NOMENCLATURE

C_p = molal heat capacity, B.t.u./lb. mole
E = internal energy, B.t.u./lb. mole
H = enthalpy, B.t.u./lb. mole
P = pressure, lb./sq. inch abs.
T = absolute temperature, °K.
t = temperature, °C.
V = molal volume-cu. ft./lb. mole
J = proportionality factor

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Vapor Pressure and Viscosity of Solutions in the Calcium Oxide-Phosphoric Oxide-Water System at 25°C.

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A diversity of interest in the properties of phosphoric acid and calcium phosphate solutions in industrial, agronomic, and biochemical fields has led to the publication of articles concerning various properties of such solutions (*2–4, 6–10, 13, 15*). The vapor pressures and viscosities of solutions in the system calcium oxide–phosphoric oxide–water, as measured by usual methods, are reported here. Compositions of the solutions were bounded by the line phosphoric oxide–water and the solubility isotherms of anhydrous dicalcium phosphate and monocalcium phosphate monohydrate (*2,8*). The solution compositions lay along lines of constant weight ratios of phosphoric oxide–calcium oxide, as shown in Figure 1.

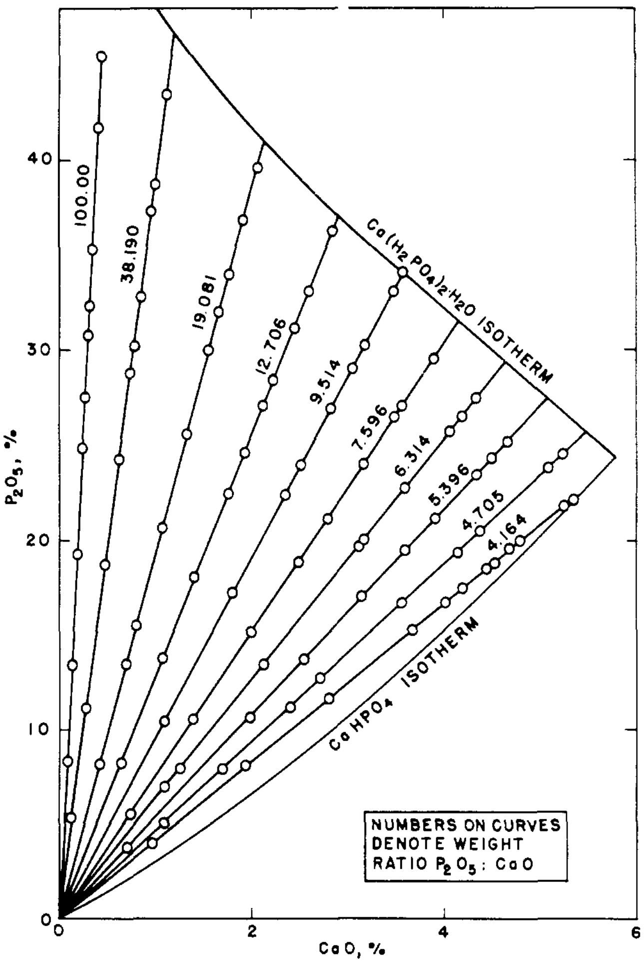

Figure 1. Composition of test solutions

PREPARATION OF SOLUTIONS

The solutions were prepared from conductance water, recrystallized phosphoric acid hemihydrate, and monocalcium phosphate monohydrate. These reagents were prepared by methods described elsewhere (*15*), and their purity was comparable to those of the same reagents used for measurements of density, conductance, and pH (*15*). Stock solutions with the phosphoric oxide–calcium oxide weight ratios shown in Figure 1 were prepared by mixing weighed amounts of monocalcium phosphate monohydrate, water, and phosphoric acid of known concentration. The stock solutions are those represented by the points of highest concentration for each phosphoric oxide–calcium oxide ratio line in Figure 1. For individual measurements, more dilute solutions were prepared by adding water to these stock solutions. The composition of each solution was checked by measuring its density (*15*) and comparing the result with tables of the density-composition relation for solutions in the system (*15*).

METHODS OF MEASUREMENT

Vapor Pressure. The vapor pressure measurements were made by a differential static method. Conductance water was the reference material. As the dimensions of the apparatus were unsuitable for measurement of the vapor pressure of water, a published value, 23.756 mm. of mercury (*14*), was used. The advantages of the differential method for measuring vapor pressures of aqueous salt solutions have been discussed (*12*). The apparatus, Figure 2, was a modification of one described by Gibson and Adams (*12*).

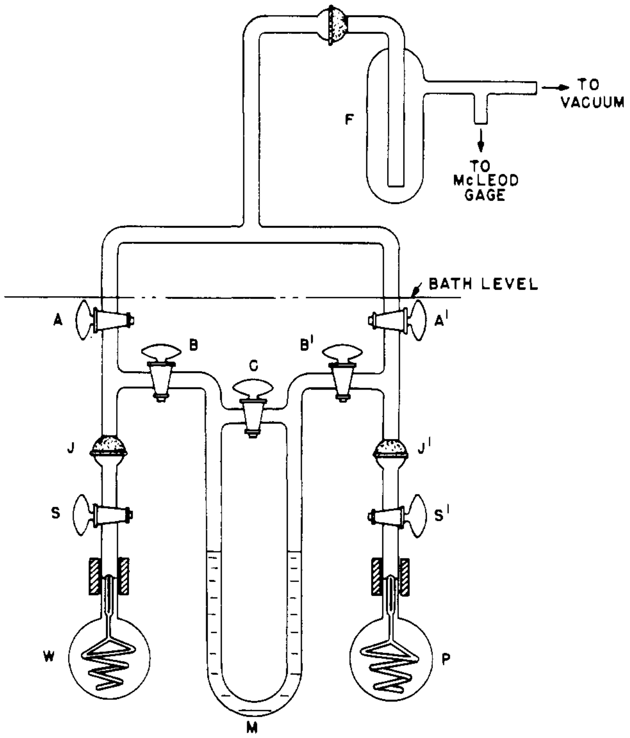

Figure 2. Modified Gibson and Adams vapor-pressure apparatus

The manometer liquid was dioctyl sebacate, a mobile oil with a density of 0.9103 gram per milliliter at 25° C. Its vapor pressure at 25° C. was about 5×10^{-8} mm. of mercury. After it was distilled into the manometer under a high vacuum, the oil was exposed only to water vapor, except on rare occasions when it was exposed to dry nitrogen for a few minutes while a stopcock was regreased. The oil showed no significant change in density with use.

The vapor pressure system was immersed to a point above stopcocks *A* and *A'* (Figure 2) in a water bath with plate glass sides. The bath water was maintained at 25° ± 0.005° C. The room temperature was maintained at 25° ± 1° C.

Differences in oil levels in the manometer were read with a microcathetometer to ±0.005 mm., which corresponds to ±0.0003 mm. of mercury. The measurements were made through a glass wall of the bath, however, and refraction increased the over-all error in the reading to about ±0.001 mm. of mercury.

Spherical joints *J* and *J'* were sealed with Apiezon W wax. With the bath water level lowered below these joints, the bulbs were attached or removed by flaming the seals.

To make a vapor pressure measurement, 50 ml. of phosphate solution and 25 ml. of conductance water were placed in solution bulb *P*. The bulb was attached to the apparatus and the bath was filled with water. The solution bulb then was evacuated, causing the solution to boil. By adjustment of stopcock *S'* the solution was boiled intermittently, with continuous magnetic stirring, to evaporate 25 ml. of water over a 2.5-hour period. The water vapor was frozen out in removable cold trap *F*. During this boiling-off process the solution became essentially degassed. Stopcock *S'* then was closed and the solution was stirred overnight at 25° C. under its own pressure. Next day the solution bulb was opened momentarily to a high vacuum (10^{-5} to 10^{-6} mm. of mercury) by slow rotation of stopcock *S'* through two complete revolutions. If the solution contained enough gas to cause bumping when opened to the high vacuum, it was degassed further by intermittently opening the bulb to the high vacuum as the solution was stirred continuously.

The solvent (conductance water) was treated in a similar way and then was left connected to the vapor pressure apparatus. It was checked for noncondensable gas in each vapor pressure measurement.

With *S* and *S'* closed, after the degassing step was completed, *A* and *A'* were closed. Bulb *W* was opened to the manometer; then bulb *P* was opened and stopcock *C* was closed. The differential pressure was measured at intervals of 15 minutes. The 30-, 45-, and 60-minute readings usually differed by no more than 0.002 mm. of mercury. When there was no trend in the measured pressure over an hour, the average of the readings for that period was taken as the final pressure. Readings over periods as long as 24 hours usually showed no significant change after 30 minutes. This rapid approach to equilibrium is to be expected (*11*) when the solutions are degassed completely and are stirred adequately during equilibration.

At the end of the pressure measurement the gas enclosed between *S'*, *A'*, and *B'* was expanded into the high vacuum (10^{-6} mm. of mercury) system which contained trap *F*, cooled in liquid nitrogen for freezing out the water. The pressure of the noncondensable gas was measured with a McLeod gage. The residual gas pressure in the vacuum system always was less than 10^{-5} mm. of mercury, which corresponds to less than 10^{-3} mm. of mercury calculated for the 75-ml. volume of the vapor pressure system.

After completion of the vapor pressure measurement, the solution was removed for viscosity and density determinations. From a knowledge of the density of the solution and its phosphoric oxide–calcium oxide weight ratio, its composition was determined from published data (*15*).

Viscosity. Viscosities were measured with an Ostwald viscometer that had a delivery time of about 80 seconds for water at 25° C. The viscometer was calibrated with conductance water at 25° C. The viscosity of water at 25° C., 0.8902 centipoise, was calculated (*5*) from the reliable value at 20° C. (*16*). The density of water at 25° C. was taken as 0.99707 gram per ml.

The measurements were made according to the conventional procedure (*1*) in a water bath maintained at 25° ± 0.005° C. Efflux times were measured with an electric timer that was read to 0.01 second. The viscosities were not corrected for kinetic energy losses, as this correction was less than the uncertainty introduced through the densities of the solutions.

Density. The densities were determined (*15*) in duplicate, and the weights corrected for the buoyancy of air. Duplicate weighings agreed to 1 part in 10,000, which corresponds to approximately 0.03% in density.

RESULTS

Data are presented in Table I. The differences in the viscosity of air-saturated and degassed solutions of the same composition were not significant, and the values tabulated are those for the air-saturated solutions. The average deviation for duplicate measurements of viscosity was ±0.05 centipoise.

The average uncertainty in the density of a given solution, ±0.004 gram per ml., corresponds to an uncertainty of ±0.04% phosphoric oxide or ±0.02% calcium oxide. An analysis of the vapor pressure–composition relationship showed that the uncertainty in composition leads to an uncertainty in vapor pressure of ±0.013 mm. of mercury at 25° C. The maximum uncertainty did not exceed ±0.02 mm. of mercury. The vapor pressure measurements are tabulated to 0.001 mm. of mercury, because the individual measurements were this precise.

In deriving empirical equations for the activity of water, a_1, and viscosity, η, as functions of composition, the solutions were regarded as solutions of monocalcium phosphate [$Ca(H_2PO_4)_2$] and phosphoric acid [H_3PO_4] in water. The symbols were

Table I. Viscosity and Vapor Pressure of Solutions in the System Calcium Oxide-Phosphoric Oxide-Water at 25° C.

Solution[a]						
	Composition					
Weight ratio P_2O_5 : CaO	P_2O_5, %	CaO, %	m_{AM}	m_M	Viscosity, Centipoises	Vapor Pressure, Mm. Hg at 0° C.
4.164	22.18	5.326	4.7518	1.4442	...	21.675
	21.85	5.246	4.6451	1.4116	4.31	21.79
	19.95	4.791	4.0615	1.2345	3.55	22.19
	19.55	4.694	3.9448	1.1987	...	22.110
	18.86	4.529	3.7484	1.1393	3.26	22.26
	18.44	4.428	3.6317	1.1038	3.15	22.27
	17.51	4.203	3.3806	1.0271	...	22.391
	16.72	4.015	3.1751	0.9650	2.71	22.49
	15.20	3.650	2.7980	0.8504	2.39	22.69
	11.74	2.819	2.0201	0.6134	...	22.974
	11.73	2.817	2.0180	0.6133	1.81	23.00
	8.12	1.950	1.3079	0.3976	1.40	23.27
	4.00	0.961	0.6006	0.1826	1.09	23.52
4.705	24.55	5.218	5.5285	1.4873	5.02	21.137
	23.83	5.065	5.2738	1.4188	4.75	21.296
	20.54	4.364	4.2136	1.1331	3.40	21.903
	19.40	4.124	3.8815	1.0444	3.19	22.109
	16.74	3.558	3.1669	0.8520	2.58	22.470
	12.77	2.715	2.2342	0.6012	1.82	22.867
	11.20	2.380	1.9029	0.5118	1.70	23.015
	7.90	1.679	1.2654	0.3404	1.36	23.268
	5.08	1.072	0.7758	0.2072	1.15	23.438
5.396	25.18	4.667	5.7156	1.3409	4.91	20.917
	24.35	4.512	5.4180	1.2707	4.55	21.124
	23.48	4.352	5.1186	1.2008	4.18	21.313
	21.16	3.921	4.3761	1.0264	3.45	21.758
	19.50	3.613	3.8900	0.9123	3.03	22.020
	17.00	3.151	3.2196	0.7553	2.51	22.382
	13.75	2.548	2.4433	0.5731	1.93	22.761
	10.63	1.970	1.7832	0.4183	1.59	23.031
	3.79	0.702	0.5663	0.1328	1.06	23.532
6.314	27.45	4.347	6.5384	1.3105	5.28	20.287
	26.67	4.225	6.2303	1.2493	5.02	20.490
	25.73	4.076	5.8745	1.1779	4.47	20.731
	22.83	3.616	4.8716	0.9766	3.56	21.415
	20.01	3.170	4.0147	0.8050	2.83	21.913
	19.67	3.115	3.9182	0.7854	2.58	22.091
	13.51	2.140	2.3824	0.4776	1.80	22.727
	7.90	1.251	1.2613	0.2528	1.29	23.242
	6.97	1.103	1.0956	0.2195	1.27	23.313
7.596	27.13	3.572	6.3580	1.0595	4.66	20.304
	26.56	3.497	6.1389	1.0230	4.25	20.470
	24.00	3.160	5.2246	0.8707	3.64	21.141
	21.15	2.785	4.3242	0.7207	2.85	21.651
	18.89	2.487	3.6845	0.6140	2.45	22.033
	15.18	1.998	2.7530	0.4586	1.89	22.539
	10.59	1.393	1.7671	0.2943	1.49	23.018
	5.58	0.734	0.8564	0.1426	1.14	23.398
9.514	34.15	3.589	9.5438	1.2695	7.32	17.784
	33.08	3.476	8.9683	1.1928	6.82	18.216
	30.34	3.188	7.6405	1.0162	5.38	19.234
	29.12	3.060	7.1082	0.9454	4.72	19.649
	26.98	2.836	6.2494	0.8315	4.03	20.289
	23.95	2.518	5.1734	0.6884	3.29	21.026
	22.43	2.358	4.6864	0.6236	3.00	21.342
	17.23	1.812	3.2375	0.4309	2.03	22.229
	10.43	1.096	1.7317	0.2303	1.40	23.006
12.706	36.26	2.854	10.6432	1.0603	...	16.799
	33.14	2.608	8.8979	0.8863	6.02	18.137
	31.18	2.453	7.9459	0.7912	5.23	18.875
	28.41	2.235	6.7546	0.6726	4.25	19,790
	27.14	2.136	6.2603	0.6236	3.98	20.160
	24.60	1.936	5.3550	0.5334	3.26	20.813
	22.45	1.767	4.6648	0.4647	2.82	21.285
	18.02	1.418	3.4235	0.4333	2.17	22.066
	13.72	1.080	2.4065	0.2398	1.69	22.622
	8.22	0.647	1.3128	0.1662	1.30	23.134
19.081	39.61	2.076	12.7117	0.8433	...	15.062
	36.89	1.934	10.8831	0.7222	6.96	16.422
	34.00	1.782	9.2391	0.6129	5.65	17.734
	31.93	1.674	8.2123	0.5449	4.89	18.535
	30.05	1.575	7.3705	0.4890	4.22	19.203
	25.61	1.342	5.6616	0.3755	3.19	20.500
	20.65	1.082	4.1118	0.2727	2.40	21.566
	15.46	0.810	2.7887	0.1849	1.78	22.358
	13.44	0.705	2.3387	0.1553	1.59	22.644
	8.17	0.428	1.3016	0.0863	1.26	23.165
38.190	43.43	1.137	15.5836	0.5164	...	12.889
	38.68	1.013	11.8709	0.3935	...	15.523
	37.98	0.994	11.4062	0.3779	...	15.870
	37.38	0.979	11.0349	0.3658	...	16.159
	32.81	0.859	8.5418	0.2830	...	18.135
	30.23	0.792	7.3841	0.2449	...	19.071
	28.78	0.754	6.7860	0.2250	...	19.513
	24.27	0.634	5.1761	0.1711	...	20.753
	18.69	0.490	3.5650	0.1183	...	21.859
	11.17	0.292	1.8650	0.0617	...	22.855
	5.35	0.140	0.8147	0.0270	...	23.385
38.190	43.90	1.149	16.0204	0.5307	10.15	...
	42.87	1.122	15.0818	0.4996	9.27	...
	40.36	1.057	13.0546	0.4327	7.52	...
	38.51	1.009	11.776	0.3903	6.69	...
	34.04	0.891	9.1530	0.3032	4.95	...
	32.44	0.849	8.3655	0.2771	4.39	...
	24.80	0.650	5.3496	0.1775	2.78	...
	18.87	0.494	3.6116	0.1197	1.96	...
	12.51	0.328	2.1362	0.0709	1.51	...
	6.82	0.179	1.0621	0.0353	1.17	...
100.00	45.47	0.455	17.3561	0.2198	9.95	11.945
	41.73	0.417	13.9650	0.1766	7.58	13.964
	35.30	0.353	9.7475	0.1234	4.96	17.098
	32.37	0.324	8.2788	0.1049	4.14	18.281
	30.79	0.308	7.5733	0.0959	3.81	18.847
	27.51	0.275	6.2684	0.0793	3.18	19.862
	24.84	0.248	5.3401	0.0675	2.67	20.637
	19.22	0.192	3.6925	0.0467	2.02	21.725
	13.39	0.134	2.3169	0.0293	1.50	22.578
	8.35	0.083	1.3305	0.0167	1.22	23.114

[a] m_M = molality of monocalcium phosphate; $m_{AM} = m_A + 2m_M$, where m_A = molality free phosphoric acid.

m_M = molality of monocalcium phosphate
m_A = molality of free phosphoric acid
$m_{AM} = m_A + 2m_M$
a_1 = activity of water
η_w = viscosity of water
η = viscosity of solutions in the system

The following equation was derived to express the values of a_1 for solutions in which m_{AM} ranged from 0.1 to 7.5

$$-\log a_1 = 0.0000385\, m_{AM}^{-\frac{1}{2}} + 0.00920\, m_{AM} - 0.00145\, m_{AM}^{\frac{3}{2}} + 0.00109\, m_{AM}^2 - 0.00625\, m_M - 0.0003\, m_M^2 - 0.0006\, m_M m_{AM} \quad (1)$$

When m_M is zero, m_{AM} is the same as m_A, and Equation 1 becomes the same as that published for the activity of water in phosphoric acid solutions in which m_A ranges from 0.1 to 7.5 (9).

When m_{AM} is greater than 7.5, the following equation applies.

$$-\log a_1 = \beta - 0.00625\, m_M - 0.0003\, m_M^2 - 0.0006\, m_M m_{AM} \quad (2)$$

Values of β, in units of $-\log a_1$, are read from a plot of published data (9) for $-\log a_1$ in phosphoric acid solutions as a function of m_A. In reading values of β, the value taken for m_A is the same as that for m_{AM} in the three-component solution being evaluated.

From the deviations between the experimental values for a_1 and those calculated by Equations 1 and 2, it is calculated that the probable error of the equation values for vapor pressure is ±0.008 mm. of mercury, with a 95% confidence limit of 0.025 mm. of mercury.

Three empirical equations are required to represent the viscosities over the range of compositions studied.

$$\eta = \eta_w + 0.223\, m_{AM} + 0.0178\, m^2_{AM} + 0.5\, m_M + 0.05\, m_M m_{AM} + 0.0138\, (m_M m_{AM})^2 \quad (3)$$

$$(m_{AM} = 0.2 \text{ to } 2.7)$$

$$\eta = \eta_w + 0.206\, m_{AM} + 0.0275\, m^2_{AM} - 0.00074\, m^3_{AM} + 0.5\, m_M + 0.05\, m_M m_{AM} + 0.0138\, (m_M m_{AM})^2 \quad (4)$$

$$(m_{AM} = 2.7 \text{ to } 5.5)$$

$$\eta = \eta_w + 0.1891\, m_{AM}^{1.33} + 0.5\, m_M + 0.05\, m_M m_{AM} + 0.0138\, (m_M m_{AM})^2 \quad (5)$$

$$(m_{AM} = 5.5 \text{ to } 18)$$

When m_M is zero, Equations 3, 4, and 5 become identical to equations for the viscosity of pure phosphoric acid solutions (*6*). For the present use, however, the viscosity equations are applied in concentration ranges that differ somewhat from those originally specified, and the empirical constants are rounded to correspond with the experimental data for the three-component system.

The probable error of viscosities calculated by use of Equations 3, 4, and 5, compared to the experimental values, is ±0.05 centipoise, with a 95% confidence limit of ±0.148 centipoise.

The activity of water in the solution has thermodynamic significance and is useful in evaluating the thermodynamics of the three-component system. In this connection, a study of the activity of calcium ions in the calcium oxide–phosphoric oxide–water system is needed.

The viscosity data are useful in engineering calculations on the handling of calcium phosphate solutions. They also are needed in theoretical calculations relating to diffusion of calcium phosphate solutions.

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Net Heat of Combustion of Aviation Gasoline and Its Correlation with Other Properties

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The work described was undertaken to determine the feasibility of finding for 115/145 grade aviation fuels relations between net heat of combustion and aniline-gravity product similar to those found by Jessup and Cragoe (*6*) and Rothberg and Jessup (*11*) for AN-F-28 and AN-F-58 aircraft fuels, and by Jessup and Cogliano (*5*) for JP-4 and JP-5 fuels. The previous work had indicated that it is not possible to make a reliable estimate of the heat of combustion of a petroleum fuel from its aniline-gravity product alone, but that such an estimate can be made for members of a definite class of fuels.

The data at present available show clearly that net heat of combustion of petroleum products is not a function of aniline-gravity product alone, but must depend to some extent upon some other variable or variables; thus, data on many pure hydrocarbons are not in accord with any such relation, the individual fuels of a given type depart from the equation for that type by considerably more than the experimental error of measurement, and different relations between aniline-gravity product and net heat of combustion are obtained for different types of fuels. It appears, therefore, that to develop a satisfactory method of estimating net heat of combustion it will be necessary to investigate the effect of other factors in addition to aniline-gravity product. In particular, it seems desirable to make an approximate determination of composition in terms of hydrocarbon type. The work described in this report, therefore, includes measurements of this type.

FUELS INVESTIGATED

In deriving an equation to represent net heat of combustion as a function of another measured property such as the aniline-gravity product, the fuels selected for measurement can be regarded as a sample from a population of fuels of similar type. To make valid inferences about the population, the fuels selected must constitute a representative sample—i.e., the fuels of the sample should have characteristics typical of the specified population. To ensure a representative sample of any given type of fuel, the following minimum requirements were imposed upon the samples to be used: