TABLE I

THE ATOMIC WEIGHT OF POTASSIUM

Anal.	Sample of KCl	KCl in vacuum, g.	Ag in vacuum, g.	Ag added, g.	Ag in vacuum, corrected, g.	Ratio KCl:Ag	Atomic weight of K
1	A	4.88482	7.06844	0.00025	7.06819	0.691099	39.099
2	A	4.08265	5.90751	.00000	5.90751	.691094	39.098
3	A	8.52040	12.32907	.00000	12.32907	.691082	39.097
4	A	8.62997	12.48729	.00020	12.48749	.691089	39.098
5	B	8.77749	12.70116	.00020	12.70096	.691089	39.098
					Average	.691085	39.098

average K^{39}/K^{41} ratio in mineral sources to be 14.25. With this abundance ratio the two values of the packing fraction give 39.093 and 39.097 for the atomic weight of potassium (conversion factor = 1.000275).

Summary

By comparison of potassium chloride with silver the atomic weight of potassium is found to be 39.098.

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[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Transition Temperatures of the Liquid–Solid Phases of Trimethyl Phosphate

BY H. ARMIN PAGEL AND WALTER A. SCHROEDER

No reference to the melting or freezing point of trimethyl phosphate could be found in the literature. The work carried out in this Laboratory showed that two solid forms can be obtained, and that these forms are monotropic.

Experimental.—Commercial grade trimethyl phosphate, obtained from the Commercial Solvents Corporation, was purified by fractional distillation at two different pressures. Distillations were carried out in a 2-liter all-glass still, fitted with an "indented" type of distilling head (similar to the Vigreux), which was in turn attached to a vertical condenser. The ground glass joint necessary for filling was sealed against leakage under reduced pressure by means of external rubber housings. A mercury trap in series with the aspirator line prevented possible moisture contamination of the ester. Essentially constant reduced pressures were maintained by the use of a specially constructed vacuum valve.

About 3 liters of the ester were fractionally distilled in 1-l. lots at 380 ± 1 mm. The approximate volumes, densities, and refractive indices of the first, middle, and residual fractions (arbitrarily labelled in order: (1–1), (2–1), and (R–1) for later reference) were: (1–1), 10%, d^{20}_4 1.19701, n^{20}_D 1.3936; (2–1) 75%, d^{20}_4 1.21439 ± 0.00001, n^{20}_D 1.3967; (R–1) 15%, d^{20}_4 1.21499, n^{20}_D 1.3968. About one-half of the total (2–1) fraction was then further fractionated at 192 ± 3 mm., labelled in order (1–2) and (R–2), yielding: (1–2) 75%, d^{20}_4 1.21436 ± 0.00000, n^{20}_D 1.3967; (R–2), 25%, d^{20}_4 1.21442, n^{20}_D 1.3967.

Since the physical properties of fractions (2–1) and (1–2) appeared to be constant, these fractions were used. Further possible purification was sought by slowly fractionally freezing 100 ml. of fraction (1–2) until about 30% of liquid remained. The remaining liquid was siphoned off, and the remelted solid used (labelled R–3).

Low temperatures were obtained with a mixture of solid carbon dioxide and alcohol. The low temperature-bath consisted of a cylindrical metal can, 11 cm. in diameter and 17 cm. tall, surrounded by rock wool insulation, 4 cm. thick. Test-tubes for maintaining seed crystals, a pentane thermometer, and a 25 mm. by 200 mm. test-tube fitted into a slightly larger glass shield tube were introduced into the bath through carefully fitted holes in a wooden cover. The shield tube arrangement was found necessary to control the temperature gradient in order to obtain slow freezing. Since alcohol and carbon dioxide vapors are soluble in trimethyl phosphate, these were constantly removed from the surface of the bath through a suitable hole in the cover connected to a filter pump.

The large test-tube described above was fitted with a cork to accommodate a double junction thermocouple and a manually operated ring type glass stirrer. Since the ester is noticeably hygroscopic, purified air was continuously passed into the upper part of the test-tube to prevent possible entrance of moist air. Samples of approximately 35 ml. were used. All temperature observations were made at one-minute intervals. In the freezing point determinations, the observations were usually continued until the solidified portion prevented further effective stirring (estimated 40 to 50% solid) whereupon the container was quickly transferred to a Dewar flask and the melting temperature observed.

Temperature measurements were made with a Leeds and Northrup Student Type potentiometer using double junction copper–constantan thermocouples made of Leeds and Northrup standardized wire. The potentiometer was checked against a calibrated Type K potentiometer at the desired values, and the thermocouples in turn checked against the transition point of sodium sulfate decahydrate, the melting point of ice and the freezing point of reagent mercury, as fixed thermometric points. Within the precision obtainable (equivalent to ±0.03°) perfect agreement with the accepted tabulated values was found.

Results

The observed liquid–solid phase transition temperatures of the two different solid forms referred to as "α" and "β" are given in Tables I and II below.

TABLE I

(α FORM)

Fraction[a,b] used	Transition[c] temp., °C.
(2-1)*a*	−46.08*f*
(2-1)*a*	−46.01*f*
(2-1)*a*	−46.03*m*
(2-1)*a*	−46.08*m*
(2-1)*b*	−46.06*m*
(2-1)*c*	−46.06*f*
(1-2)*d*	−46.15*f*
(1-2)*d*	−46.09*m*
(1-2)*e*	−46.08*f*
(R-2)*f*	−46.00*f*
(R-3)*g*	−46.08*f*

TABLE II

(β FORM)

Fraction used	Transition temp., °C.
(2-1)*a*	−62.48
(2-1)*b*	−62.59
(2-1)*b*	−62.64
(2-1)*c*	−62.39
(1-2)*e*	−62.48
(R-2)*f*	−62.38
(R-3)*g*	−62.48

[a] Samples of fractions having the same letter indicate that the same sample was used. [b] "*f*" "*m*" indicate freezing and melting, respectively. [c] All temperatures in Table II are freezing values.

The most probable temperatures for the transition of the α and β forms are believed to be −46.1 ± 0.1° and −62.5 ± 0.15°.

Discussion

No specific method for starting the crystallization of the α or the β form was found. When the ester was slowly cooled to about −60° and the walls of the container vigorously scratched with a glass rod as the cooling continued, the β form was usually obtained. Frequently, however, the α form was obtained instead, in which case nearly all of the liquid solidified almost instantly. Occasionally the α form crystallized spontaneously between the ranges of about −58 to −75°, but never above −58°. Undisturbed cooling to about −70° followed by scratching usually gave the α variety. Either form could be produced by seeding.

Within the ranges of the conditions studied the two forms appear to be monotropic. The β form is metastable, and appears to be capable of almost instant change into the α form. This transformation frequently starts spontaneously or may be started at will by seeding the liquid–solid β mixture or the completely solid β, with a trace of partially melted α seed. The rapid rate of transformation was particularly observed during a freezing point determination of the β form, in which case the liquid was allowed to solidify completely and further cooled to about −65°. Within a few seconds after a trace of α seed was added, the container split lengthwise. As soon a the potentiometer was quickly readjusted, the thermocouple junctions, about 5.5 cm. below the solid surface, already showed a temperature of −56°. The reverse transformation of α to β was never observed. Due to the tendency of spontaneous transformation, much difficulty was experienced, both in preserving solid β seed in the seed tubes and in obtaining at least ten successive freezing observations. However, in several instances thirty or more successive observations were obtained.

Regardless of the degree of supercooling or the means of inducing crystallization, the characteristic sudden temperature rise, followed abruptly by extremely constant freezing temperatures, was observed in every case, for both α and β forms. This constitutes additional proof of two definite solid phases.

Both solid forms are denser than the liquid. Although the α form remains well in suspension when constantly stirred, the β form tends to settle quite rapidly. Due in part to this, and the greater ease of melting, no reliable melting data were obtained for the β form.

Summary

1. Two solid forms of trimethyl phosphate, which appear to be monotropic, have been observed. The liquid–solid transition temperature of the α or stable form was found to be −46.1 ± 0.1° and that of the β or metastable form, −62.5 ± 0.15°.

2. Methods of obtaining each of the two forms as well as certain properties have been discussed.

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