

The Chemistry of Phosphine

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* The present article is a revised and extended version of the work previously published by Fluck and Novobilsky: *Fortschr. chem. Forsch.* 13, 125 (1969). It is especially concerned with the many new physico-chemical investigations which have been carried out on phosphine. The literature has been covered to the end of 1971 and in some cases beyond this date.

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I. Introduction

Since the discovery of phosphine by Gengembre and Kirwan ^{1,2,3}), the first published reports about its formation ^{264,265}) and the relatively early investigations of its reactions with heated alkali metals ^{4,5}) the compound has been mentioned in all text-books and compilations. The study of its chemical behaviour was, however, only carried out systematically in the last twenty years. Nuclear magnetic resonance experiments on phosphine and its inorganic derivatives and the attempted correlation of the data with the chemical properties of the compounds induced us to review the literature on phosphine and its reactions. The results of this work are presented in the following article.

II. Properties of Phosphine and its Determination

1. Physical Properties and Data

At room temperature phosphine is a *colourless gas* with a garliclike smell. Below $-87.74\text{ }^{\circ}\text{C}$ ⁶) [$-87.44\text{ }^{\circ}\text{C}$ ⁷); $-87.78\text{ }^{\circ}\text{C}$ ⁸); $-87.9\text{ }^{\circ}\text{C}$ ³⁴¹)], it is a colourless liquid which freezes at $-133.5\text{ }^{\circ}\text{C}$ ^{7,8,9}). Solid phosphorus hydride exists in four or five different forms ^{7,8,10}). The transformations occurring at -185 , -224 , -243 and $-263\text{ }^{\circ}\text{C}$ are possibly connected with the hindered rotation of the molecule. The weight of phosphine at normal temperature and pressure is 1.5307 g/l ^{11,12}), the density of liquid phosphine at $-90\text{ }^{\circ}\text{C}$ is 0.746 g/cm^3 ^{11,12,321}). The density of liquid phosphine in the temperature range between the triple-point and the boiling point can be obtained from the equation

$$d_4^t = 0.594 - (1.71 \cdot 10^{-3} t \pm 3 \cdot 10^{-5} t) \quad (1)$$

where d_4^t is the density of the hydride relative to the density of water at $4\text{ }^{\circ}\text{C}$ and t is the temperature ³⁴²). The density of solid phosphine was found to be 0.896 g/cm^3 at $-135\text{ }^{\circ}\text{C}$ ¹³). The vapour pressure over liquid phosphine below the boiling point can be determined by the equation ^{8,14,284})

$$\log p (\text{cm} \cdot \text{Hg}) = -1027.300/T - 0.0178530 T + 0.000029135 T^2 + 9.73075 \quad (2)$$

Vapour pressures of phosphine at temperatures $< 25\text{ }^{\circ}\text{C}$ were determined by A. Stock *et al.* ¹⁵) and Stephenson and Giaouque ⁸), and between 25 and $50\text{ }^{\circ}\text{C}$ by Briner ²⁶⁹). See also ^{270,271}). The vapour pressures of the system PH_3/AsH_3 in the temperature range -78.7 to $-100\text{ }^{\circ}\text{C}$ were determined by Devyatykh *et al.* ³⁴¹).

According to the most recent measurements the critical pressure is 65 at and the critical temperature $52\text{ }^{\circ}\text{C}$ ²⁷²). Earlier work gave similar values ^{16,269,273,281}). The latent heat of vapourisation of phosphine at the boiling point was

found experimentally to be 3493 ± 3 cal/mol^{6,17)}, a more recent value is 3949 cal/mol³⁴¹⁾. The molar entropy at the boiling point is 46.93 cal·grad⁻¹^{7,8)}. Earlier work gave the remarkably small value of 18.8 for the Trouton constant⁷⁾. However, the latest report of 21.3 is probably correct³⁴¹⁾.

The equilibria between the liquid and vapour of binary mixtures of phosphine and arsine were investigated by Devyatykh *et al.*³⁴¹⁾.

The surface tension of liquid phosphine at -100 °C is 22.0 dyn/cm^{319, 320,349)}.

The viscosity of phosphine at 273 K is $1073 \cdot 10^{-7}$ poise^{343,344)}. The temperature dependence can be represented by the equation

$$\eta = K \cdot T^S \quad (3)$$

where η is the viscosity coefficient ($\text{g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$), T the temperature in Kelvin, K and S are constants. For phosphine in the temperature range 193–273 K, $K = 3.648 \cdot 10^{-7}$ and $S = 1.013$ ³⁴³⁾.

Phosphine is thermally very stable and decomposes noticeably only above 550 °C^{274,275)}.

At -140 °C *solid phosphine* crystallises in a face-centred cubic form with four molecules in the unit cell¹³⁾. The lattice constant is $a = 6.31 \pm 0.01$ Å¹³⁾. Agreeing results from various different methods show that the phosphine molecule has a pyramidal structure with C_{3v} symmetry¹⁸⁻²⁴⁾. Also infra-red and Raman^{25,26)}, micro-wave²⁷⁻²⁹⁾, and nuclear magnetic resonance experiments³⁰⁾ confirm this result, as do the findings from electron diffraction experiments³¹⁻³³⁾. Helminger and Gordy³⁴⁵⁾ recently carried out thorough investigations of the micro-wave spectra (sub-millimetre wave spectra) of phosphine and deuterophosphine. Infra-red experiments suggest that the phosphine molecule in the solid state also has C_{3v} or C_3 symmetry^{10,13,328)}. X-Ray diffraction studies on solid phosphine have not yet been carried out.

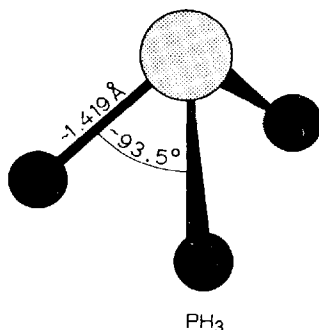


Fig. 1. PH₃ molecule (bond angle and interatomic distance)

The values obtained for the P–H bond lengths and H–P–H bond angles by different methods are collected together in Table 1. Calculations on the bond lengths in PH_3 , PH_4^+ and PH_2 have been made by Banyard and Hake⁴¹⁾. *Ab initio* SCF–LCAO–MO calculations for the phosphine molecule have been made recently by various workers and the results compared with the experimentally determined physical quantities for the molecule^{346,347)}.

Revisions of earlier data on the *heat of formation* and the bond energies of phosphine have been undertaken⁴⁰⁾. The heat of formation ΔH_{f_0} of phosphine from white phosphorus and hydrogen is 1.30 kcal/mol⁴⁰⁾, (the corresponding value for P_2H_4 is 5.0 ± 1.0 kcal/mol), the average bond energy E (P–H) was found to be 76.8 kcal.

When subjected to shock-waves, phosphine dissociates into hydrogen and red phosphorus. The radiation thus emitted is only visible in reflection. In contrast, the shock-wave induced dissociation of phosphine diluted with argon is accompanied by emission of visible light. In this case the reaction products are hydrogen and white phosphorus⁴⁶⁵⁾.

The refractive index between gaseous phosphine at 0 °C and 760 mmHg and vacuum is 1.000789 when measured with white light⁴⁶⁶⁾. The refractive indices between liquid phosphine and air were found to be, for white light at 11 °C, 1.323 and for the Na–D-line at 17.5 °C, 1.317^{467,468)}.

Measurements of the magnetic susceptibility at room temperature gave a value of $\chi = -26.2 \cdot 10^{-6} \text{ cm}^3/\text{g}$ ⁴⁶⁹⁾. The magnetic rotation (Faraday Effect) of gaseous phosphine at 0 °C, 1 atm and $\lambda = 5700 \text{ \AA}$ was measured as $[M]_{\omega} = 57 \cdot 10^{-6} \text{ rad m}^4 \text{ V}^{-1} \text{ s}^{-1} = 0.30 \text{ min cm}^2 \text{ Gauss}^{-1} \text{ mol}^{-1}$ ⁴⁷⁰⁾.

Phosphine has a *dipole moment* of 0.58 D^{42,43)}; on substituting all of the hydrogen atoms by methyl or ethyl groups it increases to 1.19 or 1.35 D, respectively⁴³⁾. In the series of compounds PH_3 to $\text{P}(\text{CH}_3)_3$ the following values for the dipole moments were measured: PH_3 0.579 D, CH_3PH_2 1.100 D, $(\text{CH}_3)_2\text{PH}$ 1.230 D, $(\text{CH}_3)_3\text{P}$ 1.192 D. These results are in close agreement with the figures calculated on the assumption that the molecules have pyramidal structures. The most probable values for the individual bond moments are m_0 (P–H) = 0.371 D and m_0 (P–C) = 0.690 D³⁴⁸⁾. The dipole moment of triethyl-phosphine is 1.35 D⁴³⁾. In contrast to phosphine, the dipole moment of ammonia (1.47 D⁴³⁾) decreases when the hydrogen atoms are replaced by alkyl groups. Both trimethyl- and triethylamine have dipole moments of 0.61 D⁴³⁾. Weaver and Parry⁴³⁾ interpreted this result as follows: the contribution of the electron lone pair to the dipole moment of phosphine is very small whereas that of the electron lone pair in ammonia is very large (see also^{44,45)}). This assumption is confirmed by the chemical behaviour and nuclear magnetic resonance spectra of phosphine, which also suggest that practically pure *p* orbitals of phosphorus are used for the P–H bonds⁴⁶⁻⁴⁸⁾.

The ¹H nuclear magnetic resonance spectrum of phosphine dissolved in liquid ammonia shows a chemical shift of $\delta_{\text{H}} = +1.66$ ppm (relative to $(\text{CH}_3)_4\text{Si}$)

Table 1. Bond lengths and bond angles in the phosphorus hydride molecule and some of its derivatives (from Corbridge ³¹⁸)

Compound	Bond length [Å] P-H or P-D	Angle [°] H-P-H	Method	Lit.
PH ₃	1.415 ± 0.005		ED/MI ^{a)}	34)
	1.44		calc.	35)
	1.437 ± 0.004		ED	33)
	1.4206 ± 0.005	93.5	MI	27)
	1.419	93.8	IR ^{a)}	20)
	1.419	93.5	MI	28)
	1.418	93.3	calc.	36)
CH ₃ PH ₂	1.414 ± 0.003	93.4	MI	37)
	1.445 ± 0.007	–	ED	31)
(CH ₃) ₂ PH	1.445 ± 0.02	–	ED	31)
PHD ₂	1.4116 ± 0.0001	93.2	MI	29)
PH ₂ D	1.4177 ± 0.0001	93.4	MI	29)
PD ₃	1.4166 ± 0.005	–	MI	27)
PH ₄ I	1.42 ± 0.02	–	NMR ^{a)}	38)
PH	1.43		IR	39)

^{a)} ED: Electron diffraction; MI: Micro-wave; IR: Infra-red; NMR: Nuclear magnetic resonance.

and a coupling constant of $J_{\text{H-P}} = 188.7$ Hz. The coupling constants in the pure liquid were reported to be $J_{\text{H-P}} = 182.2 \pm 0.3$ Hz and $J_{\text{H-H}} = 13.2 \pm 0.7$ Hz ⁴⁹⁾. Ebsworth and Sheldrick ¹⁴⁵⁾ studied the dependence of the chemical shift and H-P coupling constant of phosphine on concentration, temperature and solvent. Two phases are formed in fairly concentrated solutions of phosphine in liquid ammonia below -30 °C, one of these is phosphine-rich and the other ammonia-rich. In the phosphine-rich phase, the coupling constant, $J_{\text{H-P}}$, increases from 185.2 to 186.6 Hz on cooling from -32 to -79 °C, while in the ammonia-rich phase between the same temperatures it increases from 191.1 to 195.1 Hz.

The difference between the chemical shift, δ_{H} , for gaseous and for liquid phosphine is small ²⁶⁶⁾; this indicates that the degree of association in the liquid phase is small. Consideration of thermal data ^{267,268)} leads to the same conclusion. In comparison to water or ammonia, phosphine forms practically no hydrogen bonds.

Birchall and Jolly used ¹H NMR data for phosphine, arsine, and germane and some of their alkyl derivatives to determine the relative acidities in liquid ammonia ²⁵⁹⁾. Spin-lattice relaxation time (T_1) measurements for the ¹H nuclei in PH₃ are reported by Armstrong and Courtney ³⁵⁰⁾.

The expected 1 : 3 : 3 : 1 quartet is observed in the ^{31}P nuclear magnetic resonance spectrum. The chemical shift, δ_{P} , relative to 85% aqueous ortho-phosphoric acid, is +241.0 ppm. The high positive chemical shift of the phosphorus atom is clearly related to the fact that the bonds between the central phosphorus atom and the hydrogen atoms are almost pure $p_{\sigma}(\text{P})-s_{\sigma}(\text{H})$ bonds. This is in accord with the observed bond angle of *ca.* 93° , numerous physical data ⁴⁶⁻⁴⁸, and theoretical considerations ⁵⁰⁻⁵². Calculations of the overlap integrals of the $s-p$ functions of the phosphorus atom with the hydrogen $1s$ function show that the $3s(\text{P})-1s(\text{H})$ overlap integral is smaller than the $3p_{\sigma}(\text{P})-1s(\text{H})$ overlap integral, so that the small deviation of the bond angle from 90° probably results from mutual repulsion of the hydrogen atoms ⁵² (see also ³³⁸). The two free electrons in the valence shell remain in an s orbital and so are relatively near to the nucleus. This results in a strong shielding of the phosphorus nucleus which, in turn, causes the high chemical shift. This particular electronic configuration is also apparent from the chemical behaviour of the molecule; the nucleophilic character is not very pronounced so that phosphine is very unreactive in many respects. This inertness is particularly noticeable when the chemical behaviour of phosphine is compared with that of the alkyl-phosphines. In the latter, the σ -bond system contains a large contribution from the $3s$ orbital so that the electron lone pairs have considerable p character. In comparison to those in the phosphine molecule, these are in much more wide-reaching orbitals and can therefore take part more easily in the first step of a nucleophilic attack.

The *infra-red spectra* of gaseous phosphine have been described and interpreted by different authors ^{19,25,53-56}, that of solid phosphine has been reported by Heinemann ³²⁸. The *infra-red spectra* of solid phosphine in the temperature range 4 to 68 K have been measured by Hardin and Harvey ¹⁰. At 10 K a previously undescribed transformation was observed.

The molecular data obtained from the *infra-red spectra* (see Table 1) are in good agreement with the results from *micro-wave spectra* ^{28,29}.

The gas phase *UV-absorption spectra* of phosphine and a series of other phosphorus compounds have been studied in the long wave-length region ⁵⁷⁻⁵⁹ and recently by Halmann ⁶⁰ in the 1850–2500 Å range. In general, it is assumed that the electronic excitation process of lowest energy in compounds, such as NH_3 , H_2O , PH_3 , H_2S or HCl and their alkyl derivatives, is that which involves the promotion of non-bonding electrons of the most electronegative atom into an anti-bonding orbital, *i.e.* an $n \rightarrow \sigma^*$ transition. However, Halmann ⁶⁰ attributes a strong absorption band in the spectrum of phosphine at 1910 Å to an $n \rightarrow \delta^*$ transition. The wave lengths at which the maximum absorptions occur and their extinction coefficients are summarised in Table 2 and compared with the corresponding values for ammonia and amines ^{57,61}.

The absorption of phosphine at even shorter wave-lengths (down to 1250 Å) was measured by Walsh and Warsop ⁶². The ionisation potentials of phosphine

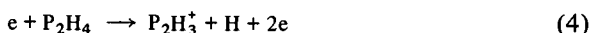
were found, from the 584 Å photoelectron spectrum, to be 10.28 and 12.90 eV³⁵¹). See also³⁵²).

Comprehensive investigations of the *mass spectra* of phosphine and diphosphine were carried out by Wada and Kiser⁶³), among others^{262,353}). The ionisation potential of phosphine was found to be 10.2 ± 0.2 eV, in good agreement with the experiments of Neuert and Clasen⁶⁴). Deviating values were reported by Saalfeld and Svec^{65,66}). The ionisation potential of diphosphine is 8.7 ± 0.3 eV. The corresponding ionisation potentials for ammonia and hydrazine are $10.15 - 10.5$ ^{67,69}) and 9.00 ± 0.1 eV⁷⁰), respectively. The $P_2H_3^+$ ions

Table 2. UV data for phosphines and amines⁶⁰)

Compound	λ_{\max} [Å]	ϵ [$l \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$]
PH ₃	1910	3400 ± 200
CH ₃ PH ₂	2010 ± 3	130 ± 30
	1960	weak
	1870	1500 ± 200
(CH ₃) ₂ PH	1890	6300 ± 500
(CH ₃) ₃ P	2010 ± 5	18800 ± 100
NH ₃	1942	5600
	1515	strong
CH ₃ NH ₂	2150	600
	1737	2200
(CH ₃) ₂ NH	2200	100
	1905	3300
(CH ₃) ₃ N	2273	900
	1990	3950

observed in the mass spectrum of diphosphine do not, according to Wada and Kiser, arise from the reaction



but from the simple ionisation of P_2H_3 radicals which are formed as intermediates in the thermal decomposition of diphosphine to PH_3 and a solid reported to have the approximate constitution P_2H . The appearance of the PH_4^+ ion in the mass spectra of phosphine results from the reaction²⁶²)



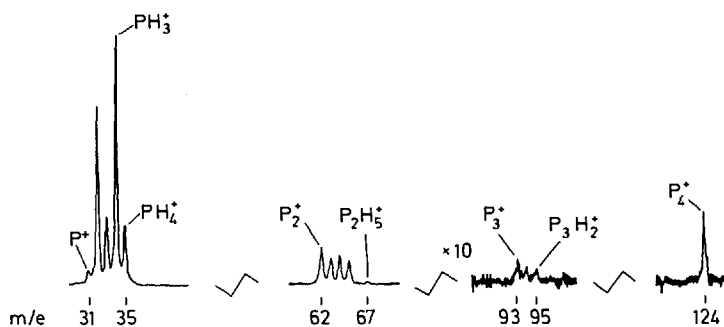


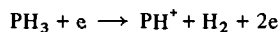
Fig. 2. ICR spectrum of the positive ions of PH_3 at $2 \cdot 10^{-5}$ Torr and 23 eV ionisation energy

Further ion-molecule reactions were identified in the gas phase by Eyler³⁵⁴⁾ using ion cyclotron single and double resonance. The ion cyclotron single resonance spectrum of phosphine is shown in Fig. 2.

As well as the PH_3^+ ion, the ions PH_2^+ , PH^+ and P^+ , caused by fragmentation are observed. Furthermore the signal for the phosphonium ion, formed according to Eq. (5), is seen. Many other, heavier ions are the products of ion molecule reactions in PH_3 . These have the general formulae

P_2H_n^+ ($n = 0 - 5$), P_3H_n^+ ($n = 0 - 2$), and P_4^+ . Analogous ions were also formed by ion molecule reactions in ammonia. The reactions listed in Table 3 were identified with the help of the ion cyclotron double resonance technique.

The results of electron-impact studies of phosphine by Halmann *et al.*⁴⁵¹⁾ are given in Table 3a. The authors used the appearance potentials, in conjunction with thermochemical data, to choose the probable reaction processes. In many simple cases the observed appearance potential $A(Z)$ for an ion fragment Z from a molecule RZ is related to its ionisation potential $I(Z)$ and to the energy of dissociation $D(\text{R}-Z)$ of the bond by the expression $A(Z) = I(Z) + D(\text{R}-Z)$. This assumes that the dissociation products are formed with little, if any, excitation energy, and that $I(Z) < I(\text{R})$. The most abundant ion species in the usual mass spectrum of phosphine is PH^+ , which is probably formed according to the following mechanism



The appearance potential for this reaction should be

$$I(\text{PH}) \leq A(\text{PH}^+) - 2\bar{D}(\text{P}-\text{H}) + D(\text{H}-\text{H}) = 13.1 - 6.7 + 4.48 = 10.9 \pm 0.5 \text{ eV.}$$

The average energy of dissociation of the $\text{P}-\text{H}$ -bond is known from thermochemical measurements, $\bar{D}(\text{P}-\text{H}) = 3.35 \text{ eV}$. The dissociation energy of the hydrogen molecule is $D(\text{H}-\text{H}) = 4.48 \text{ eV}$. The appearance potential for PH^+ formed according to the mechanism

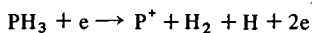
Table 3. Ion molecule reactions of phosphine
(obtained from ion cyclotron double resonance,
the neutral species are assumed) ³⁵⁴⁾

$\text{PH}_3^+ + \text{PH}_3$	\longrightarrow	$\text{PH}_4^+ + \text{PH}_2$
$\text{PH}_3^+ + \text{PH}_3$	\longrightarrow	$\text{P}_2\text{H}^+ + 2\text{H}_2 + \text{H}$
$\text{PH}_3^+ + \text{PH}_3$	\longrightarrow	$\text{P}_2\text{H}_3^+ + \text{H}_2 + \text{H}$
$\text{PH}_3^+ + \text{PH}_3$	\longrightarrow	$\text{P}_2\text{H}_4^+ + \text{H}_2$
$\text{PH}_3^+ + \text{PH}_3$	\longrightarrow	$\text{P}_2\text{H}_5^+ + \text{H}$
$\text{PH}_2^+ + \text{PH}_3$	\longrightarrow	$\text{PH}_3^+ + \text{PH}_2$
$\text{PH}_2^+ + \text{PH}_3$	\longrightarrow	$\text{P}_2\text{H}^+ + 2\text{H}_2$
$\text{PH}_2^+ + \text{PH}_3$	\longrightarrow	$\text{P}_2\text{H}_3^+ + \text{H}_2$
$\text{PH}^+ + \text{PH}_3$	\longrightarrow	$\text{PH}_4^+ + \text{P}$
$\text{PH}^+ + \text{PH}_3$	\longrightarrow	$\text{PH}_3^+ + \text{PH}$
$\text{PH}^+ + \text{PH}_3$	\longrightarrow	$\text{PH}_2^+ + \text{PH}_2$
$\text{PH}^+ + \text{PH}_3$	\longrightarrow	$\text{P}_2^+ + 2\text{H}_2$
$\text{PH}^+ + \text{PH}_3$	\longrightarrow	$\text{P}_2\text{H}_2^+ + \text{H}_2$
$\text{PH}^+ + \text{PH}_3$	\longrightarrow	$\text{P}_2\text{H}_3^+ + \text{H}$
$\text{P}^+ + \text{PH}_3$	\longrightarrow	$\text{PH}_3^+ + \text{P}$
$\text{P}^+ + \text{PH}_3$	\longrightarrow	$\text{P}_2\text{H}^+ + \text{H}_2$
$\text{P}_2^+ + \text{PH}_3$	\longrightarrow	$\text{P}_3\text{H}^+ + \text{H}_2$
$\text{P}_2^+ + \text{PH}_3$	\longrightarrow	$\text{P}_3\text{H}_2^+ + \text{H}$
$\text{P}_2\text{H}^+ + \text{PH}_3$	\longrightarrow	$\text{P}_3\text{H}_2^+ + \text{H}_2$



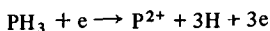
would be higher by the amount of energy of dissociation of the hydrogen molecule.

The formation of P^+ by electron impact on phosphine may be due to the following process:



The lowest appearance potential for P^+ can be predicted by the equation $A(\text{P}^+) \geq I(\text{P}) + 3\bar{D}(\text{P}-\text{H}) - D(\text{H}-\text{H})$. The ionisation potential of the phosphorus atom has been determined spectroscopically, namely $I(\text{P}) = 11.0 \text{ eV}$. Thus $A(\text{P}^+) = 11.0 + 3 \cdot 3.35 - 4.48 = 16.6 \text{ eV}$. This predicted value for the process mentioned above is close to the observed value for the "vanishing current" appearance potential of P^+ . The "linear extrapolation" value of 20 eV may be due to a process in which three hydrogen atoms are formed.

For the formation of doubly charged phosphorus ions, P^{2+} , the following mechanism is suggested



The appearance potential for this ion should thus be equal to, or larger than, the sum of the potentials for double ionisation of phosphorus, $I(\text{P}^1) + I(\text{P}^{11})$, and the dissociation energy of phosphine should be given by

$$A(\text{P}^{2+}) \geq I(\text{P}^1) + I(\text{P}^{11}) + 3\bar{D}(\text{P}-\text{H})$$

With the spectroscopic values for $I(\text{P}^1) = 11.0$ eV and $I(\text{P}^{11}) = 19.65$ eV the predicted value of $A(\text{P}^{2+})$ is 40.7 eV. The agreement between this and the observed value of 42 eV seems to support the suggested dissociation mechanism

Table 3a. Appearance potentials A for ion fragments from phosphine ⁴⁵¹⁾

Ion	m/e	Reference ion	A [eV] linear extrapol.	A [eV] vanishing current
PH_3^+	34	Ar^+	10.3 ± 0.5	10.4 ± 0.3
PH_2^+	33	Ar^+	14.4	14.0 ± 0.2
PH^+	32	Ar^+	13.6	13.1 ± 0.2
P^+	31	Ar^+	20 ± 1	16.0 ± 1.0
			Linear extrapol.	Square root plot
PH_3^{2+}	17	Kr^{2+}	15.0	15.6
PH_2^{2+}	16.5	Kr^{2+}	32.7	34.0
PH^{2+}	16	Kr^{2+}	21.2	15.1
P^{2+}	15.5	Kr^{2+}	42 ± 2	42 ± 2

The flash photolysis of phosphine, according to spectroscopic results, causes the formation of two phosphorus· and two hydrogen-containing radicals, corresponding to the dissociation of phosphine as shown in Eqs. (6) and (7) ⁷¹⁾.



In addition, Basco and Yee observed electronically excited phosphorus atoms and P_2 molecules in excited vibration states in the absorption spectra ³⁵⁵⁾. The latter were also found by Norrish and Oldershaw ⁷²⁾.

Phosphine, subjected to radiation of the 10.59 μ -line of a CO_2 laser dissociates into the elements ²⁶¹⁾.

Neutron irradiation of gaseous phosphine always results in 40 to 60 % of the ^{32}P being retained as $^{32}\text{PH}_3$ while the balance is deposited on the walls as phosphorus oxyacids⁴⁵²⁻⁴⁵⁴. This result is independent of whether the irradiation is done in the presence of an excess of various inert gases or methane (as possible moderators for hot atoms), or in the presence of substances which could possibly scavenge thermal phosphorus atoms. This indicates that "hot" phosphorus atoms do not form stable products and that phosphine itself is a very efficient scavenger for thermal phosphorus atoms. When phosphine was irradiated in a large excess of methane Halmann and Kugel⁴⁵² observed the formation of ^{32}P -labelled methyl-, dimethyl- and trimethyl-phosphines. The addition of traces of water enhanced the yields of methylphosphines. As a possible reactive intermediate Halmann and Kugel suggest $\text{H}-\text{C}\equiv\text{P}$, which may account for products such as CH_3PH_2 , $\text{CH}_3\text{P}(\text{H})(\text{O})(\text{OH})$ and $\text{CH}_3\text{PO}_3\text{H}_2$, while $(\text{CH}_2)_2\text{P}$ may be a hypothetical intermediate for dimethylphosphine and its oxidation products. Also the thermal-neutron irradiation of trimethylphosphine results in the formation of phosphine, in which, among the volatile products, most of the radioactivity is found (PH_3 40%, CH_3PH_2 1-3%, $(\text{CH}_3)_2\text{PH}$ 0.3%, $(\text{CH}_3)_3\text{P}$ 0.6-3.8% of the total activity). The activity in trimethylphosphine decreased with lower pressure. This demonstrates that there is no appreciable retention of chemical bonds of the recoiling phosphorus atoms⁴⁵⁵.

The solubility of phosphine in water is, in comparison to ammonia, very small^{73,74}. At 17 °C, only 22.8 ml of gaseous phosphine dissolve in 100 ml of water⁷³.

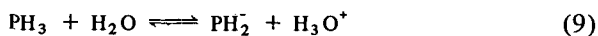
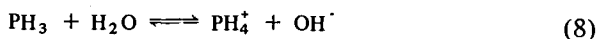
The Ostwald solubility coefficient β , *i.e.* the ratio of the concentration of the dissolved substance in the solution phase to the concentration of the dissolved substance in the gas phase is, at 297.5 K, 0.201. In the pressure range of 100 to 700 mmHg it is independent of pressure so that, at least below 1 atm, Henry's law is obeyed. With increasing temperature β decreases and reaches a value of 0.137 at 323.2 K. The enthalpy of solution calculated from the temperature dependence of β is -2.95 ± 0.1 kcal/mol⁴⁷¹.

According to earlier results, the solubilities at 18 °C in ethanol, ether and oil of turpentine are 0.5, 2 and 3.25 volumes of phosphine per volume of solvent, respectively³⁵⁷. Phosphine dissolves in cyclohexanol far more readily than in water. At 26 °C and a partial pressure of 766 mmHg, 2856 ml of phosphine dissolve in 1000 ml of cyclohexanol³²². 15,900 ml of phosphine dissolve in 1 litre of trifluoroacetic acid at 26 °C and a pressure of 653 mmHg³⁵⁸. For the solubilities of phosphine in non-polar solvents see^{312,315}.

When phosphine is liquified by pressure in the presence of water, it dissolves partly in the water, the rest floats on the solution. If the pressure is suddenly removed colourless crystals of phosphine hydrate are formed at 2.20 °C under a pressure of 2.8 atm, 11 °C under 6.7 atm, and at 20.0 °C under 151.1 atm. When the pressure is reduced too rapidly the crystals dissolve

again, also they do not form at temperatures above 28 °C. In the presence of CO₂ crystals are formed which are stable at 22 °C. In the presence of phosphine and water, CS₂ behaves similarly to CO₂ ^{472,473}). In all cases clathrate compounds are formed. The cubic unit cell of phosphine hydrate contains 46 molecules of water. Their skeleton forms 2 cavities with a coordination number of 20 and 6 with a coordination number of 24. If all the cavities were occupied by phosphine molecules a composition of PH₃ · 5.75 H₂O or 8 PH₃ · 46 H₂O would be obtained. In practice, crystals with a composition of PH₃ · 5.9 H₂O are found in the above described experiments. The dissociation pressure at 0 °C is 1.6 atm, the decomposition temperature at 1 atm is -6.4 °C and the critical decomposition temperature is 28 °C ^{474,475,476})

Aqueous solutions of phosphine show neither acidic nor basic properties. Weston and Bigeleisen ⁷⁴) investigated the deuterium exchange between D₂O and PH₃. It was found that this exchange proceeds *via* a PH₄⁺ ion in acidic solutions and *via* a PH₂⁻ ion in basic solutions. From the kinetic data and the assumed exchange mechanisms, these authors calculated the equilibrium constants at 27 °C for reactions (8) and (9) to be $K_b \approx 4 \cdot 10^{-28}$ and $K_a \approx 1.6 \cdot 10^{-29}$, respectively.



These small constants suggest that the acidic or basic properties of phosphine can only be observed under special circumstances. For example, phosphine behaves as a base when it is dissolved in very strong acids. In concentrated sulphuric acid, BF₃ · H₂O (with excess BF₃) or in BF₃ · CH₃OH (with excess BF₃), phosphine accepts a proton to form a phosphonium ion, which could be identified in solution for the first time by proton and phosphorus nuclear magnetic resonance spectroscopy. The proton spectrum ascribed to the PH₄⁺ ion in sulphuric acid consists of a 1 : 1 doublet with a coupling constant of approximately 547 Hz. Similar doublets are also observed in the spectra of PH₃ in the other solvents mentioned. The ³¹P spectra of solutions of phosphine in BF₃ · H₂O and BF₃ · CH₃OH, which are stable at room temperature, show 1 : 4 : 6 : 4 : 1 quintets. These are conclusive proof that PH₄⁺ ions exist in these solutions. The chemical shift δ_P is +217 ppm (relative to P₄O₆), while τ was found to be 3.84 [PH₃ in 98% H₂SO₄ + (CH₃)₄PCl at -43 °C] ⁷⁵).

Also fluorosulphonic acid protonates phosphine as well as organophosphines ³⁵⁶). The phosphonium ions formed are soluble in fluorosulphonic acid. The chemical shifts, δ_{31P} and δ_{1H} , of phosphine, the phosphonium ion and a series of organophosphines and the respective cations obtained by protonation are shown in Table 4.

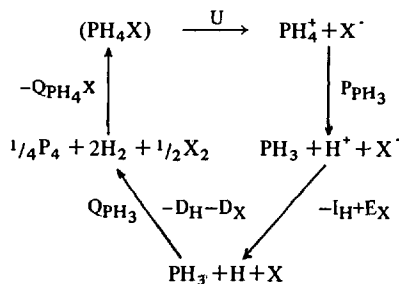
Banyard and Hake ⁴¹) calculated the molecular energies for PH₃, PH₄⁺ and PH₂⁻. From the difference between the energies for PH₃ and PH₄⁺ the proton

Table 4. N.M.R. data for phosphines and phosphonium ions ³⁵⁶⁾

	Chemical shift ^{a)} δ_P [ppm]	Chemical shift δ_H [ppm]	J_{H-P} [Hz]
Phosphine			
PH ₃	+238	2.28 (in CCl ₄)	188
P(CH ₃) ₃	+ 62.2		
P(C ₂ H ₅) ₃	+ 19.2		
P(<i>i</i> -C ₃ H ₇) ₃	- 19.3		
P(<i>t</i> -C ₄ H ₉) ₃	- 61.9		
P(<i>n</i> -C ₄ H ₉) ₃	+ 32.6		
P(<i>n</i> -C ₈ H ₁₇) ₃	+ 32.5		
P(<i>c</i> -C ₆ H ₁₁) ₃	- 11.3 (in CHCl ₃)		
P(C ₆ H ₅) ₃	+ 5.4 (in CCl ₄)		
HP(C ₆ H ₅) ₂	+ 40.7		
Phosphonium ions			
PH ₄ ⁺	+101.0	6.20	548
[HP(CH ₃) ₃] ⁺	+ 3.2	6.36	497
[HP(C ₂ H ₅) ₃] ⁺	- 22.5	5.97	471
[HP(<i>i</i> -C ₃ H ₇) ₃] ⁺	- 44.4	5.58	448
[HP(<i>t</i> -C ₄ H ₉) ₃] ⁺	- 58.3	5.46	436
[HP(<i>n</i> -C ₄ H ₉) ₃] ⁺	- 13.7	6.01	470
[HP(<i>n</i> -C ₈ H ₁₇) ₃] ⁺	- 13.0	6.04	465
[HP(<i>c</i> -C ₆ H ₁₁) ₃] ⁺	- 32.7	5.48	445
[HP(C ₆ H ₅) ₃] ⁺	- 6.8	8.48	510
[H ₂ P(C ₆ H ₅) ₂] ⁺	+ 21.2	7.88	519

a) The chemical shifts, δ_{31P} are all relative to 85% aqueous orthophosphoric acid.

affinity of phosphine is found to be 236 kcal/mol. This value is, however, too high. A lower figure was obtained by Wendlandt ⁷⁶⁾ using a Born-Haber cycle:



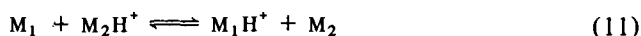
The proton affinity, P_{PH_3} , at 0 K is given by:

$$P_{\text{PH}_3} = U + Q_{\text{PH}_4\text{X}} - Q_{\text{PH}_3} + D_{\text{H}} + I_{\text{H}} + D_{\text{X}} - E_{\text{X}} - 5/2 RT \quad (10)$$

where U is the lattice energy of PH_4X , $Q_{\text{PH}_4\text{X}}$ the heat of formation of PH_4X , Q_{PH_3} the heat of formation of PH_3 , D_{H} the heat of dissociation of hydrogen, I_{H} the ionisation potential of hydrogen, D_{X} the heat of dissociation of the halogen molecule, E_{X} the electron affinity of the halogen, and R the gas constant ($1.987 \text{ cal}\cdot\text{grad}^{-1}\cdot\text{mol}^{-1}$). Using the values for phosphonium iodide, PH_4I , Eq. (10) gives the proton affinity of phosphine as $200 \pm 10 \text{ kcal/mol}$.

$U(\text{CsCl lattice})$	131.5 kcal/mol
$-Q_{\text{PH}_4\text{X}}$	15.8
Q_{PH_3}	2.21
$-D_{\text{H}}$	52.1
$-I_{\text{H}}$	311.9
$-D_{\text{X}}$	25.5
E_{X}	74.6
$5/2 RT$	1.5

Waddington⁷⁷⁾ reported an approximately similar value of $194.5 \pm 5 \text{ kcal/mol}$. Both these results agree well with that reported by Holtz and Beauchamp³⁵⁹⁾ for the proton affinity of phosphine. These workers determined the proton affinity from ion molecule reactions of the type



which take place with negligible energies of activation. Such a reaction proceeds to the right only when the proton affinity of M_1 is greater than or equal to that of M_2 . Binary mixtures of phosphine with acetaldehyde, acetone, ammonia or water were investigated at pressures in the range of 10^{-7} to 10^{-4} mmHg using ion cyclotron resonance. At pressures $> 10^{-6}$ mmHg, proton exchanges as shown by the general Eq. (11) were observed. The results of these investigations are summarised in Table 5.

Table 5. Protonation reactions

No.	Observed reaction	Proton affinity of PH_3 [kcal/mol]	Lit.
1	$\text{PH}_4^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{PH}_3$	207	362)
2	$\text{PH}_4^+ + (\text{CH}_3)_2\text{CO} \rightarrow (\text{CH}_3)_2\text{COH}^+ + \text{PH}_3$	189	364)
3	$\text{CH}_3\text{CHOH}^+ + \text{PH}_3 \rightarrow \text{PH}_4^+ + \text{CH}_3\text{CHO}$	182	364)
4	$\text{H}_3\text{O}^+ + \text{PH}_3 \rightarrow \text{PH}_4^+ + \text{H}_2\text{O}$	164	360,362)
5	$\text{C}_2\text{H}_5^+ + \text{PH}_3 \rightarrow \text{PH}_4^+ + \text{C}_2\text{H}_4$	158	360)
6	$\text{CH}_5^+ + \text{PH}_3 \rightarrow \text{PH}_4^+ + \text{CH}_4$	124	363)

The reactions 2 and 3 in Table 5 set the limits for the proton affinity of phosphine. Reaction 2 shows that it is smaller than that of acetone (186 ± 3 kcal/mol) and reaction 3 indicates that it is larger than the proton affinity of acetaldehyde (185 ± 3 kcal/mol). Thus a value of 185 ± 4 kcal/mol is obtained for the proton affinity of phosphine at room temperature.

Using the same methods ^{359,360} Eyler ³⁵⁴) obtained concurring results. Also the value reported by Haney and Franklin ³⁶¹) of 186 ± 1 kcal/mol is in agreement. The latter workers determined the proton affinity of ammonia as 207 kcal/mol ³⁶²), which is approximately 21 kcal/mol larger than that for phosphine. The greater basicity of ammonia as compared to phosphine is shown by the difference of about 20 pH units in their relative basicities in aqueous solutions. The difference in the basicities of the aqueous solutions of 23–32 kcal/mol, which is comparable to that in the gas phase, leads to the somewhat surprising conclusion that solvent effects appear to play an unessential part in the relative basicities of PH_3 and NH_3 in aqueous solutions. The proton affinities of H_2O and H_2S , 164 and 170 kcal/mol, respectively, are in the reverse order.

The bond strengths can be obtained from the proton affinities. The proton and hydrogen affinities of a molecule and its respective ion are related to the ionisation potentials according to Eq. (12)

$$PA(M) - HA(M^+) = IP(H) - IP(M) \quad (12)$$

The hydrogen affinity $HA(M^+)$ is simply the $\text{H}-M^+$ bond strength $D(\text{H}-M^+)$. A summary of the hydrogen affinities for phosphine and some isoelectronic molecules is given in Table 6.

Table 6. Bond strengths in PH_3 , PH_4^+ and isoelectronic molecules and ions^{a)}

Ion	Proton affinity ^{b,365)} [kcal/mol]	Molecule	Bond strength ³⁶⁶⁾ [kcal/mol]
NH_4^+	128	CH_4	103
PH_4^+	102	SiH_4	80
OH_3^+	141	NH_3	105
SH_3^+	97	PH_3	85

a) For literature for the values in the Table, see ³⁵⁹⁾.

b) From Eq. (12).

The substitution of a hydrogen atom in phosphine by an organic group increases the basic properties so that, for example, trimethylphosphonium salts are stable in aqueous solutions ⁷⁸⁾.

2. Toxicity of Phosphine

Phosphine is extremely poisonous. The maximum concentration of phosphine in the atmosphere must not exceed 0.1 ppm for an 8 h working day⁴⁵⁶). The smell of phosphine is first noticeable when the concentration reaches or exceeds about 2 ppm. A concentration of 50 – 100 ppm can only be withstood for a very short time without damage, a concentration of 400 ppm leads rapidly to death²²⁵⁻²²⁷). The symptoms observed by a medium-to-serious case of phosphine poisoning are: sense of anxiety, feeling of pressure in the chest, shortage of breath, pain behind the breast-bone, occasional dry cough, increased breathing noise, confusion, vertigo, and fainting. As first aid, the victim should be removed to fresh air and, when possible, given oxygen. For the toxicology of phosphine, see^{225,226,228,229}), as well as the article with an extensive bibliography by O. R. Klimmer²³⁰): Zur Frage der sog. chronischen Phosphorwasserstoffvergiftung.

3. Determination of Phosphine

Small quantities of phosphine in the air or other gases can be detected by passing the gas into a 5% aqueous solution of HgCl_2 . The HCl , liberated by the formation of $\text{P}(\text{HgCl})_3$, is then titrated potentiometrically³²⁹). The titration can be followed automatically using a Beckman Model K titrator³⁶⁷). A method for the semiquantitative determination of phosphine in the air works on the same principle³³⁰). Here the air is lead through 5 ml of a 1.5% aqueous HgCl_2 solution at pH 4.2. The solution is mixed with an indicator and the volume necessary to reduce the pH from 4.2 to 3.4 measured. By using a calibration curve, phosphine contents between 0.1 and 2.5 mg PH_3 /litre of air can be estimated within an accuracy of $\pm 5\%$. A larger concentration range of 0.03 to 150 ppm PH_3 can be measured using a simple method. A fixed amount of air is sucked through a tube containing silica gel impregnated with AuCl_3 . The phosphine concentration can be estimated from the length of the coloured zone³³¹).

Moser and Brukl⁹⁸) described a method for the gravimetric determination of phosphine. Dumas³⁶⁸) used gas chromatography for the micro-determination of phosphine in the air (0.005–0.5 mg/litre), see also³⁶⁹). An automatic gas analyser, for the determination of phosphine and other substances in gases, works on the principle of the light absorption in reflection through a paper band, on which the gas causes a colour reaction with suitable reagents³⁷⁰).

III. Preparation of Phosphine

For the laboratory preparation of phosphine, only a few of the many methods of formation are suitable. Among these the hydrolyses of calcium phosphide^{79,80-83}), magnesium phosphide⁸⁴⁻⁸⁷), aluminium phosphide⁸⁸), zinc phos-

phide and tin phosphide ^{84-86,89,90)} are the most important. As well as water, acids or bases, aqueous mixtures of acids or bases with organic solvents such as, for example, dioxane, alcohols etc. can be used for the hydrolyses ⁹¹⁻⁹³⁾.

Together with phosphine, noticeable amounts of diphosphine and higher phosphines are formed by the hydrolysis of calcium phosphide; thus, this reaction can be used for the preparation of such compounds ⁹⁴⁾. Quesnel ⁸⁹⁾ reported that the formation of diphosphine can be avoided when aqueous hydrochloric acid is added drop-wise to a mixture of calcium phosphide and copper chloride (proportions by weight, $\text{Ca}_3\text{P}_2 : \text{CuCl}_2 = 10 : 1$) in boiling alcohol, for example, methanol, or in dioxane.

When the calcium phosphide is formed by the reduction of $\text{Ca}_3(\text{PO}_4)_2$ with carbon, the phosphine obtained on hydrolysis usually contains up to 3% acetylene.

Baudler and her co-workers ⁴⁴⁰⁾ have described in detail the preparation of larger quantities of phosphine by the hydrolysis of calcium phosphide. Higher phosphines (see page 51) formed simultaneously, are thermally decomposed to phosphorus, phosphine and hydrogen. It is noteworthy that, on storage in steel cylinders the diphosphine concentration in phosphine, originally less than 1%, increases. It is, even after several months, so small that the gas is not spontaneously inflammable in contact with air, whereas, after about one year, it is spontaneously inflammable.

Our experience ⁹⁵⁾ has shown that the hydrolysis of aluminium phosphide with cold water is the most suitable method for the laboratory preparation of phosphine. Here it is important that the aluminium phosphide be as pure as possible in order to avoid the formation of spontaneously inflammable phosphine. The presence of small quantities of diphosphine and also higher phosphines are responsible for this spontaneous inflammability ^{96,276-278)}. It appears, however, that these are only formed when P-P bonds are already present in the phosphide. Accordingly the hydrolysis of aluminium phosphide, prepared from the elements with phosphorus in slight excess, always leads to spontaneously inflammable phosphine. The formation of diphosphine and higher phosphines from aluminium or alkaline earth metal phosphides, which contain excess phosphorus, can be easily understood when the lattices of these compounds are considered.

Aluminium phosphide crystallises in a zinc blende lattice ⁴⁴¹⁻⁴⁴³⁾. Both the aluminium and phosphorus atoms have a coordination number of four. The simplest picture of this is to consider the phosphide ions as forming a face-centred cubic lattice that is almost closest-packed with the aluminium ions occupying alternate tetrahedral sites. Only half of the tetrahedral sites are occupied as the compound has 1 : 1 stoichiometry and there are two tetrahedral sites associated with each phosphide ion. Because the aluminium ions occupy tetrahedral sites, it is clear that they have the coordination number four.

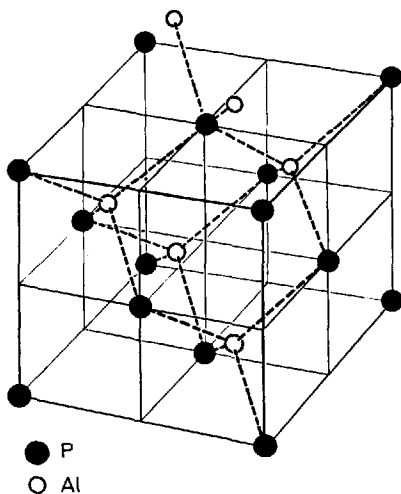


Fig. 3. Lattice of AlP (zinc blende lattice)

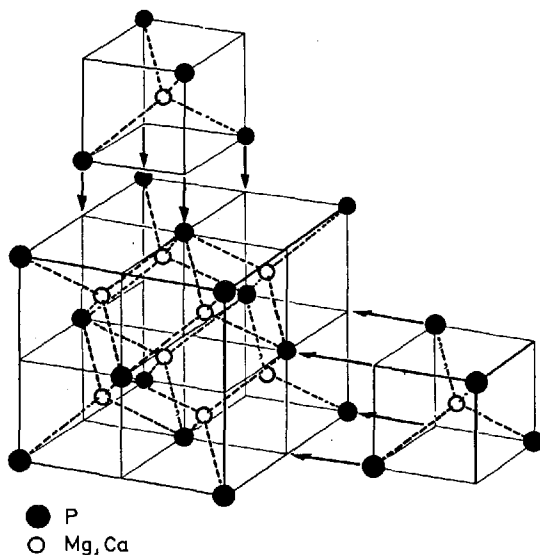


Fig. 4 Lattice of Ca_3P_2 and Mg_3P_2 (anti fluorite lattice with vacant sites)

Calcium phosphide and magnesium phosphide, crystallise in a lattice which can be deduced from the fluorite structure⁴⁴⁴⁻⁴⁴⁶. One way to describe the arrangement of the atoms in this lattice is to imagine that the phosphide ions

form a face-centred cubic lattice and the calcium or magnesium ions occupy all tetrahedral sites. This structure is related to that of aluminium phosphide in which only half the tetrahedral sites in a face-centred cubic lattice are occupied. The lattice so far described yields, however, a stoichiometry of 2 : 1 or 4 : 2. Mg_3P_2 and Ca_3P_2 have, in fact, a stoichiometry of 3 : 2. This stoichiometry is obtained by vacant sites in the partial lattice of the metal ions. One quarter of the metal ion sites in the lattice are unoccupied.

Preparation of Phosphine by the Hydrolysis of Aluminium Phosphide

The generator consists of a 1 litre-3-necked-flask, fitted with a gas-inlet tube, and which is mounted over a magnetic stirrer. A second neck of the flask is connected to a trap, cooled in dry ice/methanol, *via* an approximately 2 metre long drying tube filled with P_4O_{10} /glass wool. A wash-bottle containing concentrated H_3PO_4 is fitted between the generator and the drying tube to serve as a control of the gas flow. It is important that the inlet-tube of the wash bottle projects only a little way below the surface of the phosphoric acid.

The generator flask is filled with 650 ml of water. The whole apparatus is then purged with nitrogen. Finally, with vigorous stirring and the introduction of moderate flow of nitrogen, 20 g of finely powdered aluminium phosphide are added. After a few minutes a continuous stream of phosphine is generated. The end of the PH_3 -evolution is recognised by the change in colour of the suspension from green to grey. When necessary a further 20 g portion of aluminium phosphide can be added.

Using the above given conditions, an explosive decomposition of phosphine has never been observed. It is important, however, that no rapid change of pressure, which causes a spontaneous decomposition of phosphine into the elements, occurs because of the method of taking up of the phosphine or because of a blockage in the drying tube.

The hydrolyses of aluminium phosphide with acids ^{89,97,98)} or alkalies ^{99, 100)} do not seem to be so suitable for the preparation of phosphine.

The method, described relatively early, for the preparation of phosphine using the reaction of hot concentrated alkalies, such as NaOH, KOH or $\text{Ca}(\text{OH})_2$, on white phosphorus can also be used for the laboratory preparation. This method also produces a steady stream of phosphine, which, however, may be contaminated by up to 90% hydrogen and traces of P_2H_4 ^{1,3,85,101-106)}. Phosphine formed from the thermal decomposition of phosphorous or hypophosphorous acids or their salts is similarly contaminated with hydrogen. In cases where hydrogen interferes, the phosphine can be purified by condensation and distillation.

“Inorganic Syntheses”, Vol. IX, p. 56, contains an accurate description of the preparation of phosphine by the pyrolysis of phosphorous acid ^{107,108)}.

Very pure phosphine is formed by the hydrolysis of phosphonium iodide with water, dilute acids or dilute bases ^{2,14,17,107,109-114}, or by the reduction of phosphorus trichloride with lithium in diethyl ether ^{87,115-117}. Related to the latter is a method for the preparation of phosphine, described in the patent literature, where phosphorus trichloride vapour, diluted with nitrogen, is passed through a column filled with lithium hydride mixed with an inert material, such as sand, NaCl, KCl or similar materials ¹¹⁸.

According to a method described by Horner *et al.*, phosphine was obtained in 70% yield from the reaction of PCl_3 with finely divided sodium in toluene, followed by hydrolysis of the reaction products ²⁸⁷.

Finally, in the recent patent literature, some further processes for the preparation of phosphine were described; for example, the treatment of white phosphorus with steam in the presence of phosphoric acid at 275–285 °C. According to a British patent, phosphine is formed when white phosphorus, in aqueous acid, is brought into contact with mercury or zinc amalgam ¹¹⁹. A Japanese patent recommends the treatment of a mixture of white phosphorus and granulated zinc with acids and a small amount of methanol for the preparation of highly pure phosphine ³⁷¹. Other patents describe electrolytic processes. Finally, it is mentioned that phosphine is formed by the electrolysis of phosphorous and hypophosphorous acid, especially at mercury or lead cathodes ¹²⁰.

The purification of phosphine, from the main gaseous substances obtained by the preparation, can be achieved by fractional distillation ^{14,121,122}. Acetylene can be removed with the help of molecular sieves ¹²³.

IV. Reactions of Phosphine

1. Thermal Decomposition, Reaction with Oxygen, Reducing Properties

Phosphine decomposes only at higher temperatures. The thermal decomposition of phosphine under various conditions has been examined in detail. It is found to be a first order reaction. The rate constant for the decomposition of phosphine at 500 °C is approximately $8 \cdot 10^{-3} \text{ sec}^{-1}$ ^{57,231-233}.

The thermal decomposition of phosphine on a glass surface can be satisfactorily described as a first order reaction using Eq. (13):

$$-\frac{dp}{dt} = K \cdot p \quad (13)$$

where K is the rate constant for the decomposition and p is the pressure of phosphine. The decomposition rate on a silicon film is smaller than that on a glass surface. This decomposition also follows first order kinetics. The temperature dependence is described by the Arrhenius equation:

$$\lg K = 8.86 - 9669 \cdot \frac{1}{T} \quad (\text{glass surface}) \quad (14)$$

$$\lg K = 11.6 - 12110 \cdot \frac{1}{T} \quad (\text{silicon surface}) \quad (15)$$

The energies of activation of the decomposition on glass and silicon surfaces are 44.2 and 55.3 kcal/mol, respectively ³⁷²). See also ^{373-375, 481-492}).

Phosphine-oxygen mixtures are relatively stable above the upper and below the lower critical explosion pressures. However, on irradiation with UV-light reaction occurs. It is assumed that the reaction is initiated by the photolytic dissociation of the PH₃ molecule according to the equation:



Then the PH₂ radical reacts further by collision with an oxygen molecule. In the presence of water vapour the end-product is H₃PO₂ and/or H₃PO₄ ⁴⁷⁷⁻⁴⁸⁰).

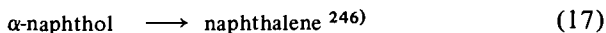
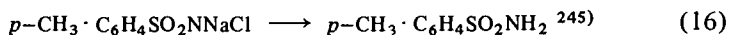
The conditions under which mixtures of phosphine and oxygen ignite were investigated by Trautz ²³⁴) and Shantarovich ²³⁵). The ignition pressure is dependent on the composition of the mixture, the water content, the temperature and the presence of foreign gases. With increasing partial pressure of phosphine the ignition pressure generally increases. Mixtures of phosphine and excess oxygen diluted with nitrogen do not react noticeably up to temperatures of 200 °C ³⁷⁶).

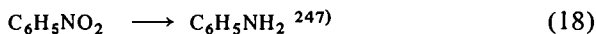
A large number of articles have been devoted to kinetic studies of the oxidation of phosphine ²³⁶⁻²⁴³). The compositions of phosphine under pressure, which are oxidised by water, have been described by Bushmakin and Frost ²⁴⁴).

Mixtures of phosphine and oxygen, both above and below the explosion limits, subjected to flash photolysis show, in the spectra, the presence of PH·, OH· and PO· radicals as well as the PH₂ radical ²⁵⁵). During the reaction of atomic oxygen with phosphine visible luminescence up to 3600 Å and UV emission were observed, which were attributed to the partial processes: O + PO → PO₂ and OH + PO → HOPO ³⁷⁷).

It is of particular interest that solutions of hydrogen peroxide of varying concentrations are not able to oxidise phosphine ²⁵⁶). Phosphine appears to simply dissolve (to a very small extent) even in 100% H₂O₂ without reacting ²⁸²). Solid sulphur trioxide oxidises phosphine to red phosphorus ²⁸³). No reactions are observed with NO and N₂O under the usual conditions ^{79, 285, 286}).

The reducing action of phosphine has been used in organic chemistry in various ways. The reactions described in the literature are summarised by the following equations:





A comprehensive study of the reducing properties of phosphine particularly with respect to aromatic nitro-compounds and aromatic sulphonyl chlorides, was published by Buckler *et al.* ²⁴⁸⁾.

2. The Question of the Existence of Phosphine Oxide OPH_3

In contrast to organo-phosphines and also many other phosphorus(III) compounds, phosphine is very unreactive and shows no tendency to react with electrophilic substances. In particular there is no substantiated evidence for an auto-oxidation of phosphine. This chemical behaviour is related to the electronic configuration of the molecule. As shown by, among other factors, H-P-H bond angles and the chemical shift, $\delta_{31\text{P}}$, in the nuclear magnetic resonance spectrum, the lone electron pair of the phosphine molecule stays predominantly in a $3s$ orbital of the phosphorus atom. The relative proximity of these two electrons to the nucleus and their, to a first approximation, spherically symmetric density distribution cause the unusually strong shielding of the phosphorus nucleus and thus the high positive chemical shift of +241 ppm (relative to 85% orthophosphoric acid) and also the small nucleophilic character of the molecule. Derivatives of phosphine which also show high positive chemical shifts in the ^{31}P NMR spectra are collected together in Table 7. In common with phosphine, they do not react either with oxygen or with sulphur to form the corresponding oxides or sulphides, nor do they react with alkyl iodides to form the corresponding phosphonium salts. The resonance signal is shifted to lower field strengths only when one or more ligands in phosphine, tris-(trimethylsilyl)-, tris-(trimethylstannyl)-, tris-(trimethylgermyl)- or tris-(triphenylstannyl)-phosphine are substituted. This is shown in the table, for example, by the series of compounds $\text{P}[\text{Si}(\text{C}_6\text{H}_5)_3]_3$, $\text{P}[\text{Si}(\text{C}_6\text{H}_5)_3]_2(\text{C}_6\text{H}_5)$, $\text{P}[\text{Si}(\text{C}_6\text{H}_5)_3](\text{C}_6\text{H}_5)_2$ and $\text{P}(\text{C}_6\text{H}_5)_3$. Parallel to this, the nucleophilic character increases, thus the usual reactivity of phosphorus(III) compounds towards electrophiles is reached step-wise. The contribution of the s electrons to the s bonding system is obviously increasing in the series, so that the orbital occupied by the electron lone pair has more and more p character. This orbital is more far-reaching and thus gives the molecule increasing nucleophilic character ³⁹³⁾. In agreement with this argument is the increased reactivity of phosphine in UV-light caused by the promotion of one electron of the lone pair to a more outlying orbital. This will be discussed in more detail later.

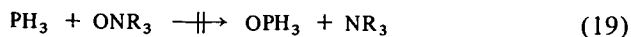
In the course of mass spectroscopic investigations of the hydrolysis products of calcium phosphide, Baudler and her co-workers could find no evidence for the existence of OPH_3 as an oxidation product of PH_3 ³⁹⁶⁾. In contrast, oxides of higher phosphines were observed, even when the hydrolysis of calcium phosphide was carried out with the strictest exclusion of oxygen. The

Table 7. N.M.R. data for phosphorus, phosphine and derivatives of phosphine

Compound	Chemical shift δ_{31P} [ppm]	Coupling constant J_{HP} [Hz]	Lit.
P ₄ , solid	460.0		378,383)
P ₄ , solution	460.0-533		378-382)
P ₄ , vapour	553.1		384)
PH ₃	238	188.2	385-391)
P[Si(CH ₃) ₃] ₃	251.2		392)
P[Sn(CH ₃) ₃] ₃	330.0		392,395)
P[Ge(CH ₃) ₃] ₃	228.0		392,395)
P(SiH ₃) ₃	378.0		339)
PH[Si(CH ₃) ₃] ₂	237.4	186	394)
PH ₂ [Si(CH ₃) ₃]	239.0	180	394)
P[Sn(C ₆ H ₅) ₃] ₃	323		395)
P[Sn(C ₆ H ₅) ₃] ₂ (C ₆ H ₅)	163		395)
P[Sn(C ₆ H ₅) ₃](C ₆ H ₅) ₂	56		395)
PH ₂ (CH ₃)	163.5		383)
PH(CH ₃) ₂	98.5		383)
P(CH ₃) ₃	62.0		383)
PH ₂ (C ₆ H ₅)	122.0		383)
PH(C ₆ H ₅) ₂	41.1		383)
P(C ₆ H ₅) ₃	8.0		383)
P[C(CH ₃) ₃] ₃	- 58		447)
P[Ge(CH ₃) ₃] ₂ CH ₃	177		447)
P[Ge(CH ₃) ₃] ₂ C ₆ H ₅	127		447)
PH[Ge(CH ₃) ₃](C ₆ H ₅) ₂	119		447)
P(GeH ₃) ₃	338		448)
P[Sn(C ₄ H ₉) ₃] ₂ C ₆ H ₅	170		448)
P[Sn(C ₄ H ₉) ₃](C ₆ H ₅) ₂	56		448)

following phosphine oxides were identified individually: P₂H₄O, P₃H₃O, P₃H₅O, P₄H₂O, P₇H₃O and P₇H₅O. PH₃O was not observed. The oxygen of the higher phosphine oxides was probably contained in the calcium phosphide used for the hydrolysis ³⁹⁶).

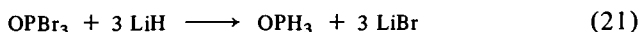
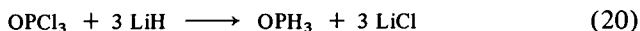
Also, attempts to convert phosphine to PH₃O using amine oxides, such as trimethylamine oxide and pyridine oxide, did not proceed to the result formulated in Eq. (19) ³⁹⁷):



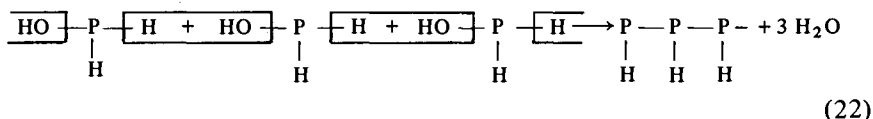
Phosphine reacts neither in aqueous solution nor direct with trimethylamine oxide. Also no reaction occurs on treatment of phosphine with pyridine oxide

in methylene chloride³⁹⁷). In contrast, PCl_3 reacts rapidly and quantitatively with pyridine oxide in methylene chloride even at -40°C to give OPCl_3 and pyridine³⁹⁸).

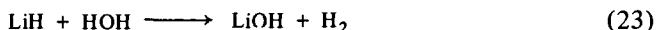
The reaction products observed from experiments to reduce the phosphoryl halides, OPCl_3 and OPBr_3 , with lithium hydride suggest that the primary reactions proceed according to Eqs. (20) and (21):



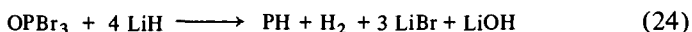
The authors assume that OPH_3 rearranges to the tautomeric form H_2POH , from which, at temperatures below -115°C , the highly polymeric $(\text{PH})_x$ is formed by condensation:



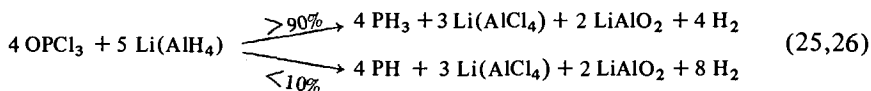
The released water reacts with excess lithium hydride to give hydrogen.



Thus, in the case of the reaction with OPBr_3 , the reaction shown in Eq. (24) was observed.



When lithium aluminium hydride, $\text{Li}(\text{AlH}_4)$, in ether solution is used instead of lithium hydride for the reduction of OPCl_3 , the OPH_3 also formed is mostly further reduced to phosphine at temperatures of about -115°C . Altogether, the reaction can be described by the following equations:



In the reaction of OPCl_3 with lithium borohydride at -115°C proceeding according to Eq. (27)



a crystalline solid $\text{H}_3\text{PO} \cdot \text{BH}_3$ is formed, which is stable up to -90°C . Thus, OPH_3 in the form of the adduct $\text{H}_3\text{PO} \cdot \text{BH}_3$ can be isolated and is stable up to -90°C , while, in the free state, it decomposes even at -115°C according to $\text{PH}_2\text{OH} \longrightarrow \text{PH} + \text{HOH}$. Above -90°C , $\text{H}_3\text{PO} \cdot \text{BH}_3$ also decomposes to hydrogen and H_2POBH_2 , which is regarded by the authors as polyborophosphene oxide $-\text{PH}_2-\text{O}-\text{BH}_2-\text{O}-\text{PH}_2-\text{O}-\text{BH}_2-$ ³⁹⁷.

SCF calculations for the hypothetical compound H_3PO were carried out by Marsmann *et al.* ⁴⁴⁹). The authors studied the effect of adding either a *d* or another *p* orbital to a phosphorus atom depicted in terms of seven *s* and three *p* Gaussian orbitals. An approximate model of H_3PO based on the valence bond method has been published by Mitchell ⁴⁵⁰).

3. Reactions with Atomic Hydrogen and Nitrogen

The reaction between phosphine and deuterophosphine on one hand and atomic hydrogen, generated by high-voltage discharge, on the other hand was intensively investigated using spectroscopic methods by Guenebaut and Pascat ^{249,252}). According to Wiles and Winkler ²⁵³), the stable end products of the reaction are red phosphorus and molecular hydrogen.

The main products from the reaction between phosphine and atomic nitrogen are molecular hydrogen and phosphorus nitride $(PN)_x$, which is formed in the α form ²⁵³). For the conversion of one mole of phosphine into (PN) , two atoms of nitrogen appear to be necessary. The primary step is the formation of PH_2 radicals which react further with the nitrogen atoms to give the nitride ²⁵⁴).

4. The Systems Phosphine/Water, Phosphine/Water/Ammonia, and Phosphine/Water/Ammonia/Methane

Electric discharges in the system phosphine/water result in the formation of water insoluble polyphosphines $H_2P-(PH)_n-PH_2$ and phosphorus as well as H_3PO_2 , H_3PO_3 and H_3PO_4 . When ammonia is also present, hypophosphate, pyrophosphate, polyphosphate and possibly polyhypophosphate are formed in addition. Finally, in the system phosphine/water/ammonia/methane, organic phosphorus compounds such as aminoalkylphosphates and aminoalkane-phosphonates and other phosphorus-free compounds such as amino-acids, ethanolamine etc. can be detected as well as the previously mentioned reaction products. The presence of phosphine or its rearrangement products seem to make the condensation reactions in the last mentioned system possible, because the ratio of the amino-acids, which are present after hydrolysis with 6N HCl, to the amino-acids which are present before the hydrolysis is larger in this system than in the system $CH_4/H_2O/NH_3$ ^{399,400}).

Irradiation of a gaseous mixture of phosphine and ammonia with ^{60}Co gamma-rays produces hydrogen, nitrogen and red phosphorus. Other products were not observed. Phosphine appears to work as a very efficient radical acceptor *via* reactions such as



and



The phosphino radical reacts further and finally produces red phosphorus and hydrogen ^{401,402}).

5. Reactions with Alkali and Alkaline Earth Metals

Alkali metals react with phosphine to form alkali dihydrogen phosphides. The reactions are generally carried out by passing the phosphine through a solution of the alkali metal in liquid ammonia ¹²⁴⁻¹²⁹). According to a patented method, phosphine can also be led through a suspension of the alkali metal in a mixture of a hydrocarbon and methoxypolyether ¹³⁰). Finally, sodium dihydrogenphosphide is also formed on leading phosphine into an ether solution of triphenylmethyl sodium ¹³¹).

Step-wise replacement of all three hydrogen atoms in phosphine by lithium can be obtained by the reaction of phosphine with an alkyl lithium compound in the corresponding molar ratio. The preparations of Li_3P and Na_3P from the elements were described by Brauer and Zintl ¹³⁴).

Of the alkali dihydrogenphosphides, potassium dihydrogenphosphide, KPH_2 , has been studied most extensively. This compound crystallises in a rock salt lattice with pseudo-rhombic distortion in the direction of a space diagonal ¹³²). An analogous structure has also been proved for rubidium dihydrogenphosphide. The density of potassium dihydrogenphosphide at 25 °C is 2.435 g/cm³ ¹³²). Potassium dihydrogenphosphide is soluble in strongly polar solvents such as tetramethylene sulphone and dimethylacetamide ¹³³). It is also well soluble in trimethylamine and dimethylformamide (10–15 g/100 ml). The chemical shift, δ_{P} , of KPH_2 in liquid ammonia is 279 ± 2 ppm (relative to 85% aqueous orthophosphoric acid), the coupling constant is $J_{\text{PH}} = 139$ Hz ⁹⁵). The proton nuclear resonance spectrum of KPH_2 dissolved in dimethylformamide consists of a doublet with a chemical shift $\delta_{\text{H}} = 1.12$ ppm (relative to $(\text{CH}_3)_4\text{Si}$), the phosphorus spectrum consists of a triplet with a chemical shift of +255.3 ppm (relative to 85% aqueous orthophosphoric acid). The coupling constant, measured from the proton spectrum, is $J_{\text{HP}} = 136.8$ Hz ¹³³). Solutions of KPH_2 in trimethylamine show a well resolved triplet in the phosphorus spectrum with a chemical shift of 272 ± 2 ppm ⁹⁵). The ¹H and ³¹P resonance spectra of solutions of NaPH_2 and KPH_2 in liquid ammonia were thoroughly investigated by Sheldrick ¹⁴⁴). As previously mentioned, the proton spectra consist of doublets and the phosphorus spectra of 1 : 2 : 1 triplets. When considerable quantities of phosphine are present in the solutions the multiplet structures collapse. The chemical shift of a 4% solution of NaPH_2 in liquid ammonia at room temperature was measured as $11.487 \pm 0.004 \tau$. This depends only slightly on temperature and is, at 2 °C $11.469 \pm 0.003 \tau$, and at -23 °C is $11.444 \pm 0.004 \tau$. The coupling constant, J_{HP} , at +22 °C is 138.71 ± 0.007 Hz. This increases with decreasing temperature and at 2 °C is 138.86 ± 0.05 and at -23 °C it is 139.05 ± 0.07 Hz. Measurements of a 2% solution of NaPH_2 in liquid ammonia

at $-60\text{ }^{\circ}\text{C}$ gave a value of $140.08 \pm 0.04\text{ Hz}$. The ^{31}P spectrum of a 5% solution of KPH_2 in liquid ammonia at $22\text{ }^{\circ}\text{C}$ shows a chemical shift of $+393\text{ ppm}$ (relative to an external P_4O_6 reference). The coupling constant obtained from this spectrum is $J_{\text{PH}} = 139 \pm 2\text{ Hz}$.

Potassium dihydrogenphosphide dissolved in dimethylformamide, is probably dissociated into ions. This is confirmed by the equivalent conductance, the value of $77.0\text{ }\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ was found for a $8 \cdot 10^{-5}\text{ mol/cm}^3$ solution. The PH_2^- ion is a strong nucleophilic reagent. The study of its chemical behaviour towards oxygen, sulphur and white phosphorus has produced, to date, no conclusive results. The reaction with the latter element results in the formation of an amorphous red-brown substance of composition KP_5H_2 which is soluble in dimethylformamide ¹³³).

Li_3P and Na_3P have the same structure as Na_3As . Each phosphorus atom is surrounded by 5 alkali metal ions at the corners of a trigonal bipyramid. The lattice contains two types of alkali metal atoms. One sort is surrounded by a trigonal prism of other alkali metal ions, in which the centres of the three vertical faces of the prism are occupied by three phosphorus atoms. The other type of alkali metal ion is surrounded by 4 phosphorus atoms in a distorted tetrahedron. Seven alkali metal ions are found at larger distances. In sodium phosphide the distance between the central phosphorus atom of the trigonal bipyramid and an axial sodium atom is 2.93 \AA and that between the phosphorus atom and an equatorial sodium atom 2.88 \AA ¹³⁴).

As well as for the preparation of alkali phosphides, the reaction of phosphine with the elements, their oxides or halides, at higher temperatures in quartz tubes have been much used recently for the preparation of other phosphides, in particular those which play important roles in semi-conductor technology. The preparations of the following phosphides using these methods have been described: for example, NdP ^{135,136}), BP ^{137,138}), GaP ^{139,140}), SmP , LaP ^{136,141}), TiP , Ti_2P (possibly Ti_3P) ^{142,143}) and InP ¹³⁹). See also Section IV.9.

Calcium reacts with phosphine in an analogous manner as the alkali metals. In liquid ammonia, solid $\text{Ca}(\text{PH}_2)_2 \cdot n\text{NH}_3$ is formed with hydrogen evolution ^{128,280}). The corresponding reaction with a solution of elemental strontium in liquid ammonia does not lead to a uniform product ²⁸⁰).

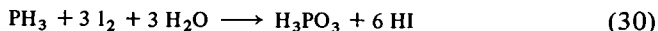
6. Reactions with Halogens and Chloramines

Phosphine burns to PCl_5 and hydrogen chloride in a chlorine atmosphere ^{79, 311,313}). An aqueous chlorine solution oxidises PH_3 to phosphoric acid (see also Section IV.7) ³¹⁴).

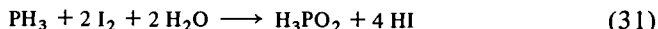
Royen and Hill ³⁰³) reported that phosphonium bromide and solid phosphorus hydride are the products from the reaction of excess phosphine with bromine at low temperatures.

From iodine and dry phosphine, P_2I_4 and hydrogen iodide, which reacts with excess phosphine to form phosphonium iodide, are formed^{316,317}.

In aqueous solution iodine reacts with phosphine according to the empirical formula (30) to form phosphorous acid and hydrogen iodide²²⁰;



According to earlier work²²¹, hypophosphorous acid should be formed according to Eq. (31):

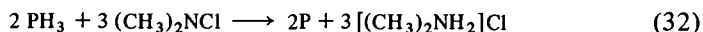


In fact, this is the first stage of the reaction. In the presence of protons released by the reaction, oxidation to phosphorous acid occurs. If the reaction mixture is kept only weakly acid throughout the whole reaction, only hypophosphite is actually formed in the solution.

Horak and Ettl²²² described two methods for the determination of phosphine in organic solvents which are based on Eq. (31). Thus,

- a) PH_3 is oxidised with excess iodine in a bicarbonate containing solution to H_3PO_2 and the excess iodine is back titrated with sodium thiosulphate solution;
- b) PH_3 mixed with twelve volumes of methanol is titrated with an aqueous iodine solution in the presence of pyridine so that H_3PO_2 is formed.

Whereas the reactions of chloramines of the type R_2NCl (where $R = H$ or an alkyl group) with tertiary phosphines have been abundantly investigated and almost without exception lead to the formation of aminophosphonium chlorides or their condensation products⁴⁰³⁻⁴⁰⁷, Highsmith and Sisler⁴⁰⁸ investigated the behaviour of primary and secondary phosphines and phosphine itself towards chloramines for the first time. With dimethylchloramine, phosphine forms red phosphorus and dimethylammonium chloride according to Eq. (32):



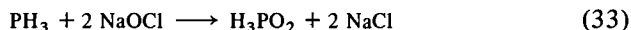
Only polymeric phosphorus hydride, P_xH_y , and not red phosphorus was observed when phosphine was treated with chloramine in ether solution^{408,409}. The authors attributed this to the expected higher basicity of a dimethylamino group in comparison to that of an amino group.

In an alkaline medium phosphine is oxidised solely to hypophosphite by N-bromosuccinimide⁴¹⁰.

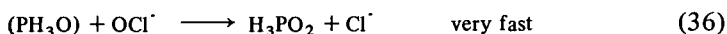
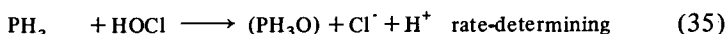
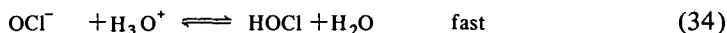
7. Reactions with Sodium Hypochlorite

Sodium hypochlorite in aqueous solutions reacts practically instantaneously with phosphine so that such solutions are particularly suitable for removing traces of phosphine from a gas stream²¹⁹.

In the pH range 12–13 the reaction follows the equation



The reaction is first order with regard to both the concentration of phosphine and the concentration of hypochlorite. It is suggested that the reaction proceeds as shown in Eqs. (34) – (36):



8. Reactions with Hydrogen Halides

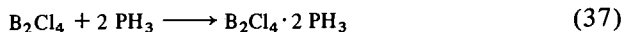
The introduction of phosphine into liquid hydrogen chloride results in the formation of PH_4Cl ^{295,328}; this was also observed earlier^{307,308}. Similarly PH_4Br can be obtained from hydrogen bromide and phosphine^{307,309,328}. Both phosphonium halides are almost completely dissociated at room temperature and normal pressure.

The reaction between dry phosphine and hydrogen iodide, first described in 1817 by J. J. Houton de la Billardière¹⁰⁹) produces phosphonium iodide. The simplest laboratory preparation of this compound is by the hydrolysis of an intimate mixture of diphosphorus tetraiodide and white phosphorus²⁷⁹). According to X-ray diffraction investigations, phosphonium iodide crystallises in a caesium chloride type lattice^{324,325}; see also³²⁶). The hydrogen atoms are tetrahedrally arranged about the phosphorus atoms; this was also shown by Raman and IR spectra^{327,328}).

9. Reactions with Metal and Non-Metal Halides

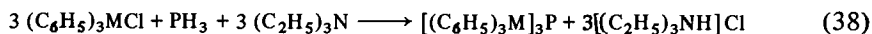
With metal halides such as AlCl_3 or InI_3 ^{93,146}) and non-metal halides such as BCl_3 or BBr_3 phosphine forms 1 : 1 adducts which, on pyrolysis, split off hydrogen halides to form the corresponding phosphides¹⁴⁷). This method for the preparation of phosphides is used in practice for the formation of semi-conducting crystals. The 1 : 1 adduct, $\text{AlCl}_3 \cdot \text{PH}_3$ reacts exothermically with alkyl halides to form hydrogen chloride and the primary phosphine. This reaction offers a relatively convenient method for the preparation of primary phosphines. The yields, especially with alkyl halides with long chain alkyl groups (more than 5 carbon atoms), are favourable and usually greater than 50%⁹³).

Phosphine reacts with B_2Cl_4 at room temperature according to equation (37)



to form the colourless solid *I* which is stable up to 65 °C but is, however, very sensitive to air³³⁴).

Tris-(triorganylmetal)phosphines are the products from the reactions between triphenyltin, triphenylgermanium and triphenyllead chlorides and phosphine^{148,149}. The reactions proceed in benzene solution in the presence of triethylamine as hydrogen chloride acceptor thus:

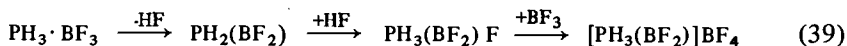


M = Sn, Ge, Pb.

To date, however, only few reactions between phosphine and a non-metal halide, in which a chemical bond is formed between phosphorus and a non-metal by HCl condensation, are known. To these, apart from the above-mentioned reactions, belongs also the reaction with CF_3SCl ²²³ which, depending upon the chosen proportions of the reactants, in a sealed tube at -95 °C leads to the formation of $(\text{CF}_3\text{S})_2\text{PH}$ or $(\text{CF}_3\text{S})_3\text{P}$ ²²⁴. Both compounds are not very stable thermally and decompose at 40–50 °C. Tris(trifluoromethylthio)-phosphine forms an unstable adduct with chlorine, which decomposes at 0 °C to give a mixture of PCl_3 , bis(trifluoromethyl)-disulphide and trifluoromethylsulphenyl chloride.

With SiH_3I phosphine probably forms silylphosphine²⁸⁸ and with $(\text{CH}_3)_2\text{BBr}$, crystalline $\text{H}_2\text{PB}(\text{CH}_3)_2$ ²⁸⁹. Germanium halides do not react with phosphine²⁹⁹.

The phase diagram of the system PH_3/BF_3 indicates the presence of two compounds²⁹⁰. On treatment of PH_3 with BF_3 at -130 °C $\text{BF}_3 \cdot \text{PH}_3$ is formed^{291,292}, which is probably converted to $[\text{PH}_3(\text{BF}_2)]\text{BF}_4$ by the following reaction mechanism^{290,292,293}:



In many other cases the course of the reaction and the nature of the reaction products resulting from the treatment of non-metal halides with phosphine are not completely clarified. To these belong the reaction products shown in Table 8.

For completeness, the alkylsilylphosphines, a class of compounds, the first member of which was synthesised by Parshall and Lindsey¹⁵⁰ must be mentioned. The alkylsilylphosphines, $(\text{CH}_3)_3\text{SiPH}_2$ (b.p. 69–73 °C), $[(\text{CH}_3)_3\text{Si}]_2\text{PH}$ (b.p. 170–172 °C) and $[(\text{CH}_3)_3\text{Si}]_3\text{P}$ (b.p. 242–243 °C), are formed by the reactions of the alkylchlorosilane with the lithium phosphides, LiPH_2 , Li_2PH and Li_3P , e.g.¹⁵⁰.

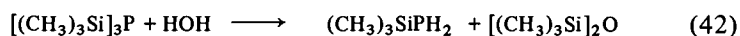
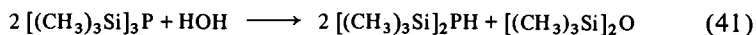


Leffler and Teach³³² described the preparation of $[(\text{CH}_3)_3\text{Si}]_3\text{P}$ from NaPH_2 and $(\text{CH}_3)_3\text{SiCl}$.

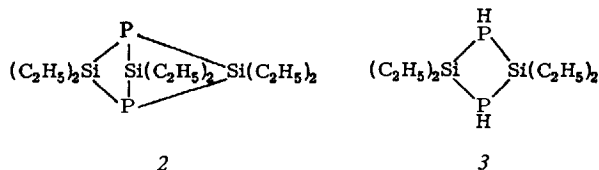
Table 8. Reaction products from phosphine and non-metal halides

Reaction of PH ₃ with	Reaction conditions	Reaction product	Lit.
BCl ₃	20 °C	PH ₃ · BCl ₃	147,158,294)
B ₂ Cl ₄	-78 °C	2 PH ₃ · B ₂ Cl ₄	296)
BBr ₃	20 °C	PH ₃ · BBr ₃	147,297)
BBr ₃	1250 °C	BP	298)
SiF ₄	-22 °C, 50 at		293)
SiCl ₄	-60 °C	No reaction	299)
SiBr ₄	Under pressure	Colourless amorphous compound	300)
PCl ₃		Solid phosphorus hydride	301)
PCl ₅	Dissolved in liq. HCl	No defined reaction	302,303)
PBr ₅	-90 °C	PH ₄ Br, solid phosphorus hydride	301,303)
AsF ₃ , AsCl ₃		Arsenous phosphide	304-306)

Bis-(trimethylsilyl)phosphine and trimethylsilylphosphine are also formed by the hydrolysis of tris-(trimethylsilyl) phosphine with the appropriate amount of water in diglyme or tetrahydrofuran ¹⁵¹⁾:



The compounds 2 and 3 were formed by treating a mixture of Li₂PH and Li₃P with diethyldichlorosilane ¹⁵⁰⁾:

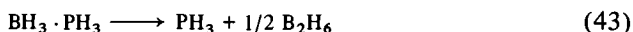


The alkylsilylphosphines are colourless liquids or low melting solids. They are very sensitive to water and oxygen but are thermally very stable.

Phosphine, primary and secondary phosphines react with Grignard reagents as "active hydrogen" compounds ^{214-216,493)}.

10. Reactions with Diborane and Monobromodiborane

Ammonia reacts with boron hydride to form a product with the empirical composition $B_2H_6 \cdot 2NH_3$ ¹⁵²⁻¹⁵⁴). Similarly, phosphine combines with diborane, in the gas phase above $-30^\circ C$ and in the liquid phase in a sealed tube above $-130^\circ C$, to give a white instable solid of constitution $BH_3 \cdot PH_3$ (m.p. $32-35^\circ C$) ^{155,156}). The dissociation pressure of $BH_3 \cdot PH_3$ is so large that the compound is already separated into its components at room temperature



Nuclear magnetic resonance spectra show that the compound exists as a monomer in the molten state; IR and Raman data show that the same molecular structure exists for the solid state ¹⁵⁶). Sawodny and Goubeau ⁴¹¹) calculated the force constants from the normal vibrations of the molecule, after they had corrected the original assignments of the bands ¹⁵⁶). A bond number of 0.78 was found for the P-B bond. The chemical shifts and coupling constants from the 1H and ^{11}B n.m.r. spectra for molten $BH_3 \cdot PH_3$ are given in Table 9 ²⁶⁰).

Table 9. N.M.R. data for molten $BH_3 \cdot PH_3$ at $37^\circ C$

Chemical shift [ppm]	Coupling constant [Hz]
δ_{BH} +0.53 ^{a)}	J_{BH} 104
δ_{PH} +4.31	J_{PH} 372
δ_B 60.8 ^{b)}	J_{PB} 27
	J_{HBPH} 8
	J_{PBH} 16

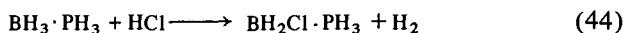
a) Relative to TMS.

b) Relative to $B(OCH_3)_3$.

The 1H n.m.r. and the vibrational spectra of $PH_3 \cdot BD_3$, $PD_3 \cdot BH_3$ and $PD_3 \cdot BD_3$ were investigated by Davis and Drake ⁴¹²). Proton n.m.r. spectra of the first two compounds show that no hydrogen-deuterium exchange takes place between boron and phosphorus. The spectrum of $BH_3 \cdot BD_3$ shows only a signal for the PH_3 group. This appears as a widely split doublet because of coupling between the protons and the phosphorus nucleus ($J_{PH} = 360$ Hz). Each component of the doublet is further split into a septet due to coupling between the protons bonded to phosphorus and the three deuterons ($I = 1$). The coupling constant J_{HD} is 1.1 Hz. The proton spectrum of $PD_3 \cdot BH_3$ consists only of a resonance for the protons on the boron atom ($I = 3/2$ for ^{11}B);

this is comprised of a 1 : 1 : 1 : 1 quartet ($J_{\text{BH}} = 103$ Hz). Each component is further split into a doublet due to coupling with the phosphorus nucleus.

Trimethylamine replaces PH_3 quantitatively in $\text{BH}_3 \cdot \text{PH}_3$ to give $\text{BH}_3 \cdot \text{N}(\text{CH}_3)_3$. Liquid or gaseous ammonia also replaces phosphine in the compound $\text{BH}_3 \cdot \text{PH}_3$ to the extent of 52–58% or up to 75%, respectively. The hydrogen atoms bonded to boron are partially, or completely, replaced by chlorine on treatment with hydrogen chloride, depending on the reaction conditions. The first stage of the reaction with hydrogen chloride is the formation of the colourless, viscous liquid $\text{BH}_2\text{Cl} \cdot \text{PH}_3$ (see below).

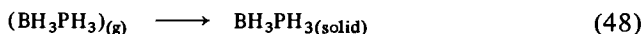
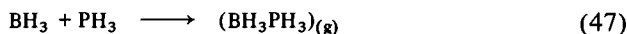
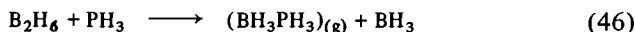


This reacts further with hydrogen chloride to give a colourless, crystalline product of composition $\text{BHCl}_2 \cdot \text{PH}_3$. The latter compound melts at about 68 °C. Finally, this is converted to $\text{BCl}_3 \cdot \text{PH}_3$ above 0 °C and under higher pressure. $\text{BCl}_3 \cdot \text{PH}_3$ is a colourless compound and was prepared earlier by Besson¹⁵⁷ from the reaction of equal volumes of PH_3 and BCl_3 below 20 °C; its properties were later investigated thoroughly by Tierney¹⁵⁸. According to this work, $\text{BCl}_3 \cdot \text{PH}_3$ is a well-crystalline solid which is partly dissociated in the gas phase (at 31 °C to about 90%). The enthalpy of the reaction

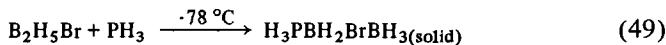


is 26 kcal/mol. In benzene the compound is probably monomeric and essentially undissociated. The dipole moment of $\text{BCl}_3 \cdot \text{PH}_3$ in benzene solution was measured as 5.2 ± 0.1 D (those for $(\text{C}_6\text{H}_5)_3\text{PBCl}_3$ and $(\text{CH}_3)_3\text{PBCl}_3$ are 7.01 ± 0.06 and 7.03 ± 0.01 D, respectively)¹⁵⁹.

By means of a kinetic investigation of the reaction between diborane and phosphine at 0 °C in the gas phase, Brumberger and Marcus¹⁶⁰ were able to describe the probable course of the reaction using the following equations:



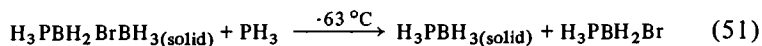
A 1 : 1 adduct is formed between monobromodiborane and phosphine at -78 °C.



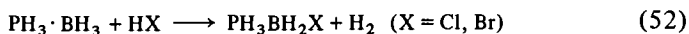
This adduct begins to decompose to diborane and $\text{H}_3\text{PBH}_2\text{Br}$ at -45 °C¹⁶¹. The latter compound is stable up to 0 °C. At this temperature it polymerises slowly by splitting off hydrogen:



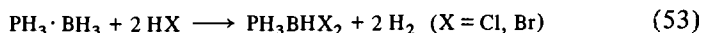
When monobromodiborane and phosphine are mixed in the proportions 1 : 2 at -78°C , equimolar amounts of $\text{H}_3\text{PBH}_2\text{Br}$ and H_3PBH_3 are obtained on melting the reaction mixture. Again, $\text{H}_3\text{PBH}_2\text{BrBH}_3$ is probably formed first but, at higher temperatures, reacts further with phosphine according to Eq. (51).



Recently Drake and Simpson²⁶³⁾ thoroughly investigated the reactions between PH_3BH_3 and $\text{PH}_3\text{BH}_2\text{Br}$ with HCl or HBr . Phosphine-borane reacted with equimolar quantities of hydrogen chloride or hydrogen bromide to give the corresponding monohaloborane adducts.



With two molar amounts of the hydrogen chloride or bromide, the dihaloborane adducts of phosphine were formed.



Similar reactions of phosphine-monobromoborane with hydrogen halides lead to $\text{PH}_3 \cdot \text{BHBrCl}$ and $\text{PH}_3 \cdot \text{BHBr}_2$. The n.m.r. data for the phosphine adducts are presented in Table 10.

Table 10. N.M.R. data for the adducts between phosphine and BH_3 or haloborane (approx. 10% solutions in CH_2Cl_2 at -20°C)²⁶³⁾

Compound	$\delta_{1\text{H}}(\text{PH}_3)^{\text{a)}$ [ppm]	J_{PH} [Hz]	J_{HH} [Hz]
$\text{PH}_3 \cdot \text{BH}_3$	4.24	369	8.0
$\text{PH}_3 \cdot \text{BH}_2\text{Cl}$	4.79	389	6.2
$\text{PH}_3 \cdot \text{BH}'\text{Cl}_2$	5.14	413	3.8 ^{b)}
$\text{PH}_3 \cdot \text{BH}_2\text{Br}$	5.08	405	6.2
$\text{PH}_3 \cdot \text{BH}'\text{Br}_2$	5.56	420	4.4
$\text{PH}_3 \cdot \text{BH}'\text{BrCl}$	5.32	417	4.0

^{a)} Relative to TMS internal reference.

^{b)} At -60°C .

As can be seen in Table 10, the coupling constant, J_{PH} , increases with increasing Lewis acidity of the borane component. The Lewis acidity increases in the following series of compounds thus: $\text{BH}_3 \ll \text{BCl}_3 < \text{BBr}_3$; $\text{BH}_3 < \text{BH}_2\text{Cl} < \text{BHCl}_2$; $\text{BH}_3 < \text{BH}_2\text{Br} < \text{BHBr}_2$ and $\text{BHCl}_2 < \text{BHBrCl} < \text{BHBr}_2$. In the series, $[\text{PH}_4]^+$, $[\text{CH}_3\text{PH}_3]^+$, $[(\text{CH}_3)_2\text{PH}_2]^+$ and $[(\text{CH}_3)_3\text{PH}]^+$, the coupling constant, J_{PH} , decreases with increasing substitution, as must be expected when the

Fermi contact term is the most important factor for coupling. The bonding in $[\text{PH}_4]^+$ is probably comprised of pure sp^3 -hybridised orbitals, so that increasing substitution by methyl groups reduces the s character of the remaining P–H bonds and simultaneously causes a reduction in the H–P–H bond angle. On the other hand, the coupling constant, J_{PH} , increases in the series PH_3 , CH_3PH_2 and $(\text{CH}_3)_2\text{PH}$ with increasing methyl substitution⁴¹³. This apparent contradiction can be explained by considering that J_{PH} is dependent upon the geometry of the molecule⁴¹⁴. The replacement of hydrogen atoms by methyl groups renders the electron lone pair more accessible (see page 7). This is shown by the fact that the H–P–H bond angle in PH_3 is only 93° whereas the C–P–C bond angle in $\text{P}(\text{CH}_3)_3$ is 98° . Therefore, among other factors, an increase in the coupling constant, J_{PH} , which indicates an increase in the s character of the P–H bonds, can occur when an electron-withdrawing group is introduced.

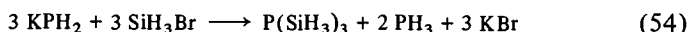
In systems derived from $\text{PH}_3 \cdot \text{BH}_3$, changes in the coupling constant, J_{PH} , are found which are similar to those seen in compounds derived from PH_3 , *i.e.* compounds with phosphorus in coordination number 3. The observation that the alteration does not correspond to that seen for derivatives of PH_4^+ suggests that the very weak donor-acceptor bond in $\text{PH}_3 \cdot \text{BH}_3$ does not affect the hybridisation of phosphorus, as compared with that in free PH_3 , as much as might at first be expected. A small increase in the electron withdrawing action by halogen substitution of the hydrogen atoms bonded to boron causes an increase in the s character of the P–H bonds.

11. Reactions with Silanes and Alkali Aluminiumhydrides

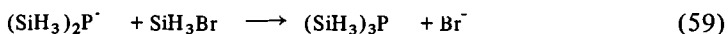
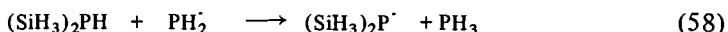
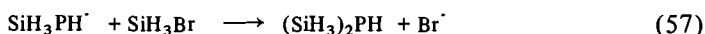
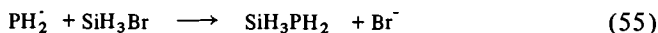
Silylphosphine, SiH_3PH_2 , can be isolated by passing equal quantities of phosphine and silane through a reaction vessel heated to 500°C and subsequently cooling the resulting gas stream immediately to the temperature of liquid nitrogen. In a sealed reaction vessel at 450°C and about 200 mmHg pressure other P- and Si-containing products were observed but not individually investigated^{162,163}.

Silylphosphine is also formed, together with disilylphosphine, $(\text{SiH}_3)_2\text{PH}$, and disilanylphosphine, $\text{Si}_2\text{H}_5\text{PH}_2$, by the application of a silent electrical discharge to a mixture of silane and phosphine. Analogous treatments of mixtures of disilane, Si_2H_6 , with PH_3 or of disilylphosphine with silane, result in the formation of disilanylphosphine and silylphosphine, respectively^{164,165}. Evidence for the existence of trisilylphosphine was found for the first time by Aylett, Emel us and Maddock¹⁶⁶) in the reactions between silyl iodide, H_3SiI , and phosphine or between silyltrialkylammonium iodide and phosphine. According to Amberger¹⁶⁷) the reaction of potassium dihydrogenphosphide with silyl bromide is suitable for the preparation of trisilylphosphine. The reaction,

which apparently even below $-100\text{ }^{\circ}\text{C}$ proceeds *via* many stages can be described by the empirical equation:



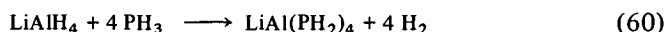
Glidewell and Sheldrick⁴¹⁵ found that the formation of trisilylphosphine occurs according to the scheme:



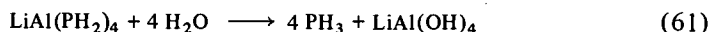
The intermediate mono- and disilylphosphines can be isolated using suitable conditions. The preferential formation of trisilylphosphine is a result of the increasing acidity of the compounds in the following order, $\text{PH}_3 > \text{H}_3\text{SiPH}_2 > (\text{H}_3\text{Si})_2\text{PH}$. Trisilylphosphine reacts with water or hydrogen chloride to form disiloxane or silyl chloride, respectively. It has a much smaller nucleophilic character than trimethylphosphine⁴¹⁵.

At room temperature trisilylphosphine is a colourless liquid, which is spontaneously inflammable in air (extrapolated boiling point, $114\text{ }^{\circ}\text{C}$). According to electron diffraction results the Si–P–Si bond angle in trisilylphosphine is $95 \pm 2^{\circ}$ ¹⁶⁸. The measured P–Si bond length of $2.247 \pm 0.005\text{ \AA}$ ¹⁶⁸ corresponds to the expected Si–P single bond length of 2.25 \AA predicted by Beagley¹⁶⁹. The ^{31}P nuclear magnetic resonance spectrum of the compound indicates that predominantly *p* orbitals of the phosphorus atom are used for the formation of the σ -bonding system³³⁹. The chemical shift of $\text{P}(\text{SiH}_3)_3$ is $+378\text{ ppm}$ (relative to 85% orthophosphoric acid); this is the largest positive shift observed to date for a compound of phosphorus.

Lithium aluminiumhydride reacts with phosphine in diglyme or tetrahydrofuran to give $\text{LiAl}(\text{PH}_2)_4$ with evolution of hydrogen¹⁷⁰

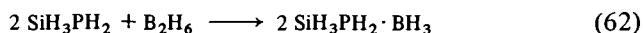


The lithium tetrakis (dihydrogenphosphido) aluminate, which is soluble in diglyme, shows typical organic and inorganic substitution reactions and can be used to introduce PH_2 groups into molecules. The compound is quantitatively hydrolysed thus:



With ethyl iodide, ethylphosphine and phosphine are formed. The reaction with excess silyl bromide results in the formation of silylphosphine⁴¹⁶.

Silylphosphine, like methylphosphine, forms an adduct with diborane⁴¹⁷



The proton n.m.r. spectra of these adducts have been intensively studied. The BH_3'' resonance in the spectrum of $\text{CH}_3\text{PH}_2' \cdot \text{BH}_3''$ consists of a 1 : 1 : 1 : 1 quartet due of coupling between the boron nucleus (^{11}B , 80% natural abundance; $I = 3/2$) and the directly bonded protons ($J_{\text{BH}''} = 99$ Hz). Each component of the quartet is further split into a doublet of triplets due to coupling with the phosphorus nucleus ($J_{\text{PH}''} = 16$ Hz) and the two protons bonded to phosphorus, respectively. The PH_2' -signal is, as is typical for phosphine-borane adducts, a doublet with $J_{\text{PH}'} = 375$ Hz. All n.m.r. data for the two types of adducts are given in Table 11.

Table 11. ^1H N.M.R. data for silyl- and methylphosphine ($^1\text{H}_3$)- and ($^2\text{H}_3$)-borane adducts (pure liquids at -20 or 25°C)⁴¹⁷

Compound	Chemical shift [ppm]			Coupling constant [Hz]						
	$\delta(\text{SiH})$ or $\delta(\text{CH})$	$\delta(\text{PH})$	$\delta(\text{BH})$	J_{HH}	$J_{\text{H}'\text{H}''}$	J_{PH}	$J_{\text{PH}'}$	$J_{\text{PH}''}$	$J_{\text{BH}''}$	$J_{\text{H}'\text{D}}$
$\text{SiH}_3\text{PH}_2' \cdot \text{BH}_3''$	4.0	3.8	0.8							
$\text{Si}(\text{HD})_3\text{PH}_2' \cdot \text{B}(\text{HD}'')_3$	4.0	3.8	0.7							
$\text{CH}_3\text{PH}_2' \cdot \text{BH}_3''$	1.30	4.58	0.53							
$\text{CH}_3\text{PH}_2' \cdot \text{BD}_3$	1.30	4.52								
$\text{SiH}_3\text{PH}_2' \cdot \text{BH}_3''$	4	8	13.5	358	ca. 16	101				
$\text{Si}(\text{HD})_3\text{PH}_2' \cdot \text{B}(\text{HD}'')_3$	4.5		14.0	255		102				
$\text{CH}_3\text{PH}_2' \cdot \text{BH}_3''$	7	7	ca. 13	375		102				
$\text{CH}_3\text{PH}_2' \cdot \text{BD}_3$	6.5		ca. 13	376						1

12. Reactions with Heavy Metals and their Ions

Heavy metal salt solutions react with phosphine in many cases to give normal phosphides. In this way, for example, Ag_3P , Au_3P , Hg_3P_2 , Pb_3P_2 and Cd_3P_2 can be prepared^{256, 257}. The reaction of phosphine with nickel salt solutions generally results in the formation of a precipitate of composition varying from $\text{Ni}_{0.4}\text{P}$ to NiP . The nickel phosphides, Ni_5P_2 , Ni_2P and NiP can only be isolated by using specific conditions²⁵⁸.

No new results about the reactions of phosphine with copper salts, their aqueous solutions or with metallic copper are available. The earlier literature

is often contradictory. According to Rose ⁴⁵⁷⁾ PH_3 reacts with CuCl_2 to give HCl and Cu_3P_2 , whereas aqueous solutions of CuCl_2 are not attacked by phosphine ⁴⁵⁸⁾. Results on the behaviour of phosphine towards copper (I) compounds have been confirmed. With acidified CuCl solution $\text{CuCl} \cdot \text{PH}_3$ is formed; $\text{CuBr} \cdot \text{PH}_3$ and $\text{CuI} \cdot \text{PH}_3$ can be prepared analogously ^{459,460)}. Under pressure the compounds $\text{CuCl} \cdot 2 \text{PH}_3$ and $\text{CuBr} \cdot 2 \text{PH}_3$ are formed ⁴⁶¹⁾. Only an earlier literature report about the reaction of PH_3 with metallic copper, in which it is reported that at $180\text{--}200^\circ\text{C}$ Cu_3P is formed, exists ⁴⁵⁸⁾. Also the behaviour of phosphine towards silver compounds is still unclear in many respects. On passing PH_3 into an alcoholic solution of AgI , $\text{AgI} \cdot 5 \text{PH}_3$ is obtained, while no addition compounds are formed between PH_3 and AgCl or AgBr ⁴⁶⁰⁾. According to a more recent report, a mixture of Ag_3P and elemental silver is obtained on treating a dilute alcoholic solution of silver nitrate with phosphine. Unstable $\text{Ag}_3\text{P} \cdot 3 \text{AgNO}_3$ is formed on passing phosphine into a concentrated aqueous solution of silver nitrate ⁴⁶²⁾. Uranium salts in aqueous solution are not attacked by PH_3 ⁴⁶³⁾. The corresponding diphosphides are formed by heating the metals Ti , Zr , V , Nb , Ta , Cr , Mo , and W with phosphine in a hydrogen atmosphere in an electric oven at 800°C ⁴⁶⁴⁾.

13. Reactions with Aldehydes

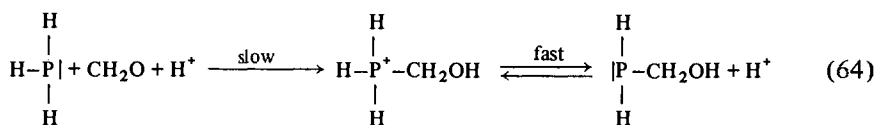
a) Aliphatic Aldehydes

Reactions between phosphine and aldehydes were observed relatively early by Messinger and Engels ^{171,172)}. By passing phosphine through ethereal solutions of acetaldehyde, propionaldehyde or butyraldehyde in the presence of hydrogen halides they obtained tetrakis(hydroxyethyl)-, tetrakis(hydroxypropyl)- or tetrakis(hydroxybutyl)-phosphonium halides, respectively. Tetrakis(hydroxyethyl)phosphonium iodide was isolated several years earlier by Girard ¹⁷³⁾ as the reaction product from phosphonium iodide and acetaldehyde.

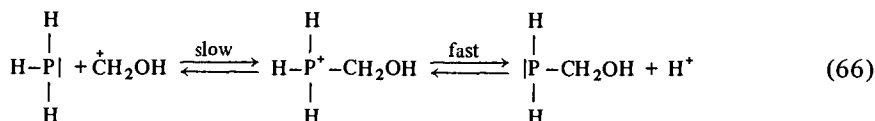
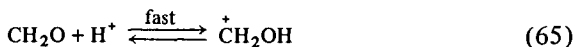
Little attention was paid to these reactions until 1921 when Hoffman ¹⁷⁴⁻¹⁷⁶⁾ prepared tetrakis(hydroxymethyl)phosphonium chloride by passing phosphine into a warm, aqueous hydrochloric acid solution of formaldehyde. The product was obtained in the form of colourless crystals by evaporation of the reaction solution.

A kinetic study of the reaction between phosphine and formaldehyde showed that it is of the first order with respect to phosphine and to the aldehyde. It is catalysed by HCl . At hydrogen chloride concentrations of less than 0.2 mol/l the rate of reaction is proportional to the HCl -content of the solution, at higher concentrations the rate is independent of the HCl -content ¹⁷⁷⁾. The dependencies found can be accounted for by both bi- and trimolecular mechanisms. In the latter case, a simultaneous interaction between one molecule of aldehyde, one of phosphine and a proton must be assumed:

E. Fluck

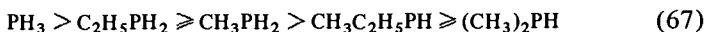


The hydroxymethylphosphonium ion first formed changes into mono-hydroxymethylphosphine by releasing a proton. This phosphine reacts further in the same way as phosphine itself until finally the quarternary phosphonium ion is formed. For a bimolecular reaction mechanism, the first stage must be assumed to be the formation of a carbonium ion from the aldehyde molecule and a proton. This ion then reacts with phosphine.



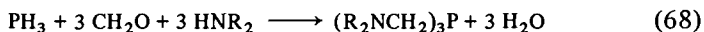
In the presence of heavy metal salts, such as HgCl_2 , AgNO_3 or PtCl_4 , the reaction between phosphine and formaldehyde is also catalysed by acids weaker than hydrochloric acid. Thus, in this way, phosphonium acetate, oxalate, lactate or fluoride can be obtained directly. According to studies by Raver^{178, 179} phosphine reacts with formaldehyde even in the absence of acids when metal salts such as HgCl_2 , NiCl_2 , $\text{Cr}_2(\text{SO}_4)_3$, PtCl_4 or finely divided metals are present in catalytic amounts^{310, 323}. Tetrakis (hydroxymethyl)phosphonium hydroxide is thus formed.

The reactions of substituted phosphines with formaldehyde show that the rate of the reaction is determined by the nucleophilic character of the phosphorus atom. The energies of activation decrease in the order¹⁸⁰:



On the other hand, fluorine-containing substituents reduce the electron donating power of the phosphorus atom.

1,1,2,2-Tetrafluoroethylphosphine only reacts with CH_2O in the presence of hydrochloric acid to give $\text{CHF}_2\text{CF}_2\text{P}(\text{CH}_2\text{OH})_2$ (b.p. 100 - 110 °C/0.18 mmHg, with decomposition). The corresponding phosphonium compound is not formed¹⁸¹. Phosphine reacts with aqueous solutions of formaldehyde in the presence of secondary amines to give tris(dialkylaminomethyl)phosphines in good yields¹⁸²:

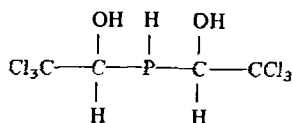


Secondary phosphines of the type $(\text{CHCl}_2\text{CHOH})_2\text{PH}$, $(\text{CCl}_3\text{CHOH})_2\text{PH}$ or $(\text{CH}_3\text{CHClCCl}_2\text{CHOH})_2\text{PH}$ are formed by the reactions of phosphine with

the corresponding aldehyde in the presence of HCl with tetrahydrofuran as reaction medium ^{183,184}.

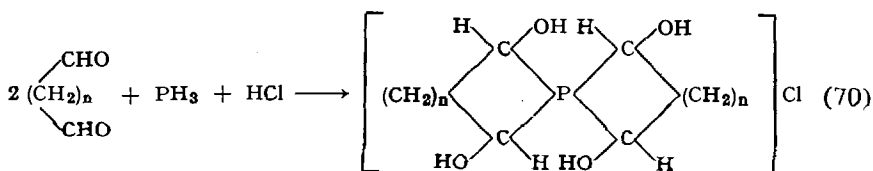
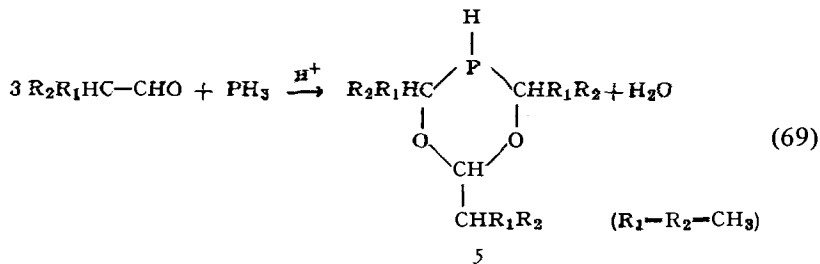
Tetrakis(1-hydroxyalkyl)phosphonium salts were prepared from phosphine and various aliphatic aldehydes using similar reaction conditions ¹⁸⁵.

Chloral hydrate and chloral alcoholate react with phosphine in the presence of HCl to give compound 4 in the form of its monohydrates ³³³. The preparation of this compound from chloral hydrate and phosphonium iodide has been previously described by Girard ¹⁸⁴.



4

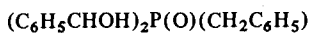
The reactions of phosphine with α -branched aldehydes follow a different pathway. They lead to the formation of stable, heterocyclic, secondary phosphines of the following type, 5 ¹⁸⁶. With suitable dialdehydes, spirocyclic phosphonium salts are obtained ^{186,187}; these are very difficult to prepare by other methods ¹⁸⁸:



b) Aromatic Aldehydes

As previously mentioned, the first reactions between phosphine and aromatic aldehydes were carried out by Messinger and Engels ^{171,172}, although the nature of the reaction products could only be clarified in the last few years.

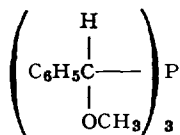
When a stream of phosphine is passed into an ether solution of benzaldehyde saturated with HCl, a colourless, crystalline solid, insoluble in the reaction mixture is formed. The infra-red spectrum of this product shows an absorption band at 1145 cm^{-1} which is typical for the $\text{P}=\text{O}$ group of a tertiary phosphine oxide. This, together with the chemical behaviour, indicates that the product is benzyl-bis(α -hydroxybenzyl)phosphine oxide, 6, ¹⁸⁹.



6

p-Methylbenzaldehyde and *p*-chlorobenzaldehyde produce the corresponding phosphine oxides in analogous reactions ¹⁸⁹.

When methanol is used as reaction solvent for the treatment of benzaldehyde with phosphine, however, the product is tris(α -methoxybenzyl)phosphine, 7, ¹⁹⁰:



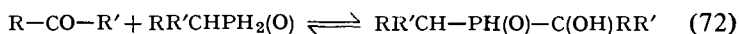
7

The use of ethanol or isopropanol as solvent results in the formation of tris(α -ethoxybenzyl)- or tris(α -isopropoxybenzyl)-phosphine, respectively, in yields of up to 85% ¹⁹⁰.

Kinetic investigations of the reactions discussed here have been made by Ettel and Horak ¹⁹⁰.

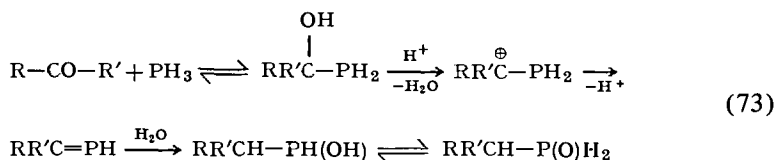
14. Reactions with Ketones

Simple ketones react with PH_3 in strongly acid media to form primary phosphine oxides and 1-hydroxyalkyl-sec.phosphine oxides ¹⁹¹⁻¹⁹³.



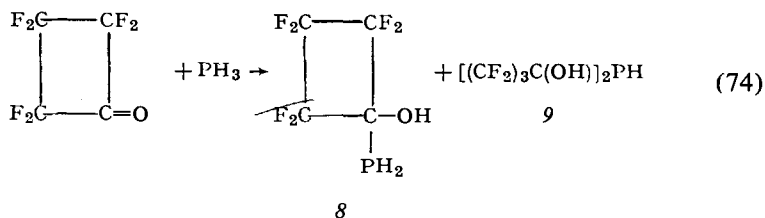
The proportions of primary and secondary phosphine oxide formed are dependent mainly on steric effects.

Buckler and Epstein ^{192,193} suggested the following reaction mechanism to account for the formation of primary phosphine oxides:



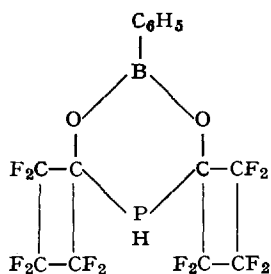
The first step corresponds to a normal carbonyl addition, as is also observed with aliphatic aldehydes; but here the equilibrium does not lie so far to the right. A strongly acidic medium is necessary for the next stage, the formation of a carbonium ion. For example, it is found that PH_3 only reacts with acetone when the solution is more than 8-molar in hydrochloric acid. By analogy, the formation of a double bond between carbon and phosphorus, which in our opinion, however is improbable, is assumed to be the third stage. Finally, this is followed by the addition of water and tautomeric rearrangement to the primary phosphine. In this way, phosphine, which is present in technical acetylene, and because of its good solubility in acetone concentrates in the commercial steel cylinders, forms with acetone, isopropylphosphine oxide and possibly, secondary products⁴¹⁸⁾.

One of the most reactive, with respect to phosphine, ketones, hexafluorocyclobutanone, produces with phosphine primary and secondary 1-hydroxy-fluorocyclobutylphosphines instead of phosphine oxides¹⁹⁴⁾:

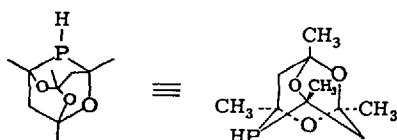
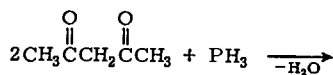


The proportions of primary and secondary phosphine formed are dependent on the molar ratio of the reaction components. Excess of phosphine leads mainly to 8, while an excess of ketone produces a practically quantitative yield of 9. The two phosphines 8 and 9 are both hydrolytically stable but, however, are oxidised to oily products by air. The secondary phosphine 9 reacts with diethylphenylboronate to give the ester 10 in high yield¹⁹⁴⁾.

Similar to ketones, diketones also react readily with phosphine in aqueous, strong hydrochloric acid media¹⁹⁵⁾. Thus, 2,4-pentadione gives a colourless crystalline substance of composition $\text{C}_{10}\text{H}_{17}\text{O}_3\text{P}$ in good yield. On the basis of spectroscopic studies and the chemical properties of the compound the authors suggest the structure 11.



10

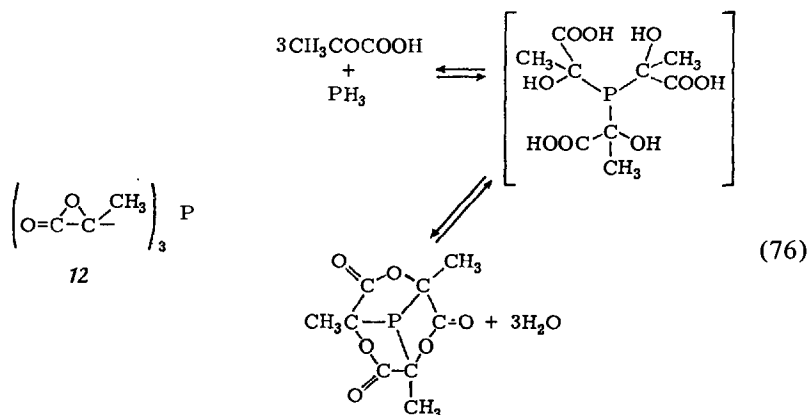


(75)

11

Analogous products are obtained from reactions between 2,4-pentadione and various primary phosphines.

Structure 12 was originally proposed for the product, with the composition $\text{C}_9\text{H}_9\text{O}_6\text{P}$, obtained by passing a mixture of phosphine and HCl into an ether solution of pyruvic acid, an α -keto acid^{171,172}. However, the infra-red and nuclear magnetic resonance spectra can only be interpreted in terms of the structure 13, recently proposed by Buckler¹⁸⁹. This structure also ac-



(76)

13

counts for the chemical behaviour of the compound. A normal carbonyl addition followed by cyclisation with the splitting off of water was assumed to account for the formation of compound 13.

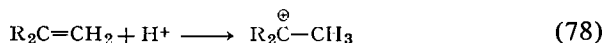
15. Reactions with Olefins

The addition of phosphine to olefins provides today a generally applicable method for the syntheses of organophosphines. Stiles, Rust and Vaughan ¹⁹⁶⁾ were the first to study the reaction systematically. It is catalysed by organic peroxides such as, for example, di-*t*-butyl peroxide, by α , α' -azobis-isobutyro-nitrile ¹⁹⁷⁾, by other free radical sources or by exposing the reaction mixture to UV- or X-radiation ¹⁹⁷⁾. The PH_2 radicals, produced according to Eq. (77), react further with olefins thus producing PH_2 radicals continually.

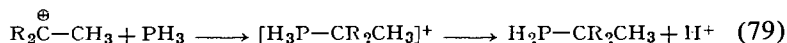


On treatment of phosphine with 1-butene, cyclohexene, allyl alcohol, allylamine or allyl chloride, the corresponding primary, secondary and tertiary organophosphines are obtained in yields ranging from 2 to 67%. The reaction between phosphine and 1-butene is, among others, used for the industrial preparation of tributylphosphine ¹⁹⁸⁾.

The addition of phosphine to olefins is accelerated by acidic ¹⁹⁹⁾ and basic ²⁰⁰⁾ catalysts. Under the influence of non-oxidising acids or Lewis acid such as, for example, methanesulphonic acid, benzenesulphonic acid, trifluoroacetic acid or boron trifluoride ²⁰¹⁾ phosphine is quickly added to olefins at pressures of 20–40 at, and temperatures of 30–60 °C. It is assumed that the reaction proceeds *via* a carbonium ion which is first formed thus:

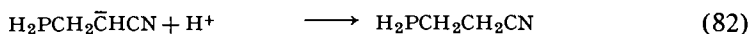
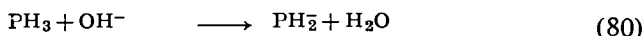


This reacts further with phosphine to give the monoalkylphosphonium ion and which finally splits off a proton to form the corresponding phosphine.

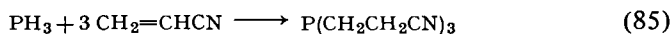
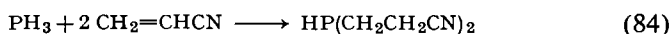
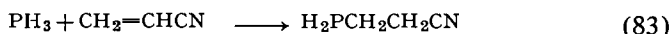


This assumption is supported by the fact that tertiary phosphines react especially readily under analogous conditions.

With strongly basic catalysts, in contrast, it is assumed that, in spite of the extremely weak acid character of phosphine, the reaction formally follows the Michael mechanism, *i.e.* it proceeds according to the sequence of reactions (80), (81) and (82) ²⁰²⁾.

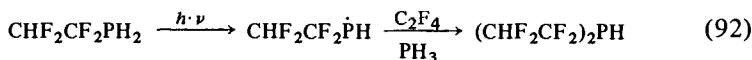
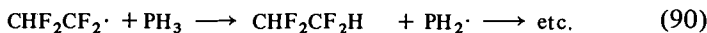
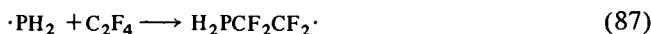


By the use of base catalysts phosphine and phenylphosphine for example can be cyanoethylated. Acrylonitrile and phosphine react together at room temperature in the presence of aqueous potassium hydroxide solution to give, depending on the reaction conditions, primary, secondary and tertiary 2-cyanoethyl-phosphines²⁰⁰):



In place of potassium hydroxide, strong organic bases or suitable ion exchangers, such as, for example, Dowex-2, can also be used.

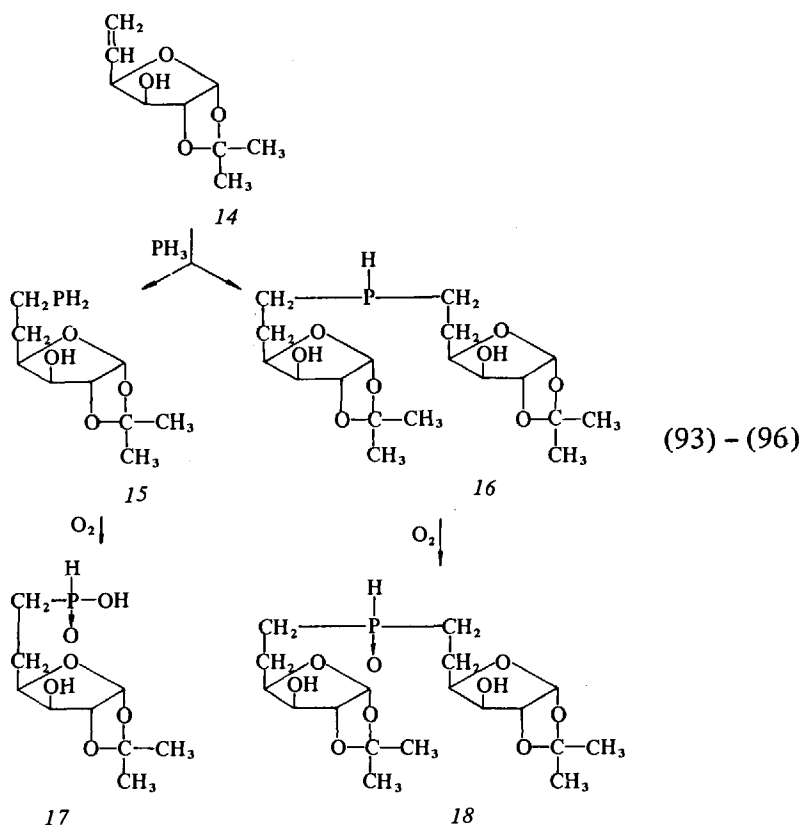
Haszeldine and co-workers investigated the reactions between phosphine and polyfluoro-olefins very carefully^{203,204}). These, initiated by UV-radiation^{203,204}), or carried out in sealed tubes at higher temperatures,^{205,206}) lead to primary and secondary polyfluoroalkylphosphines. 1,1,2,2-tetrafluoroethylene, for example, forms 1,1,2,2-tetrafluoroethylphosphine in 86% yield. In addition, the reaction product also contains tetrafluoroethylenediphosphine, whereas the reaction of ethylene with phosphine produces no ethylenediphosphine. The conditions under which the reaction proceeds and the nature of the final products suggest the mechanism described by the following equations²⁰³).



An equi-molar mixture of chlorotrifluoroethylene and phosphine reacts in UV light to give a 91% yield of chlorotrifluoroethylphosphine, $\text{ClCHFCF}_2\text{PH}_2$, *i.e.* phosphine attacks the CF_2 group, as is known from other radicals²⁰³). In

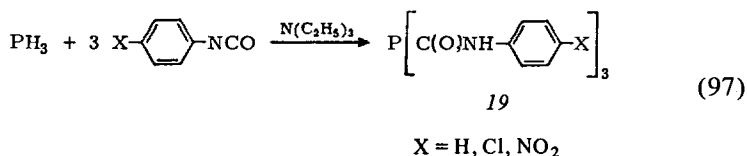
contrast, 1,1-difluoroethylene with phosphine gives $\text{CHF}_2\text{CH}_2\text{PH}_2$ as main product as well as the secondary phosphine $(\text{CHF}_2\text{CH}_2)_2\text{PH}$, *i.e.* here the attack occurs only at the CH_2 group of 1,1-difluoroethylene. Surprisingly $\text{FCIC}=\text{CFCl}$ does not react with phosphine. Finally the photochemical reaction of phosphine with trifluoroethylene results in the formation of $\text{CF}_3\text{CHFCF}_2\text{PH}_2$ and $\text{CF}_3\text{CF}(\text{PH}_2)\text{CHF}_2$ in the ratio 85 : 15.

The addition of phosphine to 5,6-dideoxy-1,2-O-isopropylidene-D-xylo-hex-5-enfuranose (*14*) takes place when the reaction mixture is irradiated with UV light. A mixture of 5,6-dideoxy-1,2-O-isopropylidene- α -D-xylo-hexa-furanose-phosphine (*15*) and bis-(5,6-dideoxy-1,2-O-isopropylidene- α -D-xylo hexanose)phosphine (*16*) is probably formed but the components could not be separated. In the presence of atmospheric oxygen these are converted to the corresponding phosphinous acid (*17*) and the secondary phosphine oxide (*18*), respectively ⁴¹⁹.



16. Reactions with Isocyanates

Phosphine reacts with aryl isocyanates to form tricarbamoylphosphines (19)^{207,208}:



The yields from the reactions, carried out at room temperature and a pressure of 2–4 at, increase with increasing electronegativity of the substituent X. The yield with phenyl isocyanate is 13%, with *p*-chlorophenyl isocyanate 55% and with *p*-nitrophenyl isocyanate it is 100%. Primary and secondary carbamoylphosphines cannot be isolated even when equi-molar quantities of phosphine and isocyanate are used. Their intermediate formation is probable but apparently they are more reactive towards isocyanates than phosphine itself. Similarly, phosphine does not react with free cyanic acid whereas primary and secondary phosphines react with cyanic acid, as with isocyanates, to form the corresponding carbamoylphosphines²⁰⁹). Attempts to make phosphine react with phenyl isothiocyanate did not succeed²¹⁰).

17. Reactions with Aromatic Acid Chlorides

Aromatic acid chlorides react with phosphine at 50 °C in absolute pyridine to form mono-, di- and triacylphosphines. For example, PH₃ and benzoyl chloride give tribenzoylphosphine, a yellow crystalline compound which is resistant to water and dilute acids but is hydrolysed to PH₃ and alkali benzoate by alkalis^{217,218}).

18. Reactions with Trimethylindium

When phosphine is passed through a benzene solution of trimethylindium at 0–25 °C, an exothermic reaction occurs and a pale yellow precipitate is formed. This is probably (CH₃In · PH)_{*n*}; it is insoluble in the usual organic solvents and is spontaneously inflammable in air.

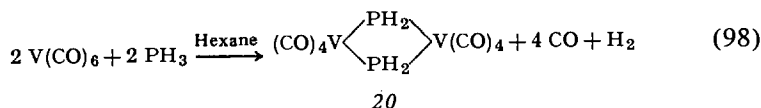
In water it decomposes to methane and phosphine. At 100–120 °C the substance sometimes decomposes with evolution of smoke or explosively. On heating to 250–270 °C, indium phosphide is formed as the residue²¹²).

Trimethylindium is readily soluble in liquid phosphine. A 1 : 1 adduct, (CH₃)₃In · PH₃, is probably formed at –123 °C. Above this temperature, at

about -112°C , it decomposes to $(\text{CH}_3)_3\text{In}$ and phosphine. At still higher temperatures, above about -78°C , condensation of the monomeric molecules occurs with the evolution of methane. The polymer of empirical composition $\text{CH}_3\text{In}\cdot\text{PH}$ thus formed, is stable up to about 95°C and decomposes at higher temperatures to CH_4 and InP ²¹³).

19. Phosphine as Ligand in Coordination Compounds

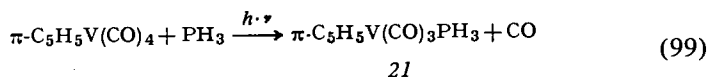
A deep-blue solution of $\text{V}(\text{CO})_4\text{PH}_2$ is formed on passing PH_3 into a hexane solution of vanadium hexacarbonyl at room temperature ²¹¹). A molecular weight determination of a benzene solution of the diamagnetic compound gave a value of twice the formula weight. Thus, apparently, a dimeric complex is formed. The infra-red spectrum confirms that PH_2 bridging groups with σ -bonds between vanadium and phosphorus are present.



Di- μ -phosphino-bis(tetracarbonylvandium), 20, is very soluble in hexane, benzene and methylene chloride and can be kept under a nitrogen atmosphere.

Mono- and diphenylphosphine also give the corresponding dimeric complexes with vanadium hexacarbonyl.

Whereas the above described reactions result only in dimeric compounds of the type 20, E. O. Fischer and co-workers ³³⁵) were recently able to prepare a carbonyl compound in which phosphine acts as a mono-dentate ligand. Tricarbonylcyclopentadienylphosphine vanadium, $\pi\text{-C}_5\text{H}_5\text{V}(\text{CO})_3\text{PH}_3$, 21, was obtained by exposing a solution of $\pi\text{-C}_5\text{H}_5\text{V}(\text{CO})_4$ in tetrahydrofuran or benzene under a phosphine atmosphere to UV light for several hours according to Eq. (99).



The ^1H n.m.r. spectrum shows a doublet with a chemical shift of $\tau = 6.81$ and a coupling constant $J_{\text{P-H}}$ of 324 Hz.

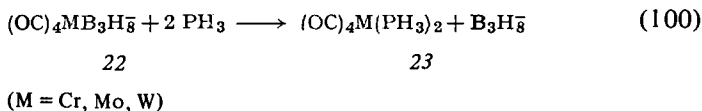
The following compounds can be obtained from analogous reactions:

- $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{PH}_3$ (red-brown, m.p. 72°C ; $\tau_{\text{PH}_3} = 6.76$; $J_{\text{P-H}} = 327$ Hz)
- $\text{Cr}(\text{CO})_5\text{PH}_3$ (pale yellow, m.p. 116°C , $\tau_{\text{PH}_3} = 7.55$; $J_{\text{P-H}} = 337.5$ Hz)
- $\text{Fe}(\text{CO})_4\text{PH}_3$ (bright yellow, m.p. 36°C , $\tau_{\text{PH}_3} = 7.85$; $J_{\text{P-H}} = 365$ Hz)
- $\text{Mo}(\text{CO})_5\text{PH}_3$ (colourless, m.p. 112°C (decomp.) $\tau_{\text{PH}_3} = 7.69$; $J_{\text{P-H}} = 327$ Hz)
- $\text{W}(\text{CO})_5\text{PH}_3$ (colourless, m.p. 120°C , $\tau_{\text{PH}_3} = 7.49$; $J_{\text{P-H}} = 341$ Hz)

Phosphine can also replace a carbonyl group in bromopentacarbonyl manganese³³⁶⁾. The compound, $\text{BrMn}(\text{CO})_4\text{PH}_3$, shows a doublet in the ^1H n.m.r. spectrum, $\tau = 6.58$, $J_{\text{P-H}} = 355$ Hz.

PF_3 as well as CO , as ligand in coordination compounds, can also be partially replaced by PH_3 ³³⁷⁾. $\text{HCo}(\text{PF}_3)_3\text{PH}_3$, a light yellow, sublimable compound (m.p. 25°C) is obtained when a mixture of $\text{HCo}(\text{PF}_3)_4$ and PH_3 is exposed to sunlight or to UV radiation from a mercury lamp, or when $\text{HCo}(\text{PF}_3)_3\text{CO}$ is treated with PH_3 . The ^1H n.m.r. spectrum of liquid $\text{HCo}(\text{PF}_3)_3\text{PH}_3$ shows a doublet of quartets, $\tau = 6.12$, $J_{\text{P-H}} = 352$, $J_{\text{F}_3\text{P-H}} = 17.6$ Hz, for the PH_3 group and a broad signal at $\tau = 24.4$ for the hydrogen atom bonded to cobalt. The hydrogen atom and the PH_3 group probably occupy axial positions of the trigonal bipyramid and the PF_3 groups the equatorial positions.

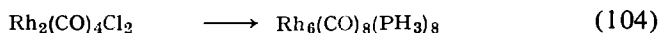
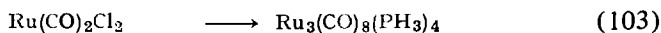
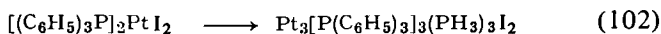
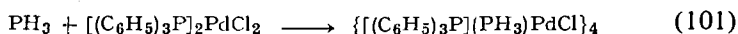
Klanberg and Muetterties³³⁶⁾ described the introduction of two phosphine ligands into a carbonyl compound. They reacted the octahydrotriboro-tetracarbonyl-metal anions (22), where $\text{M} = \text{Cr}, \text{Mo}$ or W , with phosphine and obtained the sublimable bisphosphino-metal tetracarbonyls (23) which are stable in air:

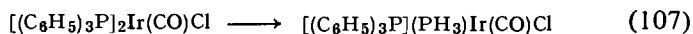
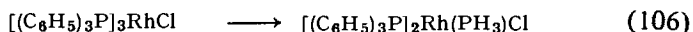


The chemical shifts in the ^1H and ^{31}P n.m.r. spectra of the molybdenum and tungsten compounds are $\tau = 6.31$ and 5.98 and $\delta_{\text{P}} = 155$ and 175 ppm (relative to H_3PO_4), respectively. The coupling constants, are 324 and 338 Hz, respectively.

Recently a compound with three PH_3 ligands bonded to a central atom was reported. Phosphine reacted rapidly and quantitatively at room temperature with a solution of tricarbonyl-hexamethylborazine chromium(0) in cyclohexane to give the octahedral tricarbonyltris(phosphine)chromium(0) in the *cis* configuration³⁴⁰⁾.

The structure of a series of other coordination compounds containing the PH_3 ligand, the preparations of which were described by Klanberg and Muetterties³³⁶⁾ according to the following Eqs. (101) to (107), are not individually known.





The authors strongly emphasise the facility with which metal clusters are apparently formed by these reactions.

V. Diphosphine and Higher Phosphines

Diphosphine, P_2H_4 , is a liquid at room temperature. The vapour pressure at 0°C is 73.0 mmHg, at -33.5°C it is 10 mmHg⁴²⁰. The average values for the extrapolated boiling point and the latent heat of evaporation of diphosphine are 63.5°C and 6889 cal/mol, respectively⁴²⁰⁻⁴²². The results are calculated from the values reported in the literature for the vapour pressure at various temperatures; however, some of these values vary greatly from one another. The melting point has been reported to be -99°C ⁴²¹. The heat of formation, calculated from the heat of explosion, for the formation of P_2H_4 from the elements was reported to be $H_{298}^0 = 5 \pm 1.0$ kcal/mol⁴²³. The most recent determination of the density of liquid diphosphine has shown that it is less dense than water⁴²⁴. Earlier, the density of liquid phosphine at 16°C was reported to be 1.016 g/cm³⁴²². Solid diphosphine has a density of 0.9 g/cm³⁴²⁴. At -136°C the lattice is built of monoclinic, and possibly also rhombic, unit cells each containing 2 molecules (space group C_2^1 or C_s^1)⁴²⁴.

The point group of the molecule is probably C_2 ⁴²⁴⁻⁴²⁶. The distances between the nuclei, calculated from the force constants, are $d(\text{P}-\text{P}) = 2.11$ Å and $d(\text{P}-\text{H}) = 1.44$ Å⁴²⁵. The IR and Raman spectra of diphosphine were carefully studied by Baudler and Schmidt⁴²⁵ and by Nixon⁴²⁴ and the n.m.r. spectra by Lynden-Bell⁴²⁷.

Diphosphine is formed by the hydrolysis of calcium phosphide^{422,424,425,428,429} and also by the hydrolysis of other phosphides when these contain P-P linkages. Thus, for example, it is reported that the phosphine obtained by the hydrolysis of aluminium phosphide, which has been prepared from the elements with phosphorus in excess, is spontaneously inflammable. This is caused by the diphosphine formed at the same time. When the aluminium phosphide is prepared using stoichiometric or even excess amounts of aluminium, the formation of diphosphine is not observed on hydrolysis. The diphosphine, formed in large quantities by the hydrolysis of calcium phosphide, can be separated from the phosphine and hydrogen evolved simultaneously by cool-

ing the gas mixture to -78°C and diphosphine can be subsequently purified by distillation under high vacuum ⁴²⁵). Diphosphine can also be obtained from the reaction of pure white phosphorus with potassium hydroxide solution at 60°C ⁴²¹). The formation of diphosphine has also been observed in the following reactions: by heating red phosphorus in a stream of hydrogen ⁴³⁰), by heating a mixture of red phosphorus and $\text{Ba}(\text{OH})_2$ ⁴³¹), by the action of atomic hydrogen on red phosphorus ⁴³²) and by the reaction of H_3PO_4 with acetyl chloride ⁴³³).

With B_2H_6 , diphosphine forms an adduct, $\text{P}_2\text{H}_4 \cdot \text{B}_2\text{H}_6$; with boron trifluoride at low temperatures the adduct $\text{P}_2\text{H}_4 \cdot 2\text{BF}_3$ is formed ⁴³⁴). On heating or exposure to light, diphosphine decomposes to PH_3 and higher phosphorus-hydrogen compounds ^{420,421,422,428,435}).

Triphosphine, P_3H_5 , has been identified as a product from the hydrolysis of Ca_3P_2 or Mg_3P_2 in acidic media by mass spectroscopy ⁴³⁸). In addition, using mass spectroscopic analysis Baudler and her co-workers ^{436,437}) were able to identify the following higher phosphines formed during the hydrolysis or the disproportionation of diphosphine:

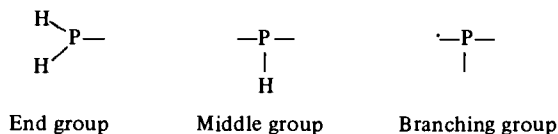
	$\text{P}_n\text{H}_{2n+2}$	P_nH_n	P_nH_{n-2}	P_nH_{n-4}	Others
Triphosphine	$\text{P}_3\text{H}_5^{\text{a)}$	$\text{P}_3\text{H}_3^{\text{a)}$			
Tetraphosphine	$\text{P}_4\text{H}_6^{\text{a)}$	$\text{P}_4\text{H}_4^{\text{a)}$	P_4H_2		
Pentaphosphine	P_5H_7	$\text{P}_5\text{H}_5^{\text{b)}$	$\text{P}_5\text{H}_3^{\text{b)}$		
Hexaphosphine	P_6H_8	P_6H_6	$\text{P}_6\text{H}_4^{\text{b)}$	P_6H_2	
Heptaphosphine	P_7H_9	P_7H_7	P_7H_5	$\text{P}_7\text{H}_3^{\text{b)}$	
Octaphosphine		P_8H_8	P_8H_6	$\text{P}_8\text{H}_4^{\text{b)}$	
Nonaphosphine		P_9H_9		P_9H_5	$\text{P}_9\text{H}_3^{\text{b)}$
Decaphosphine		$\text{P}_{10}\text{H}_{10}$	P_{10}H_8		$\text{P}_{10}\text{H}_4, \text{P}_{10}\text{H}_2^{\text{b)}$
Undecaphosphine					$\text{P}_{11}\text{H}_6, \text{P}_{11}\text{H}_3^{\text{b)}$
Dodecaphosphine					P_{12}H_4
Tetradecaphosphine					$\text{P}_{14}\text{H}(?)$

a) Main products.

b) Predominant products for the particular value of n .

The spontaneously inflammable nature of the higher phosphines decreases with increasing phosphorus content. At room temperature or on exposure to light, phosphorus-rich, yellow, solid phosphines are rapidly formed; these can also be obtained directly by thermal decomposition of diphosphine. The literature on these types of higher phosphorus hydrides which are, in general, solid and are thus referred to as "solid phosphorus hydrides" is abundant and

often contradictory ⁴³⁹). These are probably not discreet compounds but highly polymeric substances with no stoichiometric composition. They are probably composed of the following structural units:



The solid phosphorus hydrides are insoluble in all solvents generally used. They are relatively stable in air but are oxidised by strong oxidising agents.

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VI. Literature

- 1) Gengembre, P.: *Hist. Mém. Acad. Roy. Soc.* 10, 651 (1785).
- 2) Gengembre, P.: *Ann. Crell* 1789, I, 450.
- 3) Kirwan, R.: *Phil. Trans. Roy. Soc. (London)* 76, 11 (1786).
- 4) Gay-Lussac, L. J., Thénard, L. J.: *Rech. Phys.-Chim.* 1, 184 (1811).
- 5) Davy, H.: *Schweiggers J. Chem. Phys.* 1, 473 (1811); 7, 494 (1813).
- 6) Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S., Jaffé, I.: *Natl. Bur. Std. (U.S.), Circ. No. 500,571* (1952).
- 7) Clusius, K., Frank, A.: *Z. Physik. Chem.* B 34, 405 (1936).
- 8) Stephenson, C. C., Giauque, W. F.: *J. Chem. Phys.* 5, 149 (1937).
- 9) Clusius, K., Weigand, K.: *Z. Physik. Chem.* B 46, 1 (1940).
- 10) Hardin, A. H., Harvey, K. B.: *Can. J. Chem.* 42, 84 (1964).
- 11) Ritchie, M.: *Proc. Soc. (London)* A 128, 551 (1930).
- 12) Moles, E.: *Bull. Soc. Chim. Belges* 62, 67 (1953).
- 13) Natta, G., Casazza, E.: *Gazz. Chim. Ital.* 60, 851 (1930).
- 14) Ter Gazarian, G.: *J. Chim. Phys.* 7, 337 (1909), 9, 101 (1911); *Compt. Rend.* 148, 1397 (1909).
- 15) Stock, A., Henning, F., Kuss, E.: *Ber. Deut. Chem. Ges.* 54 B, 1119 (1921).
- 16) Skinner, S.: *Proc. Roy. Soc. (London)* 42, 283 (1887).
- 17) Frank, A., Clusius, K.: *Z. Physik. Chem.* B 42, 395 (1939).
- 18) Herzberg, G.: *The structure of diatomic molecules.* New York: Van Nostrand 1950.
- 19) McConaghie, V. M.: *Proc. Natl. Acad. Sci. U.S.* 34, 455 (1948).
- 20) McConaghie, V. M., Nielsen, H. H.: *J. Chem. Phys.* 21, 1836 (1953).
- 21) Nielsen, H. H.: *J. Chem. Phys.* 20, 759 (1952).
- 22) Weston, R. E., Sirvetz, M. H.: *J. Chem. Phys.* 20, 1820 (1952).
- 23) Morse, P. M., Stükelberg, E. C. G.: *Helv. Phys. Acta* 4, 337 (1931).
- 24) Sundaram, S., Suszek, F., Cleveland, F. F.: *J. Chem. Phys.* 32, 251 (1960).
- 25) Siebert, H.: *Z. Anorg. Allgem. Chem.* 274, 24 (1953).
- 26) Yost, M., Anderson, T. F.: *J. Chem. Phys.* 2, 624 (1934).

- 27) Burrus, C. A., Jacke, A., Gordy, W.: *Phys. Rev.* *95*, 706 (1954).
- 28) Loomis, C. C., Strandberg, M. W. P.: *Phys. Rev.* *81*, 798 (1951).
- 29) Sirvetz, M. H., Weston, R. E.: *J. Chem. Phys.* *21*, 898 (1953).
- 30) Van Wazer, J. R., Callis, C. F., Shoolery, J. N., Jones, R. C.: *J. Am. Chem. Soc.* *78*, 5715 (1956).
- 31) Bartell, L. S.: *J. Chem. Phys.* *32*, 832 (1960).
- 32) Bartell, L. S., Brockway, L. O.: *J. Chem. Phys.* *32*, 512 (1960).
- 33) Bartell, L. S., Hirst, R. C.: *J. Chem. Phys.* *31*, 449 (1959).
- 34) Kuchitsu, K.: *J. Mol. Spectry.* *7*, 399 (1961).
- 35) Lippincott, E. R., Dayhoff, M. O.: *Spectrochim. Acta* *16*, 807 (1960).
- 36) Moccia, R.: *J. Chem. Phys.* *37*, 910 (1962).
- 37) Kojima, T., Breig, E. L., Lin, C. C.: *J. Chem. Phys.* *35*, 2139 (1960).
- 38) Pratt, L., Richards, R. E.: *Trans. Faraday Soc.* *50*, 670 (1954).
- 39) Van Wazer, J. R.: *Phosphorus and its compounds*, Vol. I. New York: Interscience Publ. 1958.
- 40) Cottrell, T. L.: *The strength of chemical bonds*, p. 271. London: Butterworth's 1958.
- 41) Banyard, K. E., Hake, R. B.: *J. Chem. Phys.* *43*, 2684 (1965).
- 42) Burrus, C. A.: *J. Chem. Phys.* *28*, 427 (1958).
- 43) Weaver, J. R., Parry, R. W.: *Inorg. Chem.* *5*, 718 (1966).
- 44) Gibbs, J. H.: *J. Phys. Chem.* *59*, 644 (1955).
- 45) Gibbs, J. H.: *J. Chem. Phys.* *22*, 1460 (1954).
- 46) Wilmshurst, J. K.: *J. Chem. Phys.* *33*, 813 (1960).
- 47) Van Wazer, J. R.: *J. Am. Chem. Soc.* *78*, 5709 (1956).
- 48) Paddock, N. L.: *Structure and reactions in phosphorus chemistry*, The Royal Institute of Chemistry, Lecture Series 1962, No. 2, p. 4.
- 49) Lynden-Bell, R. M.: *Trans. Faraday Soc.* *57*, 888 (1961).
- 50) Gillespie, R. J.: *J. Am. Chem. Soc.* *82*, 5978 (1960).
- 51) Mulliken, R. S.: *J. Am. Chem. Soc.* *77*, 887 (1955).
- 52) Hutchinson, D. A.: *Can. J. Chem.* *44*, 2711 (1966).
- 53) Fung, L. W., Barker, E. F.: *Phys. Rev.* *45*, 238 (1934).
- 54) Howard, J. B.: *J. Chem. Phys.* *3*, 207 (1935).
- 55) Lee, E., Wu, C. K.: *Trans. Faraday Soc.* *35*, 1366 (1939).
- 56) McKean, D. C., Schatz, P. N.: *J. Chem. Phys.* *24*, 316 (1956).
- 57) Melville, H. W.: *Nature* *129*, 546 (1932).
- 58) Cheesman, G. H., Emeléus, H. J.: *J. Chem. Soc.* *1932*, 2847.
- 59) Mayor, L., Walsh, A. D., Warsop, P.: *J. Mol. Spectry.* *10*, 320 (1963).
- 60) Halmann, M.: *J. Chem. Soc.* *1963*, 2853.
- 61) Stevenson, D. P., Coppinger, G. M., Forbes, J. W.: *J. Am. Chem. Soc.* *83*, 4350 (1961).
- 62) Walsh, A. D., Warsop, P. A.: *Advan. Mol. Spectry.* *2*, 582 (1962).
- 63) Wada, Y., Kiser, R. W.: *Inorg. Chem.* *3*, 174 (1964).
- 64) Neuert, H., Clasen, H.: *Z. Naturforsch.* *7a*, 410 (1952).
- 65) Saalfeld, F. E., Svec, H. J.: *Inorg. Chem.* *2*, 46 (1963).
- 66) Saalfeld, F. E., Svec, H. J.: *Inorg. Nucl. Chem.* *18*, 98 (1961).
- 67) Watanabe, K.: *J. Chem. Phys.* *26*, 542, 1773 (1957).
- 68) Frost, D. C., McDowell, C. A.: *Can. J. Chem.* *36*, 39 (1958).
- 69) Varsel, C. J., Morrell, F. A., Resnik, F. E., Powell, W. A.: *Anal. Chem.* *32*, 182 (1960).
- 70) Dibeler, V. H., Franklin, J. L., Reese, R. M.: *J. Am. Chem. Soc.* *81*, 68 (1959).
- 71) Kley, D., Welge, K. H.: *Z. Naturforsch.* *20a*, 124 (1965).
- 72) Norrish, R. G. W., Oldershaw, G. A.: *Proc. Roy. Soc. (London)* *A 262*, 1 (1961).
- 73) Weston, R. E.: *J. Am. Chem. Soc.* *76*, 1027 (1954).
- 74) Weston, R. E., Bigeleisen, J.: *J. Am. Chem. Soc.* *76*, 3074 (1954).

- 75) Sheldrick, G. M.: *Trans. Faraday Soc.* 1967, 1077.
- 76) Wendlandt, W.: *Science* 122, 831 (1955).
- 77) Waddington, F. C.: *Trans. Faraday Soc.* 61, 2652 (1965).
- 78) Sheldon, J. C., Tyree, S. Y.: *J. Am. Chem. Soc.* 80, 2117 (1958).
- 79) Thomson, T.: *Ann. Phil. Thomson* [2] 8, 87 (1816).
- 80) Pearson, G.: *Phil. Trans. Roy. Soc. (London)* 1792, 289.
- 81) Thénard, P.: *Compt. Rend.* 18, 652 (1844); 19, 313 (1844); *Ann. Chim. Phys.* [3], 14, 5 (1845).
- 82) Moissan, H.: *Compt. Rend.* 128, 787 (1899).
- 83) Dalton, J.: *Ann. Phil. Thomson* [2] 11, 7 (1818).
- 84) Schwarz, H.: *Dinglers Polytech. J.* 191, 396 (1869).
- 85) Brandstätter, F.: *Z. Phys. Chem. Unterricht* 11, 65 (1898).
- 86) Lüpke, R.: *Z. Phys. Chem. Unterricht* 3, 280 (1890).
- 87) Saalfeld, F. E., Svec, H. J.: *IS-386*, 68 (1961); *C.A.* 57, 236 (1962).
- 88) Fonzes-Diacon, H.: *Compt. Rend.* 130, 1314 (1900).
- 89) Quesnel, G.: *Compt. Rend.* 253, 1450 (1961).
- 90) Bodroux, F.: *Bull. Soc. Chim. France* [3] 27, 568 (1902).
- 91) Kuznetsov, E. V., Valetdinov, R. K., Zavlina, P. M.: *USSR Pat.* 125 551 (1960).
- 92) Kuznetsov, E. V., Valetdinov, R. K., Roitburd, T. Ya., Zakharova, L. B.: *Tr. Kazakhsk. Khim.-Tekhnol. Inst.* 1960, 20; *C.A.* 58, 547 (1963).
- 93) Pass, F., Steininger, E., Zorn, H.: *Monatsh. Chem.* 93, 230 (1962).
- 94) Bädler, M., Ständeke, H., Borgardt, M., Strabel, H., Dobbbers, J.: *Naturwissenschaften* 53, 106 (1966).
- 95) Fluck, E., Novobilsky, V.: Unpublished results.
- 96) Landolt, H.: *Liebigs Ann. Chem.* 116, 193 (1860).
- 97) Matignon, C.: *Compt. Rend.* 130, 1391 (1900).
- 98) Moser, L., Brukl, A.: *Z. Anorg. Allgem. Chem.* 121, 73 (1922).
- 99) White, W. E., Bushey, A. H.: *J. Am. Chem. Soc.* 66, 1666 (1944).
- 100) Montignie, E.: *Bull. Soc. Chim. France* 1946, 276.
- 101) Dumas, J. B. A.: *Ann. Chim. Phys.* [2] 31, 113 (1826).
- 102) Rose, H.: *Ann. Physik* [2] 24, 109, 295 (1832); 32, 467 (1834).
- 103) Weyl, T.: *Ber. Deut. Chem. Ges.* 39, 1307 (1906).
- 104) Commaille, A.: *J. Pharm.* [2] 8, 321 (1868).
- 105) Hofmann, A. W.: *Ber. Deut. Chem. Ges.* 4, 200 (1871).
- 106) Wartik, T., Apple, E. F.: *J. Am. Chem. Soc.* 80, 6155 (1958).
- 107) Rose, H.: *Ann. Physik* [2] 8, 191 (1826); 24, 109 (1832).
- 108) Martin, D. R., Dial, R. E.: *J. Am. Chem. Soc.* 72, 852 (1950).
- 109) Houton de la Billardière, J. J.: *Ann. Chim. Phys.* 6, 304 (1817).
- 110) Lepsius, B.: *Ber. Deut. Chem. Ges.* 23, 1642 (1890).
- 111) Rammelsberg, C.: *Ber. Deut. Chem. Ges.* 6, 88 (1873).
- 112) Messinger, J., Engels, C.: *Ber. Deut. Chem. Ges.* 21, 326 (1888).
- 113) Stock, A., Henning, F., Kuss, E.: *Ber. Deut. Chem. Ges.* 54 B, 1119 (1921).
- 114) Robertson, R., Fox, J. J., Hiscocks, E. S.: *Proc. Roy. Soc. (London)* A 120, 149 (1928).
- 115) Paddock, N. L.: *Nature* 167, 1070 (1951).
- 116) Gunn, S. R., Green, L. G.: *J. Phys. Chem.* 65, 779 (1961).
- 117) Wiberg, E., Müller-Schiedmayer, G.: *Chem. Ber.* 92, 2372 (1959).
- 118) *Niederl. Pat.-Anm.* 6 504 634 (1965); *C.A.* 64, 13803 (1966).
- 119) Palmer, M. G.: *Brit. Pat.* 943 281 (1963); *C.A.* 60, 6524 (1964).
- 120) Baudler, M., Schellenberg, D.: *Z. Anorg. Allgem. Chem.* 340, 113 (1965).
- 121) Matignon, C., Trannoy, R.: *Compt. Rend* 148, 167 (1909).

- 122) Royen, P., Hill, K.: *Z. Anorg. Allgem. Chem.* 229, 112 (1936).
- 123) Addison, W. E., Plummer, J.: *Chem. Ind. (London)* 1961, 935.
- 124) Joannis, A.: *Ann. Chim. Phys.* [8] 7, 101 (1906).
- 125) Joannis, A.: *Compt. Rend.* 119, 557 (1894).
- 126) Royen, P., Zschaage, W., Wutschel, A.: *Angew. Chem.* 67, 75 (1955).
- 127) Knunyants, I. L., Sterlin, R. N.: *Dokl. Akad. Nauk SSSR* 56, 49 (1947); *C.A.* 42, 519 (1948).
- 128) Wagner, R. I., Burg, A. B.: *J. Am. Chem. Soc.* 75, 3869 (1953).
- 129) Legoux, C.: *Compt. Rend.* 207, 634 (1938).
- 130) Teach, E. G., Leffler, A. J.: *USP* 2964379.
- 131) Albers, H., Schuler, W.: *Ber. Deut. Chem. Ges.* 76, 23 (1943).
- 132) Bergerhoff, G., Schultze-Rhonhoff, E.: *Acta Cryst.* 15, 420 (1962).
- 133) Knoll, F., Bergerhoff, G.: *Monatsh. Chem.* 97, 808 (1966).
- 134) Brauer, G., Zintl, E.: *Z. Physik. Chem.* 37 B, 323 (1937).
- 135) Endrzheevskaya, S. N., Samsonov, G. V.: *Zh. Obshch. Khim.* 35, 1983 (1965); *C.A.*, 64, 6064 (1966).
- 136) Samsonov, G. V., Vereikina, L. L., Endrzheevskaya, S. N., Tikhonova, N. N.: *Ukr. Khim. Zh.* 32, 115 (1966); *C.A.* 64, 15348 (1966).
- 137) Vickery, R. C.: *Nature* 184, 268 (1959).
- 138) Williams, F. V., Ruehrwein, R. A.: *J. Am. Chem. Soc.* 82, 1330 (1960).
- 139) Effer, D., Antell, G. R.: *J. Electrochem. Soc.* 107, 252 (1960).
- 140) Samsonov, G. V., Vereikina, L. L., Titkov, Yu. V.: *Zh. Neorgan. Khim.* 6, 749 (1961); *C.A.* 56, 15 125 (1962); *Pat. USSR* 136327 (1961); 55, 21511 (1961).
- 141) Tikhonova, N. N.: *Azerb. Khim. Zh.* 1965, 139; *C.A.* 64, 18935 (1966).
- 142) Vereikina, L. L., Samsonov, G. V.: *Zh. Neorgan. Khim.* 5, 1888 (1960); *C.A.* 57, 1834 (1962).
- 143) Samsonov, G. V., Vereikina, L. L.: *USSR Pat.* 127 028 (1960); *C.A.* 54, 18912 (1960).
- 144) Sheldrick, G. M.: *Trans. Faraday Soc.* 1967, 1065.
- 145) Ebsworth, E. A. V., Sheldrick, G. M.: *Trans. Faraday Soc.* 1967, 1071.
- 146) Fischer, H., Wiberg, E.: *DBP* 1042539 (1958); *C.A.* 54, 20519 (1960); *C.Z.* 1959, 6593.
- 147) Vickery, R. C.: *Nature* 184, 268 (1959).
- 148) Schumann, H., Schwabe, P., Schmidt, M.: *Inorg. Nucl. Chem. Letters* 2, 309 (1966).
- 149) Schumann, H., Roth, A., Stelzer, O., Schmidt, M.: *Inorg. Nucl. Chem. Letters* 2, 311 (1966).
- 150) Parshall, G. W., Lindsey, R. V.: *J. Am. Chem. Soc.* 81, 6273 (1959).
- 151) Bürger, H.: Personal communication.
- 152) Stock, A., Kuss, E.: *Ber. Deut. Chem. Ges.* 56 B, 789 (1923).
- 153) Stock, A., Pohland, E.: *Ber. Deut. Chem. Ges.* 59 B, 2215 (1926).
- 154) Stock, A., Wiberg, E., Martini, H., Nicklas, A.: *Ber. Deut. Chem. Ges.* 65 B, 1711 (1932).
- 155) Gamble, E. L., Gilmont, P.: *J. Am. Chem. Soc.* 62, 717 (1940).
- 156) Rudolph, R. W., Parry, R. W., Farran, C. F.: *Inorg. Chem.* 5, 723 (1966).
- 157) Besson, A.: *Compt. Rend.* 110, 516 (1890).
- 158) Tierney, P. A., Lewis, D. W., Berg, D.: *J. Inorg. Nucl. Chem.* 24, 1163 (1962).
- 159) Phillips, G. M., Hunter, J. S., Sutton, L. E.: *J. Chem. Soc.* 1945, 146.
- 160) Brumberger, H., Marcus, R. A.: *J. Chem. Phys.* 24, 741 (1956).
- 161) Drake, J. E., Simpson, J.: *Inorg. Nucl. Chem. Letters* 3, 87 (1967).
- 162) Fritz, G.: *Z. Naturforsch.* 8b, 776 (1953).
- 163) Fritz, G.: *Z. Anorg. Allgem. Chem.* 280, 332 (1955).
- 164) Gokhale, S. D., Jolly, W. L.: *Inorg. Chem.* 4, 596 (1965).

- 165) Gokhale, S. D., Jolly, W. L.: *Inorg. Chem.* 3, 1141 (1964).
- 166) Aylett, B. J., Emeléus, H. J., Maddock, A. G.: *J. Inorg. Nucl. Chem.* 1, 187 (1955).
- 167) Amberger, E., Boeters, H. D.: *Chem. Ber.* 97, 1999 (1964).
- 168) Beagley, B., Robiette, A. G., Sheldrick, G. M.: *Chem. Commun.* 1967, 601.
- 169) Beagley, B.: *Chem. Commun.* 1966, 388.
- 170) Finholt, A. E., Helling, C., Imhof, V., Nielsen, L., Jacobson, E.: *Inorg. Chem.* 2, 504 (1963).
- 171) Messinger, J., Engels, C.: *Ber. Deut. Chem. Ges.* 21, 326 (1888).
- 172) Messinger, J., Engels, C.: *Ber. Deut. Chem. Ges.* 21, 2919 (1888).
- 173) de Girard, J.: *Ann. Chim. Phys., Ser. VII*, 2, 2 (1884).
- 174) Hoffman, A.: *J. Am. Chem. Soc.* 43, 1684 (1921).
- 175) Hoffman, A.: *J. Am. Chem. Soc.* 52, 2995 (1930).
- 176) Reeves, W. A., Flynn, F. F., Guthrie, J. D.: *J. Am. Chem. Soc.* 77, 3923 (1955).
- 177) Horak, J., Ettel, V.: *Collection Czech. Chem. Commun.* 26, 2401 (1961).
- 178) Raver, K. R., Bruker, A. B., Soborovskii, L. Z.: *Zh. Obshch. Khim.* 32, 588 (1962); *C.A.* 58, 6857 (1963).
- 179) Raver, K. R., Soborovskii, L. Z.: *SSSR Pat.*, 143 395; *C.A.* 57, 9882 (1962).
- 180) Bruker, A. B., Baranaev, M. K., Grinshtein, E. I., Novoselova, R. I., Prokhorova, V. V., Soborovskii, L. Z.: *Zh. Obshch. Khim.* 33, 1919 (1963); *C.A.* 59, 11207 (1963).
- 181) Emeléus, H. J.: *J. Chem. Soc.* 1954, 2979.
- 182) Coates, H., Hoyer, P. A.: *Brit. Pat.*, 854.182 (1960).
- 183) Buckler, S. A., Doll, L.: *U.S. Pat.*, 2,999,882 (1959).
- 184) de Girard, A.: *Ann. Chim.* [6] 2, 11 (1884).
- 185) Buckler, S. A.: *U.S. Pat.*, 3,013,085 (1961); *C.A.* 57, 11236 (1962).
- 186) Buckler, S. A., Wystrach, V. P.: *J. Am. Chem. Soc.* 80, 6454 (1958).
- 187) Buckler, S. A., Wystrach, V. P.: *J. Am. Chem. Soc.* 83, 168 (1961).
- 188) Hart, F. A., Mann, F. G.: *J. Chem. Soc.* 1955, 4107.
- 189) Buckler, S. A.: *J. Am. Chem. Soc.* 82, 4215 (1960).
- 190) Ettel, V., Horak, J.: *Collection Czech. Chem. Commun.* 26, 1949 (1961).
- 191) Buckler, S. A., Epstein, M.: *J. Am. Chem. Soc.* 82, 2076 (1960).
- 192) Buckler, S. A., Epstein, M.: *Tetrahedron* 18, 1211 (1962).
- 193) Buckler, S. A., Epstein, M.: *Tetrahedron* 18, 1221 (1962).
- 194) Parshall, G. W.: *Inorg. Chem.* 4, 52 (1965).
- 195) Epstein, M., Buckler, S. A.: *J. Am. Chem. Soc.* 83, 3279 (1961).
- 196) Stiles, A. R., Rust, F. F., Vaughan, W. E.: *J. Am. Chem. Soc.* 74, 3282 (1952); *U.S. Pat.* 2,803,597 (1959).
- 197) Rauhut, M. M., Currier, H. A., Semsel, A. M., Wystrach, V. P.: *J. Org. Chem.* 26, 5138 (1961).
- 198) Bereslavsky, E. V.: *U.S. Pat.* 2,797,153 (1957).
- 199) Brown, H. C.: *U.S. Pat.* 2,584,112 (1952).
- 200) Rauhut, M. M., Hechenbleikner, I., Currier, H. A., Schaefer, F. C., Wystrach, V. P.: *J. Am. Chem. Soc.* 81, 1103 (1959).
- 201) Hoff, M. C., Hill, P.: *J. Org. Chem.* 24, 356 (1959).
- 202) Ingold, C. K.: *Structure and mechanism in organic chemistry*, p. 691. Ithaca, N. Y.: Cornell University Press 1953.
- 203) Burch, G. M., Goldwhite, H., Haszeldine, R. N.: *J. Chem. Soc.* 1963, 1083.
- 204) Fields, R., Goldwhite, H., Haszeldine, R. N., Kirman, J.: *J. Chem. Soc.* 1966, 2075.
- 205) Parshall, G. W., England, D. C., Linsey, R. V.: *J. Am. Chem. Soc.* 81, 4801 (1959).
- 206) England, D. C., Parshall, G. W.: *U.S. Pat.* 2,879,302 (1959).
- 207) Buckler, S. A.: *J. Org. Chem.* 24, 1460 (1959).
- 208) Buckler, S. A.: *U.S. Pat.* 2,969,390 (1961).

- 209) Papp, G. P., Buckler, S. A.: *J. Org. Chem.* 31, 588 (1966).
210) Hunter, R. F.: *Chem. News* 1930, 50.
211) Hieber, W., Winter, E.: *Chem. Ber.* 97, 1037 (1964).
212) Coates, G. E., Whitcombe, R. A.: *J. Chem. Soc.* 1956, 3351.
213) Didchenko, R., Alix, J. E., Toeniskoetter, R. M.: *J. Inorg. Nucl. Chem* 14, 35 (1960).
214) Job, A., Dusollier, G.: *Compt. Rend.* 184, 1454 (1927).
215) Lecoq, H.: *Bull. Soc. Chim. Belges* 42, 199 (1933).
216) Mann, F. G., Miller, I. T.: *J. Chem. Soc.* 1952, 3039.
217) Tyka, R., Plazek, E.: *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* 9, 577 (1961).
218) Plazek, E., Tyka, R.: *Roczniki Chem.* 33, 549 (1959).
219) Lawless, J. J., Searle, H. T.: *J. Chem. Soc.* 1962, 4200.
220) Svehla, P.: *Collection Czech. Chem. Commun.* 31, 4712 (1966); *C.A.* 66, 61329 (1967).
221) Paris, R., Tardy, P.: *Compt. Rend.* 223, 242 (1946).
222) Horak, J., Ettel, V.: *Sb. Vysoke Skoly Chem.-Technol. Praze, Org. Technol* 5, 93 (1960); *C.A.* 62, 12440 (1965).
223) Haszeldine, R. N., Kidd, J. M.: *J. Chem. Soc.* 1953, 3219.
224) Emeléus, H. J., Nabi, S. N.: *J. Chem. Soc.* 1960, 1103.
225) Flury, F., Zernik, F.: *Schädliche Gase*, S. 170. Berlin 1931.
226) Flury, F.: *Arch. Exptl. Pathol. Pharmakol.* 138, 71 (1928).
227) Kloos, E. J., Spinetti, L., Raymond, L. D.: *U.S. Bureau of Mines, Inform. Circ.* Nr. 8291, 7 (1966).
228) Wiesner, H.: *Monatsschr. Kinderheilk.* 105, 312 (1957).
229) Hallermann, W., Pribilla, O.: *Arch. Toxikol.* 17, 219 (1959).
230) Klimmer, O. R.: *Arch. Toxikol.* 24, 164 (1969).
231) Trautz, M., Bhandarkar, D. S.: *Z. Anorg. Allgem. Chem.* 106, 95 (1919).
232) Hinshelwood, C. N., Topley, B.: *J. Chem. Soc.* 125, 393 (1924).
233) Melville, H. W., Roxburgh, H. L.: *J. Chem. Soc.* 1933, 586.
234) Trautz, M., Gabler, W.: *Z. Anorg. Allgem. Chem.* 180, 321 (1929).
235) Shantarovich, P. S.: *Acta Physiochim. USSR* 6, 65 (1937); *C.A.* 31, 7304 (1937).
236) Melville, H. W., Roxburgh, H. L.: *J. Chem. Soc.* 1934, 264.
237) Andreev, E. A., Kavtaradze, N. N.: *Probl. Kinetiki i Kataliza, Akad. Nauk SSSR* 6, 293 (1949); *C.A.* 47, 5776 (1953).
238) Andreev, E. A., Kavtaradze, N. N.: *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1952, 1021; *C.A.* 47, 5777 (1953).
239) Dalton, R. H., Hinshelwood, C. N.: *Proc. Roy. Soc. (London) A* 125, 294 (1929).
240) Dalton, R. H.: *Proc. Roy. Soc. (London) A* 128, 263 (1930).
241) Gray, S. C., Melville, H. W.: *Trans. Faraday Soc.* 31, 452 (1935).
242) Melville, H. W., Roxburgh, H. L.: *J. Chem. Phys.* 2, 739 (1934).
243) Bushmakina, I. N., Vvedenskii, A. A., Frost, A. V.: *J. Gen. Chem. (USSR)* 2, 415 (1932); *C.A.* 27, 1806 (1933).
244) Bushmakina, I. N., Frost, A. V.: *J. Appl. Chem. (USSR)* 6, 607 (1933); *C.A.* 28, 3677 (1934).
245) Bendall, J. R., Mann, F. G., Purdie, D.: *J. Chem. Soc.* 1942, 157.
246) Wichelhaus, H.: *Ber. Deut. Chem. Ges.* 38, 1725 (1905).
247) Weyl, T.: *Ber. Deut. Chem. Ges.* 39, 4340 (1906).
248) Buckler, S. A., Doll, L., Lind, F. K., Epstein, M.: *J. Org. Chem.* 27, 794 (1962).
249) Guenebaut, H., Pascat, B.: *J. Chim. Phys.* 61, 592 (1964).
250) Guenebaut, H., Pascat, B.: *Compt. Rend.* 267, 677 (1963).
251) Guenebaut, H., Pascat, B.: *Compt. Rend.* 295, 2412 (1964).
252) Guenebaut, H., Pascat, B., Berthou, J. M.: *J. Chim. Phys.* 62, 867 (1965).

- 253) Wiles, D. M., Winkler, C. A.: *J. Phys. Chem.* *61*, 620 (1957).
- 254) Guenebaut, H., Pascat, B.: *Compt. Rend.* *256*, 2850 (1963).
- 255) Norrish, R. G. W., Oldershaw, G. A.: *Proc. Roy. Soc. (London) A* *262*, 10 (1961).
- 256) Moser, L., Brukl, A.: *Z. Anorg. Allgem. Chem.* *121*, 78 (1922).
- 257) Brukl, A.: *Z. Anorg. Allgem. Chem.* *125*, 252 (1922).
- 258) Scholder, R., Apel, A., Haken, H. L.: *Z. Anorg. Allgem. Chem.* *232*, 1 (1937).
- 259) Birchall, T., Jolly, W. L.: *Inorg. Chem.* *5*, 2177 (1966).
- 260) Rudolph, R. W., Parry, R. W.: *J. Am. Chem. Soc.* *89*, 1621 (1967).
- 261) Borde, C., Henry, A., Henry, L.: *Compt. Rend. Acad. Sci. Paris, Ser. A, B* *263 B*, 619 (1966).
- 262) Halmann, M., Platzner, I.: *J. Phys. Chem.* *71*, 4522 (1967).
- 263) Drake, J. E., Simpson, J.: *J. Chem. Soc. (London) A* *1968*, 974.
- 264) Fourcroy, A. F., de Vauquelin, L. D.: *Ann. Chim. (Paris)* *21*, 189 (1797).
- 265) Davy, H.: *Phil. Trans. Roy. Soc. (London)* *1809*, 39, 450.
- 266) Schneider, W. G., Bernstein, H. J., Pople, J. A.: *J. Chem. Phys.* *28*, 601 (1958).
- 267) Staveley, L. A. K., Tupman, W. J.: *J. Chem. Soc.* *1950*, 3597.
- 268) Durrant, A. A., Pearson, T. G., Robinson, P. L.: *J. Chem. Soc.* *1934*, 730.
- 269) Briner, E.: *J. Chim. Phys.* *4*, 476 (1906).
- 270) Berl, E.: *Chem. Met. Eng.* *53*, 130 (1946).
- 271) Kordes, E.: *Z. Elektrochem.* *57*, 731 (1953).
- 272) Pickering, S. F.: *Natl. Bur. Std. (U.S.) Circ. No.* *279*, 1 (1926).
- 273) Leduc, A., Sacerdote, P.: *Compt. Rend.* *125*, 379 (1897).
- 274) Fritz, G.: *Z. Naturforsch.* *8b*, 776 (1953).
- 275) Fritz, G.: *Z. Anorg. Allgem. Chem.* *280*, 332 (1955).
- 276) Leverrier, U. J. J.: *Ann. Chim. Phys.* *60*, 174 (1835).
- 277) Amato, D.: *Gazz. Chim. Ital.* *14*, 57 (1884).
- 278) Retgers, J. W.: *Z. Anorg. Allgem. Chem.* *7*, 265 (1894).
- 279) *Inorganic syntheses*, Vol. II, p. 141. New York: McGraw-Hill Book Co. 1946.
- 280) Legoux, C.: *Compt. Rend.* *209*, 47 (1939).
- 281) de Guye, P.: *Bull. Soc. Chim. France* *5*, 339 (1909).
- 282) Matheson, G. L., Maass, O.: *J. Am. Chem. Soc.* *51*, 674 (1929).
- 283) Rose, H.: *Ann. Physik* [2] *24*, 109 (1832).
- 284) Kelley, K. K.: *U.S. Bur. Mines Bull. Nr.* *383*, 1 (1935).
- 285) Dalton, J.: *Ann. Phil. Thomson* [2] *11*, 7 (1818).
- 286) Steacie, E. W. R., McDonald, R. D.: *Can. J. Res.* *12*, 711 (1924).
- 287) Horner, L., Beck, P., Hoffmann, H.: *Chem. Ber.* *92*, 2088 (1959).
- 288) Aylett, B. J., Emeléus, H. J., Maddock, A. G.: *J. Inorg. Nucl. Chem.* *1*, 187 (1955).
- 289) Burg, A. B., Wagner, I.: *J. Am. Chem. Soc.* *75*, 3872 (1953).
- 290) Martin, D. R., Dial, R. E.: *J. Am. Chem. Soc.* *72*, 852 (1950).
- 291) Wiberg, E., Heubbaum, U.: *Z. Anorg. Allgem. Chem.* *225*, 270 (1935).
- 292) Parry, R. W., Bissot, T. C.: *J. Am. Chem. Soc.* *78*, 1524 (1956).
- 293) Besson, A.: *Compt. Rend.* *110*, 80 (1890).
- 294) Besson, A.: *Compt. Rend.* *110*, 516 (1890).
- 295) Waddington, T. C., Klanberg, F.: *J. Chem. Soc.* *1960*, 2332.
- 296) Wartik, T., Apple, E. F.: *J. Am. Chem. Soc.* *80*, 6155 (1958).
- 297) Besson, A.: *Compt. Rend.* *113*, 78 (1891).
- 298) Fischer, A.: *Z. Naturforsch.* *13a*, 105 (1958).
- 299) Höltje, R.: *Z. Anorg. Allgem. Chem.* *190*, 241 (1930).
- 300) Besson, A.: *Compt. Rend.* *110*, 240 (1890).
- 301) Stock, A., Böttcher, W., Lenger, W.: *Ber. Deut. Chem. Ges.* *42*, 2839 (1909).
- 302) Waddington, T. C., Nabi, S. N.: *Proc. Pakistan Sci. Conf.* *12*, Pt 13, C 7 (1960);

- C.A. 56, 9678 (1962).
- 303) Royen, P., Hill, K.: *Z. Anorg. Allgem. Chem.* 229, 112 (1936).
- 304) Besson, A.: *Compt. Rend.* 110, 1258 (1890).
- 305) Janovsky, J. V.: *Ber. Deut. Chem. Ges.* 8, 1936 (1875).
- 306) Gutmann, V.: *Z. Anorg. Allgem. Chem.* 266, 331 (1951).
- 307) Ogier, J.: *Bull. Soc. Chim. France* [2] 32, 483 (1879); *Compt. Rend.* 89, 705 (1879); *Ann. Chim. Phys.* [5] 20, 5 (1880).
- 308) Skinner, S.: *Proc. Roy. Soc. (London)* 42, 283 (1887).
- 309) Sérullas, G. S.: *Ann. Chim. Phys.* 48, 87 (1831).
- 310) Reuter, M., Orthner, L.: *DBP* 1041957 (1958); C.A. 55, 1444 (1961).
- 311) de Fourcroy, A. F.: *Ann. Chim. Phys.* 4, 249 (1790).
- 312) Horak, J.: *Chem. Listy* 55, 1278 (1961).
- 313) Stock, A.: *Ber. Deut. Chem. Ges.* 53, 837 (1920).
- 314) Solovev, V. K.: *Gorn. Zh.* 115, 34 (1939); *Chem. Zentralbl.* 1940, I, 3967.
- 315) Devyatykh, G. G., Ezheleva, A. E., Zorin, A. D., Zueva, M. V.: *Zh. Neorgan. Khim.* 8, 1307 (1963).
- 316) Hofmann, A. W.: *Liebigs Ann. Chem.* 103, 355 (1857).
- 317) Holt, A., Myers, J. E.: *Z. Anorg. Allgem. Chem.* 82, 278 (1913).
- 318) Corbridge, D. E. C.: *Topics in phosphorus chemistry*, Vol. 3, p. 91. New York: Interscience Publ. 1966.
- 319) Durrant, A. A., Pearson, T. G., Robinson, P. L.: *J. Chem. Soc.* 1934, 730.
- 320) Steele, B. D., McIntosh, D.: *Z. Phys. Chem.* 55, 140 (1906).
- 321) Dobinski, S.: *Z. Physik* 83, 129 (1933).
- 322) Cauquil, G.: *J. Chim. Phys.* 24, 53 (1927).
- 323) Reuter, M., Orthner, L.: *DBP* 1035135 (1958); C.A. 54, 14125 (1960).
- 324) Coniglio, L., Caglioti, V.: *Rend. Accad. Sci. Fis. Mat. Soc. Nazl. Sci. Napoli* 33, 154 (1927).
- 325) Dickinson, R. G.: *J. Am. Chem. Soc.* 44, 1489 (1922).
- 326) Levy, H. A., Peterson, S. W.: *J. Am. Chem. Soc.* 75, 1536 (1953).
- 327) Gopal, N.: *Indian J. Phys.* 7, 285 (1932).
- 328) Heinemann, A.: *Ber. Bunsenges. Physik. Chem.* 68, 280 (1964).
- 329) Zugravescu, P. G., Zugravescu, M. A.: *Rev. Chim. (Bucharest)* 17, 704 (1966); C.A. 66, 101326 (1967).
- 330) Taylor, R. W. D.: *Chem. Ind. (London)* 33, 1116 (1968).
- 331) Kobayashi, Y., Meguro, T.: *Bunseki Kagaku* 16, 1359 (1967); C.A. 68, 107679 (1968).
- 332) Leffler, A. J., Teach, E. G.: *J. Am. Chem. Soc.* 82, 2710 (1960).
- 333) Ettl, V., Horak, J.: *Collection Czech. Chem. Commun.* 26, 2087 (1961).
- 334) Wartik, T., Apple, E. F.: *J. Am. Chem. Soc.* 80, 6155 (1958).
- 335) Fischer, E. O., Louis, E., Schneider, R. J. J.: *Angew. Chem.* 80, 122 (1968).
- 336) Klanberg, F., Muetterties, E. L.: *J. Am. Chem. Soc.* 90, 3296 (1968).
- 337) Campbell, J. M., Stone, F. G. A.: *Angew. Chem.* 81, 120 (1969).
- 338) Boyd, D. B., Lipscomb, W. N.: *J. Chem. Phys.* 46, 910 (1967).
- 339) Siebert, H., Eints, J., Fluck, E.: *Z. Naturforsch.* 23b, 1006 (1968).
- 340) Fischer, E. O., Louis, E., Kreiter, C. G.: *Angew. Chem.* 81, 397 (1969).
- 341) Devyatykh, G. G., Zorin, A. D., Postnikova, T. K., Umilin, V. A.: *Zh. Neorgan. Khim.* 14, 1626 (1969); C.A. 71, 64783 (1969).
- 342) Zorin, A. D., Runovskaya, I. V., Lyakhmanov, S. B., Yudanova, L. V.: *Zh. Neorgan. Khim.* 12, 2529 (1967); C.A. 68, 43402 (1968).
- 343) Vlasov, S. M., Devyatykh, G. G.: *Zh. Neorgan. Khim.* 11, 2681 (1966); C.A. 67, 5929 (1967).

- 344) Rankine, A. O., Smith, C. J.: *Phil. Mag.* **42**, 601 (1921).
- 345) Helminger, P., Gordy, W.: *Phys. Rev.* **188**, 100 (1969).
- 346) Lehn, J. M., Munsch, B.: *J. Chem. Soc. (London) D* **1969**, 1327.
- 347) Hillier, I. H., Saunders, V. R.: *J. Chem. Soc. (London) D* **1970**, 316.
- 348) Raevskii, O. A., Khalitov, F. G.: *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 2368; *C.A.* **74**, 117213 (1971).
- 349) Devyatikh, G. G., Zorin, A. D., Runovskaya, I. V.: *Dokl. Akad. Nauk SSSR* **188**, 1082 (1969); *C.A.* **72**, 47751 (1970).
- 350) Armstrong, R. L., Courtney, J. A.: *J. Chem. Phys.* **51**, 457 (1969).
- 351) Frost, D. C., McDowell, C. A., Sandhu, J. S., Vroom, D. A.: *Advan. Mass Spectrometry* **1968**, 781.
- 352) Branton, G. R., Frost, D. C., McDowell, C. A., Stenhouse, I. A.: *Chem. Phys. Letters* **5**, 1 (1970).
- 353) Giardini-Guidoni, A., Volpi, U. G. G.: *Nuovo Cimento* **17**, 919 (1960).
- 354) Eyler, J. R.: *Inorg. Chem.* **9**, 981 (1970).
- 355) Basco, N., Yee, K. K.: *Nature* **216**, 998 (1967); *C.A.* **68**, 25388 (1968).
- 356) Olah, G. A., McFarland, C. W.: *J. Org. Chem.* **34**, 1832 (1969).
- 357) Graham, T.: *Phil. Mag.* **3** **5**, 401 (1834).
- 358) Fujioka, G. S., Cady, G. H.: *J. Am. Chem. Soc.* **79**, 2451 (1957).
- 359) Holtz, D., Beauchamp, J. L.: *J. Am. Chem. Soc.* **91**, 5913 (1969).
- 360) Beauchamp, J. L., Buttrill, S. E.: *J. Chem. Phys.* **48**, 1783 (1968).
- 361) Haney, M. A., Franklin, J. L.: *J. Phys. Chem.* **73**, 4328 (1969).
- 362) Haney, M. A., Franklin, J. L.: *J. Chem. Phys.* **50**, 2028 (1969).
- 363) Guyon, P.-M.: *J. Chim. Phys.* **66**, 468 (1969).
- 364) Berechnet aus Daten von Harrison, A. G., Ivko, A., Van Raalte, D.: *Can. J. Chem.* **44**, 1625 (1966) und Refaey, K. M. A., Chupka, W. A.: *J. Chem. Phys.* **48**, 5205 (1968).
- 365) Ionization potentials, appearance potentials, and heats of formation of gaseous positive ions, NSRDS-NBS 26. Washington, D.C.: U.S. Government Printing Office 1969.
- 366) Vedenev, V. I., Gurvich, L. V., Kondratev, V. N., Medvedev, V. A., Frankevich, Ye. L.: *Bond energies, ionization potentials, and electron affinities*. New York, N.Y.: Scripta Technica Ltd., St. Martin's Press 1966.
- 367) Hild, K., Heidemann, W.: *Beckman Rep.* **3/4**, 12 (1966); *C.A.* **70**, 74030 (1969).
- 368) Dumas, T.: *J. Agr. Food Chem.* **17**, 1164 (1969); *C.A.* **71**, 128321 (1969).
- 369) Berck, B., Westlake, W. E., Gunther, F. A.: *J. Agr. Food Chem.* **18**, 143 (1970).
- 370) Agranov, Kh. I.: *Nov. Obl. Prom., Sanit. Khim.* **1969**, 60; *C.A.* **71**, 116275 (1969).
- 371) Sonobe, K., Nakaoka, T.: *Japan. Pat.* 26387 (1968); *C.A.* **71**, 5007 (1969).
- 372) Devyatikh, G. G., Kedyarkin, V. M., Zorin, A. D.: *Zh. Neorgan. Khim* **14**, 2011 (1969); *C.A.* **71**, 97898 (1969).
- 373) Trautz, M., Bhandarkar, H.: *Z. Anorg. Allgem. Chem.* **106**, 95 (1919).
- 374) Hinshelwood, C. N., Topley, B.: *J. Chem. Soc.* **125**, 393 (1924).
- 375) van't Hoff, J. H., Kooj, D. M.: *Z. Phys. Chem.* **12**, 125 (1893).
- 376) Strater, K., Mayer, A.: *Semicond. Silicon, Internat. Sympos. Pap. 1st, 1969*, 469; *C.A.* **71**, 108630 (1969).
- 377) Davies, P. B., Trush, B. A.: *Proc. Roy. Soc. Ser. A* **302**, 243 (1967).
- 378) Heckmann, G., Fluck, E.: *Z. Naturforsch.* **24b**, 953 (1969).
- 379) Heckmann, G., Fluck, E.: *Z. Naturforsch.* **24b**, 1092 (1969).
- 380) Heckmann, G., Fluck, E.: *Z. Naturforsch.* **25b**, 1226 (1970).
- 381) Heckmann, G., Fluck, E.: *Z. Naturforsch.* **26b**, 63 (1971).
- 382) Heckmann, G., Fluck, E.: *Z. Naturforsch.* **26b**, 282 (1971).
- 383) Fluck, E.: *Die kernmagnetische Resonanz und ihre Anwendung in der anorganischen Chemie*. Berlin-Heidelberg-New York: Springer 1963.

- 384) Heckmann, G., Fluck, E.: *Mol. Phys.* 23, 175 (1972).
- 385) Gutowsky, H. S., McCall, D. W., Slichter, C. P.: *J. Chem. Phys.* 21, 279 (1953).
- 386) Gutowsky, H. S., McCall, D. W.: *J. Chem. Phys.* 22, 162 (1954).
- 387) Van Wazer, J. R., Callis, C. F., Shoolery, J. N., Jones, R. C.: *J. Am. Chem. Soc.* 78, 5715 (1956).
- 388) Parks, J. R.: *J. Am. Chem. Soc.* 79, 757 (1957).
- 389) Morin, C.: *Bull. Soc. Chim. (France)* 1961, 1446.
- 390) Jones, R. A. Y., Katritzky, A. R.: *Angew. Chem.* 74, 60 (1962).
- 391) Manatt, S. L., Juvinal, G. L., Elleman, D. D.: *J. Am. Chem. Soc.* 85, 2664 (1963).
- 392) Schumann, H., Stelzer, O., Kuhlmeij, J., Niederreuther, U.: *J. Organometal. Chem.* 28, 105 (1971).
- 393) Fluck, E.: *Chemiker-Ztg.* 94, 833 (1970).
- 394) Fluck, E., Bürger, H., Götze, U.: *Z. Naturforsch.* 22b, 912 (1967).
- 395) Engelhardt, G., Reich, P., Schumann, H.: *Z. Naturforsch.* 22b, 352 (1967).
- 396) Baudler, M., Ständeke, H., Dobbers, J., Borgardt, M., Strabel, H.: *Naturwissenschaften* 53, 251 (1966).
- 397) Wiberg, E., Müller-Schiedmayer, G.: *Z. Anorg. Allgem. Chem.* 308, 352 (1961).
- 398) Ramirez, F., Aguiar, A.: 134. Meeting Am. Chem. Soc., 42N, Sept. 1958.
- 399) Rabinowitz, J.: *Helv. Chim. Acta* 53, 53 (1970).
- 400) Rabinowitz, J., Woeller, F., Flores, J., Krebsbach, R.: *Nature (London)* 224, 796 (1969).
- 401) Buchanan, J. W., Hanrahan, R. J.: *Radiation Res.* 44, 296 (1970); *C.A.* 74, 17986 (1971).
- 402) Buchanan, J. W., Hanrahan, R. J.: *Radiation Res.* 42, 244 (1970); *C.A.* 72, 138289 (1970).
- 403) Sisler, H. H., Sarkis, A., Ahujo, H. S., Drago, R. J., Smith, N. L.: *J. Am. Chem. Soc.* 81, 2982 (1959).
- 404) Hart, W. A., Sisler, H. H.: *Inorg. Chem.* 3, 617 (1964).
- 405) Clemens, D. F., Sisler, H. H.: *Inorg. Chem.* 4, 1222 (1965).
- 406) Vetter, H. J., Nöth, H.: *Z. Anorg. Allgem. Chem.* 330, 233 (1964).
- 407) Jain, S. R., Krannich, L. K., Highsmith, R. E., Sisler, H. H.: *Inorg. Chem.* 6, 1058 (1967).
- 408) Highsmith, R. E., Sisler, H. H.: *Inorg. Chem.* 7, 1740 (1968).
- 409) Petrov, K. A., Parshina, V. A., Orlov, B. A., Tsypina, G. M.: *Zh. Obshch. Khim.* 32, 4017 (1962); *J. Gen. Chem. USSR* 32, 3944 (1962).
- 410) Jaura, K. L., Maini, B. K., Kaushik, R. L.: *Res. Bull. Panjab Univ.* 18, 165 (1967); *C.A.* 69, 26738 (1968).
- 411) Sawodny, W., Goubeau, J.: *Z. Anorg. Allgem. Chem.* 356, 289 (1968).
- 412) Davis, J., Drake, J. E.: *J. Chem. Soc. A* 1970, 2959.
- 413) Manatt, S. L., Junivall, G. L., Ellemann, D. D.: *J. Am. Chem. Soc.* 85, 2664 (1963).
- 414) Sheldrick, G. M.: *Trans. Faraday Soc.* 63, 1077 (1967).
- 415) Glidewell, C., Sheldrick, G. M.: *J. Chem. Soc. A* 1969, 350.
- 416) Ebsworth, E. A. V., Glidewell, C., Sheldrick, G. M.: *J. Chem. Soc. A* 1969, 352.
- 417) Davis, J., Drake, J. E., Goddard, N.: *J. Chem. Soc. A* 1970, 2962.
- 418) Strizhevskii, I. I., Slizovskaya, L. V.: *Svarochn. Proizvod.* 1968, 43; *C.A.* 70, 79530 (1969).
- 419) Whistler, R. L., Wang, Chih-Cheng, Inokawa, S.: *J. Org. Chem.* 33, 2495 (1968).
- 420) Evers, C., Street, E. H.: *J. Am. Chem. Soc.* 78, 5726 (1956).
- 421) Royen, P., Hill, K.: *Z. Anorg. Allgem. Chem.* 229, 97 (1936).
- 422) Gattermann, L., Haussknecht, W.: *Ber. Deut. Chem. Ges.* 23, 1174 (1890).
- 423) Gunn, S. R., Green, L. G.: *J. Phys. Chem.* 65, 779 (1961).
- 424) Nixon, E. R.: *J. Phys. Chem.* 60, 1054 (1956).

- 425) Baudler, M., Schmidt, L.: *Z. Anorg. Allgem. Chem.* 289, 219 (1957).
426) Wheatley, P. J.: *J. Chem. Soc.* 1956, 4514.
427) Lynden-Bell, R. M.: *Trans. Faraday Soc.* 57, 888 (1961).
428) Thénard, P.: *Compt. Rend.* 18, 652 (1844).
429) Hofmann, A. W.: *Ber. Deut. Chem. Ges.* 7, 530 (1874).
430) Retgers, J. W.: *Naturw. Rundschau* 10, 384 (1895).
431) Datta, J.: *J. Indian Chem. Soc.* 29, 751 (1952).
432) Wiles, D. M., Winkler, C. A.: *J. Phys. Chem.* 61, 620 (1957).
433) Michaelis, A., Pitsch, M.: *Liebigs Ann. Chem.* 310, 45 (1900).
434) Beichl, G. J., Evers, E. C.: *J. Am. Chem. Soc.* 80, 5344 (1958).
435) Berthelot, D., Gaudechon, H.: *Compt. Rend.* 156, 1243 (1913).
436) Baudler, M., Ständeke, H., Borgardt, M., Strabel, H., Dobbers, J.: *Naturwissenschaften* 53, 106 (1966).
437) Baudler, M., Schmidt, L.: *Naturwissenschaften* 46, 577 (1959).
438) Royen, P., Rocktäschel, C., Mosch, W.: *Angew. Chem.* 76, 860 (1964).
439) Gmelins Handbuch der anorganischen Chemie, 8th edit., System No. 16, Part C, p. 53. Weinheim: Verlag Chemie 1965.
440) Baudler, M., Ständeke, H., Dobbers, J.: *Z. Anorg. Allgem. Chem.* 353, 122 (1967).
441) White, W. E., Bushey, A. H.: *J. Am. Chem. Soc.* 66, 1666 (1944).
442) Welker, H.: *Z. Naturforsch.* 7a, 744 (1952).
443) Addamiano, A.: *Acta Cryst.* 13, 505 (1960).
444) Stackelberg, v. M., Paulus, R.: *Z. Physik. Chem. (B)* 22, 305 (1933).
445) Zintl, E., Husemann, E.: *Z. Physik. Chem. (B)* 21, 138 (1933).
446) Stackelberg, v. M.: *Z. Physik. Chem. (B)* 27, 53 (1934).
447) Engelhardt, G.: *Z. Anorg. Allgem. Chem.* 387, 52 (1972).
448) Cradock, S., Ebsworth, E. A. V., Davidson, G., Woodward, L. A.: *J. Chem. Soc. (London) A* 1967, 1229.
449) Marsmann, H., Groenweghe, L. C. D., Schaad, L. J., Van Wazer, J. R.: *J. Am. Chem. Soc.* 92, 6107 (1970).
450) Mitchell, K. A. R.: *Can. J. Chem.* 46, 3499 (1968).
451) Fischler, J., Halmann, M.: *J. Chem. Soc.* 1964, 31.
452) Halmann, M., Kugel, L.: *J. Inorg. Nucl. Chem.* 25, 1343 (1963).
453) Halmann, M.: *Chem. Rev.* 64, 689 (1964).
454) Halmann, M., Kugel, L.: *J. Chem. Soc.* 1964, 4025.
455) Halmann, M.: *Chemical effects of nuclear transformations*, p. 195. Vienna: Int. Atomic Energy Agency 1961.
456) Mitteilung VII der Kommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe, Deutsche Forschungsgemeinschaft 1971.
457) Rose, H.: *Ann. Physik* [2] 6, 199 (1826); 24, 295 (1832).
458) Rubenovitch, E.: *Compt. Rend.* 128, 1398 (1899).
459) Riban, J.: *Compt. Rend.* 88, 581 (1879); *Bull. Soc. Chim. France* [2] 31, 385 (1897).
460) Scholder, R., Pattock, K.: *Z. Anorg. Allgem. Chem.* 220, 250 (1934).
461) Höltje, R., Schlegel, H.: *Z. Anorg. Allgem. Chem.* 243, 246 (1940).
462) Moser, L., Brukl, A.: *Z. Anorg. Allgem. Chem.* 121, 73 (1922).
463) Boettger, R.: *Beitr. Phys. Chem.* 2, 116 (1840).
464) Schönberg, N.: *Acta Chem. Scand.* 8, 226 (1954).
465) Guenebaut, H., Pascat, B.: *Compt. Rend.* 255, 1741 (1962).
466) Dulong, P. L.: *Ann. Chim. Phys.* [2] 31, 154 (1826).
467) Bleekrode, L.: *Proc. Roy. Soc. (London)* 37, 339 (1884).
468) Smith, C.: *Proc. Roy. Soc. (London) A* 87, 366 (1912).
469) Barter, C., Meisenheimer, R. G., Stevenson, D. P.: *J. Phys. Chem.* 64, 1312 (1960).

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- 470) Malleman de, R., Gabiano, P.: *Compt. Rend.* 199, 600 (1934).
- 471) Weston, R. E.: *J. Am. Chem. Soc.* 76, 1027 (1954).
- 472) Cailletet, L., Bordet, L.: *Compt. Rend.* 95, 58 (1882).
- 473) Skinner, S.: *Proc. Roy. Soc. (London)* 42, 283 (1887).
- 474) Claussen, W. F.: *J. Chem. Phys.* 19, 1425 (1951).
- 475) Stackelberg, v. M., Müller, H. R.: *Z. Elektrochem.* 58, 25 (1954).
- 476) Powell, H. M.: *J. Chem. Soc.* 1954, 2658.
- 477) Melville, H. W.: *Proc. Roy. Soc. (London)* A 139, 541 (1933).
- 478) Melville, H. W., Bolland, J. L., Roxburgh, H. L.: *Proc. Roy. Soc. (London)* A 160, 406 (1937).
- 479) Hinshelwood, C. N., Clusius, K.: *Proc. Roy. Soc. (London)* A 129, 589 (1930).
- 480) Fluck, E.: In press.
- 481) Drummond, D. H.: *J. Am. Chem. Soc.* 49, 1901 (1927).
- 482) Ipatiev, W. N., Frost, A. W.: *Ber. Deut. Chem. Ges.* 63, 1104 (1930); *Zh. Russ. Fiz.-Khim. Obshchestva Chast'Khim.* 62, 1123 (1930).
- 483) Sanderson, R. T.: *J. Chem. Phys.* 20, 535 (1952).
- 484) Kooij, D. M.: *Z. Physik. Chem.* 12, 155 (1893).
- 485) Dushman, S.: *J. Am. Chem. Soc.* 43, 397 (1921).
- 486) Yamazaki, E.: *J. Tokyo Chem. Soc.* 40, 606 (1919); *C.A.* 1919, 3053.
- 487) Bodenstein, M.: *Z. Elektrochem.* 35, 535 (1929).
- 488) Barber, R. M.: *Trans. Faraday Soc.* 32, 490 (1936).
- 489) Laidler, K. J., Glasstone, S., Eyring, H.: *J. Chem. Phys.* 8, 667 (1940).
- 490) Lewis, W. C. M.: *Phil. Mag.* [6] 39, 26 (1920).
- 491) Roy, S. C.: *Proc. Roy. Soc. (London)* A 110, 543 (1926).
- 492) Temkin, M.: *Acta Physicochim. USSR* 8, 141 (1938).
- 493) Kharasch, M. S., Reinmuth, O.: *Grignard reactions of molecular substances*, p. 1335. New York: Prentice Hall 1954.

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