0.854	0.646	0.324	1.240	0.917	0.605	0.305
800	26.250	25.750	25.070	24.330	1.595	1.117	0.806	0.400	1.598	1.172	0.779	0.393
1000	22.010	21.450	20.750	20.140	1.838	1.333	0.925	0.463	1.901	1.409	0.935	0.475
1250	18.810	17.800	16.990	16.451	2.072	1.544	1.035	0.527	2.250	1.659	1.108	0.555
1500	16.632	15.612	14.825	13.771	2.256	1.695	1.126	0.575	2.511	1.878	1.255	0.629
2000	14.451	13.555	12.500	11.577	2.533	1.898	1.268	0.651	3.038	2.260	1.491	0.758
2500	13.499	12.562	11.561	10.580	2.718	2.048	1.371	0.702	3.467	2.568	1.678	0.860
3000	12.750	11.782	10.800	9.685	2.862	2.161	1.446	0.736	3.828	2.842	1.839	0.951
3500	12.175	11.091	10.025	8.880	2.974	2.245	1.498	0.760	4.151	3.095	1.981	1.039
4000	11.680	10.451	9.361	8.199	3.067	2.315	1.536	0.775	4.451	3.329	2.118	1.119
4500	11.250	9.882	8.724	7.675	3.148	2.368	1.565	0.784	4.739	3.552	2.245	1.191
5000	10.950	9.451	8.299	7.350	3.247	2.416	1.585	0.785	5.017	3.780	2.360	1.260
	Temperature 280° F.				$X_{C_2H_6} \times 10^4$				$X_{C_2H_6} \times 10^4$			
200					0.400	0.767	1.100	1.520	0.410	0.900	1.180	2.500
400					0.800	1.540	2.200	2.880	0.780	1.660	2.290	2.500
500	100.20	105.50	104.90	104.50	0.939	1.905	2.731	3.505	0.945	1.990	2.815	3.830
600	91.51	89.85	89.11	88.24	1.050	2.231	3.101	4.125	1.105	2.300	3.288	4.440
800	69.65	69.39	68.85	67.42	1.230	2.613	3.612	5.015	1.385	2.859	4.159	5.579
1000	58.97	57.97	56.91	55.76	1.415	2.835	4.000	5.495	1.648	3.340	4.960	6.570
1250	49.83	48.79	47.87	45.99	1.496	3.025	4.401	5.989	1.920	3.836	5.759	7.660
1500	44.00	42.79	41.25	39.34	1.579	3.170	4.685	6.295	2.159	4.259	6.410	8.530
2000	36.95	35.26	33.78	32.02	1.729	3.439	5.075	6.726	2.525	4.928	7.399	9.800
2500	33.12	31.29	29.30	27.49	1.861	3.675	5.411	7.110	2.788	5.430	8.145	10.778
3000	30.70	28.60	26.40	24.45	1.991	3.889	5.725	7.441	2.959	5.808	8.760	11.630
3500	29.28	26.79	24.55	22.44	2.109	4.091	6.021	7.765	3.081	6.108	9.281	12.385
4000	28.07	25.43	22.89	20.81	2.219	4.285	6.310	8.080	3.160	6.359	9.755	13.090
4500	26.83	24.22	21.52	19.70	2.321	4.468	6.588	8.380	3.210	6.561	10.185	13.760
5000	26.10	23.38	20.49	18.79	2.421	4.645	6.861	8.671	3.235	6.740	10.585	13.440

[a] $Y_{H_2O} \times 10^3$ = mole fraction of water in vapor phase. [b] $X_{C_2H_4} \times 10^3$ = mole fraction of ethylene in water. [c] $X_{C_2H_6} \times 10^4$ = mole fraction of ethane in water.

Table III. New Vapor Phase Data for Ethane-Water Binary

Temp., ° F.	Pressure, p.s.i.a.	Mole Fraction Water × 10^3
100.1	508.2	1.956
99.9	496.7	1.817
	916.7	0.666
	1003.7	0.602
	1512.2	0.543
	2000.5	0.516
	3014.7	0.500
	4017.7	0.531
	5027.7	0.462
160.1	504.7	9.899
160.0	998.7	4.699
160.1	1501.7	3.019
	2031.7	2.717
160.2	3013.7	2.368
160.1	4027.7	2.241
	5009.7	2.032
220.0	1509.2	12.16
220.1	2004.7	10.48
	3009.7	8.363
220.2	4039.7	7.226

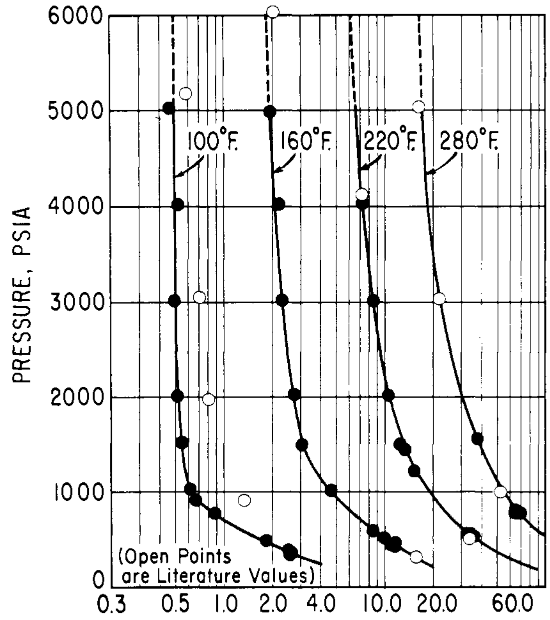

Figure 2. Water content in ethane-water vapor

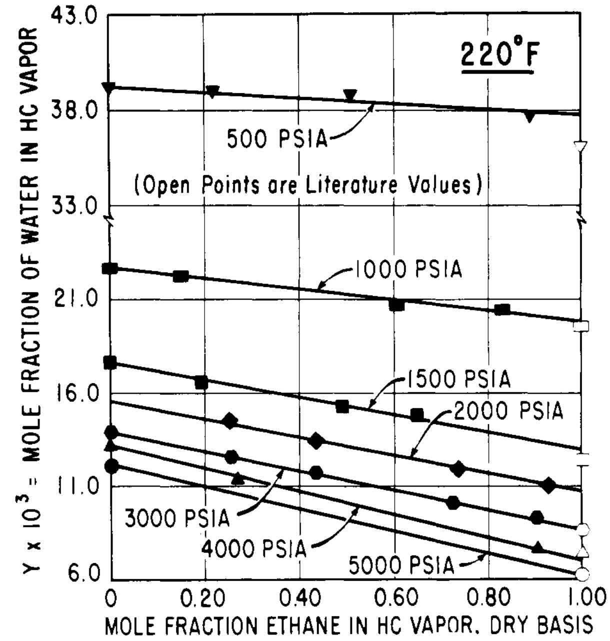

Figure 3. Water content in ternary vapor

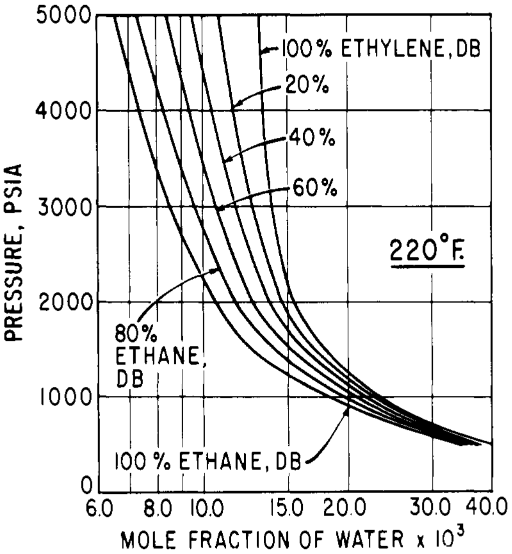

Figure 4. Effect of pressure on water content in ternary vapor

curvature is observed at 3000, 4000, and 5000 p.s.i.a. at 100°, 160°, and 220° F.

This curvature indicates that ethylene causes a slight increase in solubility of ethane over that which would be predicted by a straight line through the origin and binary points. However, this increase is so small (less than 10%) that this procedure could be used to predict solute concentrations for a ternary from binary data for the two families, olefins and paraffins. Wehe and McKetta (*19*) observed straight lines on similar plots for the *n*-butane-1-butene-water ternary in the three-phase region. The effect of pressure on the solubilities of ethylene and ethane in water for the ternary at 220° F. is illustrated in Figures 7 and 8.

THERMODYNAMIC PRESSURE EFFECT

An equation similar to that used by Krichevsky and Kasarnovsky (*8*, *9*) and Kobayashi (*7*) for binary systems is also applicable to ternary systems if the moles of components j, $i \neq j$ are held constant. This equation was used to plot the solubilities of ethane and ethylene in water for the ternary system at constant temperature and constant composition of ethane (ethylene) in the vapor phase.

This equation is

$$\ln \left(\frac{f_i}{X_i}\right)_L = \frac{\bar{V}_i}{RT} P + \ln H' \tag{1}$$

where

$$\ln H' = \frac{\bar{V}_i P_s}{RT} + \ln H$$

The assumptions in Equation 1 are constant temperature and constant moles of components i, and $\bar{V}_i$ is independent of pressure and of the change in composition of component i with pressure.

The value of $(f_i)_L$ at equilibrium is equal to $(f_i)_v$, which may be set equal to $(X_i)_v(f^{\circ}_i)_i$, provided the Lewis and Randall rule for ideal solutions applies to the system.

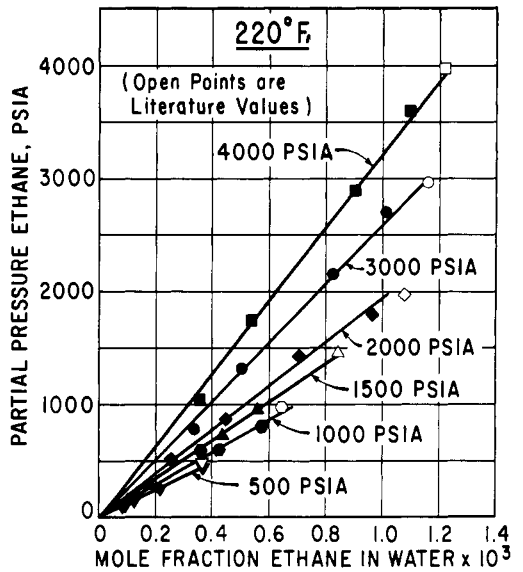

Figure 5. Solubility of ethane in water for ternary

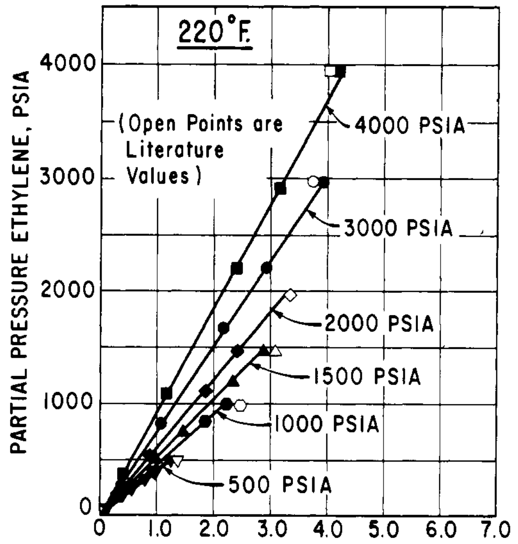

Figure 6. Solubility of ethylene in water for ternary

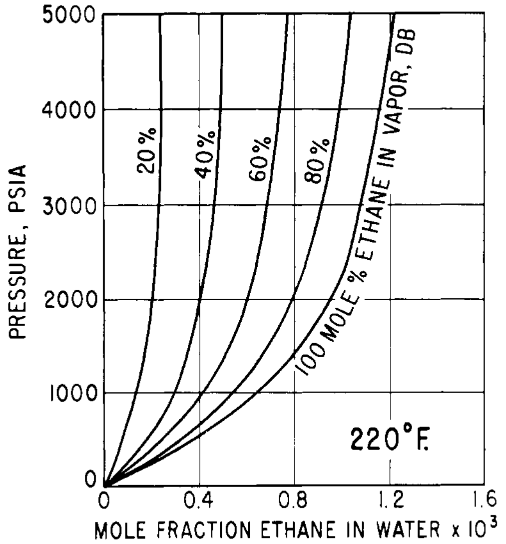

Figure 7. Effect of pressure on ethane solubility for ternary

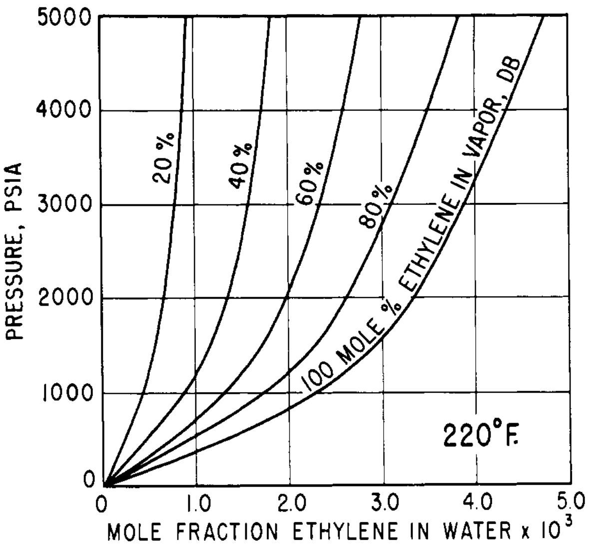

Figure 8. Effect of pressure on ethylene solubility for ternary

The value of the fugacity of the pure hydrocarbon vapor may be obtained from experimental data, from a generalized fugacity coefficient chart, or from an adequate equation of state. If, in addition, the value of Henry's law constant, H, and a value of the partial molal volume of component i in the liquid are known, the value of X_i in the liquid may be calculated from Equation 1.

Equation 1 may also be used to extrapolate experimental solubility data at low pressures to theoretical solubilities at high pressures by treating H' and $\bar{V}_i$ as empirical constants. The experimental data should, according to Equation 1, form a straight line when $\ln(f_i/X_i)_L$ is plotted against P.

The graphically smoothed data at vapor concentrations of 20, 40, 60, and 80% ethane (dry basis) were used with Equation 1 to evaluate the partial molal volumes, and modified Henry's constants for ethane and ethylene dissolved in water (Table IV). Figure 9 illustrates the type of curves obtained for each temperature. Partial molal volumes and modified Henry's law constants are reported for the cases where the effect of water in the vapor is considered negligible [dry basis, $(X_{\text{ethane}})_v + (X_{\text{ethylene}})_v = 1.0$ and wet basis $(X_{\text{ethane}})_v + (X_{\text{ethylene}})_v + (X_{H_2O})_v = 1.0$]. The Benedict-Webb-Rubin equation of state for mixtures was used to calculate fugacities of ethane and ethylene (*3*).

This equation has been derived and applied by Krichevsky and Kasarnovsky (*8*) to calculate solubilities of hydrogen and nitrogen in water and by Wiebe and Gaddy (*20*) to calculate solubilities of carbon dioxide in water. By use of experimental values of Henry's law constant and partial molar volumes of each gas in water, the solubility was calculated at pressures as high as 1000 atm. with excellent accuracy.

Kobayashi (*7*) plotted the solubilities of methane and other light hydrocarbons in water and Brooks and McKetta (*5*) and Leland and McKetta (*10*) plotted the solubility of 1-butene in water by use of Equation 1. Anthony and McKetta (*2*) used this equation to show the effect of pressure on ethylene solubility for the ethylene-water binary. Each of these investigators found that for the hydrocarbon systems this equation exhibited considerable deviation from linearity as the pressures approach that of a phase change.

Table IV. Modified Henry's Law Constants and Partial Molal Volumes for Ternary Ethane-Ethylene-Water

Ethane Compn. in Vapor Dry Basis, %[a]		100° F.		160° F.		220° F.		280° F.	
		DB[b]	WB	DB	WB	DB	WB	DB	WB
20	$\bar{v}_2$	0.5112	0.5150	0.6365	0.6391	0.8885	0.9101	0.9626	1.0563
	$\ln H_2'$	13.2959	13.2934	13.7117	13.7058	13.7863	13.7631	13.7119	13.6423
	$\bar{v}_3$	0.7177	0.7188	0.7296	0.7413	0.7293	0.7564	0.7267	0.8564
	$\ln H_3'$	12.2241	12.2396	12.6366	12.6266	12.6362	12.7384	12.7531	12.6688
40	$\bar{v}_2$	0.6764	0.6756	0.7745	0.7804	0.9334	0.9855	1.0175	1.1208
	$\ln H_2'$	13.2899	13.2890	13.6602	13.6535	13.7448	13.7087	13.6787	13.6065
	$\bar{v}_3$	0.7093	0.7123	0.6364	0.6449	0.6573	0.8014	0.6548	0.7648
	$\ln H_3'$	12.2548	12.2522	12.6881	12.6795	12.6805	12.7281	12.7586	12.6797
60	$\bar{v}_2$	0.6387	0.6404	0.6910	0.6966	0.7969	0.8279	0.8790	0.9856
	$\ln H_2'$	13.3070	13.3053	13.7226	13.7161	13.8069	13.7815	13.7192	13.6468
	$\bar{v}_3$	0.6627	0.6634	0.8040	0.8125	0.8049	0.8014	0.7666	0.8822
	$\ln H_3'$	12.2745	12.2722	12.6030	12.5946	12.6602	12.7331	12.7496	12.6698
80	$\bar{v}_2$	0.7382	0.7396	0.7909	0.7976	0.7302	0.6813	0.9194	1.0274
	$\ln H_2'$	13.2885	13.2872	13.6987	13.6922	13.8382	13.8268	13.7080	13.6358
	$\bar{v}_3$	0.6783	0.6765	0.8007	0.8118	0.7983	0.8031	0.6464	0.7643
	$\ln H_3'$	12.2638	12.2633	12.5987	12.5897	12.5998	12.7323	12.7609	12.6824

[a] 2 ethane solute. 3 ethylene solute. [b] DB, dry basis. WB, wet basis.

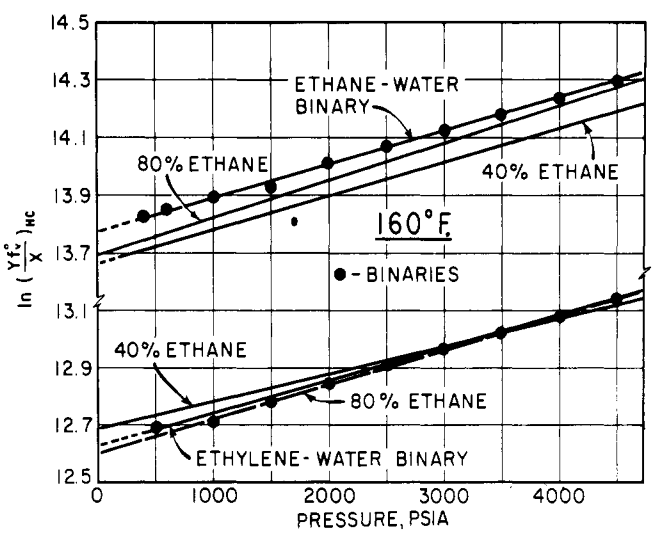

Figure 9. Equation 1 plotted for ternary

GENERAL OBSERVATIONS

Each ternary hydrocarbon-water system which has been studied at elevated temperatures and pressures has some unique characteristics—i.e., molecular weight effects are minimized, both hydrocarbon components are above or below the critical temperatures, or one hydrocarbon is above and one is below their respective critical temperatures. However, certain similarities concerning the behavior of the ternary systems have been observed. In the two-phase region, the concentration of water in the vapor phase for each isotherm and isobar varies linearly between the concentration of water in each of the respective hydrocarbon-water binaries. In the three-phase region, the water concentration in the vapor phase varies linearly between the binaries for each temperature in the *n*-butane-1-butene-water system. However, this was not the case for the methane-*n*-butane-water system. The probable cause of this difference in the behavior of these two ternary systems is that in the 1-butene-*n*-butane-water ternary both hydrocarbon components are below their respective critical temperatures, whereas in the methane-*n*-butane-water ternary, one component is above its critical temperature and the other is below.

For the two ternaries, 1-butene-*n*-butane-water and ethane-ethylene-water, very little curvature is observed when the partial pressure of a hydrocarbon (Y_hP) is plotted against its concentration in the water phase. This result is very interesting, especially when none of the binary systems obey Henry's law at the temperatures and pressures studied. Wiebe and Gaddy (*20*) observed similar results for the nitrogen-hydrogen-water ternary and used it as a basis for predicting total gas solubility in water.

A minimum hydrocarbon solubility is also observed for the ternary as well as for the binary systems.

ACKNOWLEDGMENT

The Phillips Petroleum Co. supplied the hydrocarbons used in the study.

NOMENCLATURE

f = fugacity
f°_i = fugacity of pure component i at temperature and pressure of system
$\bar{V}_i$, $\bar{v}_i$ = partial molal volume of component i in water phase
P = pressure
H = Henry's constant
H' = modified Henry's constant as defined by Equation 1
T = temperature
X = mole fraction of hydrocarbon in water
$(X_i)_v$, Y = mole fraction of water in vapor phase

SUBSCRIPTS

v = vapor
i = component i
h = hydrocarbon
s = vapor pressure of water (solvent) at temperature and pressure of system
L = water-rich liquid phase

LITERATURE CITED

(1) Anthony, R. G., Ph.D. dissertation, University of Texas, 1966.
(2) Anthony, R. G., McKetta, J. J., J. CHEM. ENG. DATA **12,** 17 (1967).
(3) Benedict, M., Webb, G. W., Rubin, L. C., *Chem. Eng. Progr.* **47,** 419 (1951).
(4) Bradbury, E. J., McNulty, D., Savage, R. L., McSweeny, E. E., *Ind. Eng. Chem.* **44,** 211–12 (1952).
(5) Brooks, W. B., McKetta, J. J., *Petrol. Refiner* **34,** 143 (February 1955).
(6) Culberson, O. L., McKetta, J. J., *Trans. Am. Inst. Mining Met. Engrs., Petrol. Branch* **189,** 319–22 (1950).
(7) Kobayashi, R., Katz, D. L., *Ind. Eng. Chem.* **45,** 440–51 (1953).
(8) Krichevsky, I. R., Kasarnovsky, J. S., *J. Am. Chem. Soc.* **57,** 2168–71 (1935).
(9) *Ibid.*, pp. 2171–2.
(10) Leland, T. W., McKetta, J. J., Kobe, K. A., *Ind. Eng. Chem.* **47,** 1265–71 (1955).
(11) Li, C. C., Ph.D. dissertation, University of Texas, 1962.
(12) Li, C. C., McKetta, J. J., J. CHEM. ENG. DATA **8,** 271 (1963).
(13) McKetta, J. J., Katz, D. L., *Ind. Eng. Chem.* **40,** 853–63 (1948).
(14) Reamer, H. H., Olds, R. H., Sage, B. H., Lacey, W. N., *Ibid.*, **35,** 790–3 (1943).
(15) *Ibid.*, **36,** 381–3 (1944).
(16) Sage, B. H., Lacey, W. N., Monograph on API Research Project 37, "Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen," American Petroleum Institute, New York, 1950.
(17) Villarreal, J. F., Bissey, L. T., Nielsen, R. F., *Producers Monthly* **18,** No. 7, 15–17 (May 1954).
(18) Wehe, A. H., Ph.D. dissertation, University of Texas, 1960.
(19) Wehe, A. H., McKetta, J. J., J. CHEM. ENG. DATA **6,** 167 (1961).
(20) Wiebe, R., Gaddy, V. L., *J. Am. Chem. Soc.* **61,** 315 (1939).

RECEIVED for review May 26, 1966. Accepted September 30, 1966. Project carried out under a National Science Foundation Grant.

Liquid and Vapor Phase Enthalpy of Monomethylamine

ROBERT A. MACRISS
Institute of Gas Technology, Chicago, Ill.

Enthalpy data have been obtained for liquid and vapor monomethylamine in the range of approximately 75° to 225° F. and pressures from 50 to 650 p.s.i.a. The data obtained are believed to be accurate to within ±1% of the actual enthalpy change relative to a base temperature of 75° F. The flow calorimeter used to make the measurements consists of a closed system in which the test fluid is recirculated at a constant and measurable rate and constant pressure through the calorimeter. A calorimeter fluid used to cool the test fluid is evaporated in the process. From the rate of evaporation of the calorimeter fluid and its known latent heat of vaporization, the enthalpy change of the test fluid can be calculated.

IN THE application of gas absorption and separation, data are required on specific heats of liquids and vapors and heats of vaporization, which sometimes cover wide ranges of temperature and pressure. Specifically, consideration of monomethylamine as a refrigerant in an absorption-refrigeration system requires knowledge of these properties in the temperature region of approximately 40° to 250° F. and pressures of 50 to 500 p.s.i.

Specific heat data available in the literature cover temperatures only to approximately 120° F. and for the saturated states. This paper presents data on the heat capacity of monomethylamine liquid and vapor at temperatures from 75° to 225° F. and pressures from 50 to 650 p.s.i.a. The experimental equipment is described also.

EXPERIMENTAL EQUIPMENT

The experimental technique employed and the principle of operation of the calorimeter have been described in part (*6*) and are patterned after those of Storvick (*7*). A schematic diagram of the flow system and essential pieces of equipment is given in Figure 1.

The adiabatic flow calorimeter is the most important item in the apparatus (Figure 2). The function of the calorimeter is to transfer to the boiling Freon (Freon 11–trichloromonofluoromethane, the calorimeter fluid) an amount of heat exactly equal to the decrease in energy of the methylamine that passes through the calorimeter coil. The amount of energy transferred is related to the quantity of vaporized Freon which is collected, condensed, and measured. With knowledge of the heat of vaporization of Freon, the enthalpy change of the methylamine between the temperatures at the

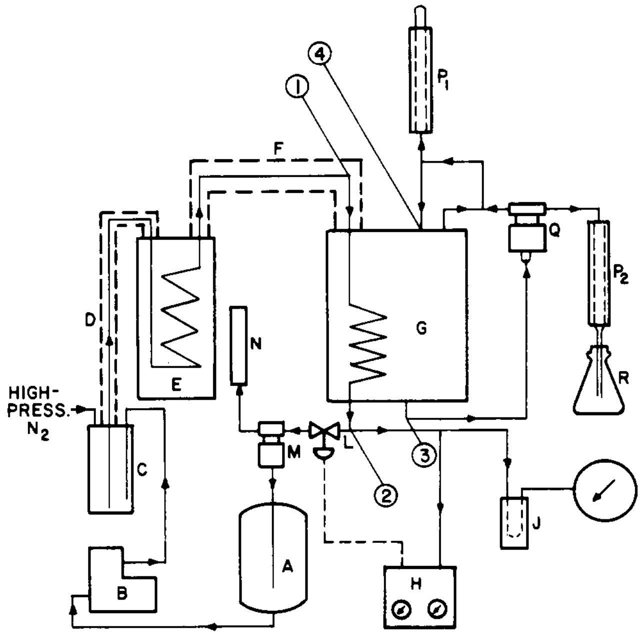

Figure 1. Schematic diagram of calorimeter unit