

A Standard for the Measurement of the pH of Blood and Other Physiological Media

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A buffer solution containing potassium dihydrogen phosphate (0.008695 molal) and disodium hydrogen phosphate (0.03043 molal) is proposed as a pH standard for the physiologically important range, pH 7 to 8. The proposed standard solution is prepared by dissolving 1.179 g (air weight) of potassium dihydrogen phosphate and 4.303 g (air weight) of disodium hydrogen phosphate in ammonia-free water and diluting to 1 liter at 25 °C. The ionic strength is 0.1.

Standard pH values (pH_s) were assigned to this reference solution at temperatures from 0 to 50 °C by means of emf measurements of hydrogen-silver chloride cells without liquid junction. The activity coefficient of chloride ion, upon which the assignment of pH_s depends, was evaluated by means of a recently proposed convention. By this means, standard values precise to ± 0.001 unit could be derived from the emf data. At 25 °C pH_s is 7.414, and at 38 °C it is 7.382. The operational consistency of these standard values with those for the 0.025-*m* equimolar phosphate buffer (one of the NBS primary standards) was demonstrated.

1. Introduction

The acid-base behavior of blood and other physiological fluids has been widely studied in recent years in medical and biological laboratories in an attempt to discover the relationships that exist among physiological functions, pathological conditions, and pH . Many of these fluids are well buffered, and the detection of any systematic variation of pH with physiological condition would therefore be expected to require precise measuring equipment. Such equipment is readily available commercially in the form of the newer highly-sensitive pH meters with a glass electrode.

Experience has shown that, with the exercise of care, the investigator or clinician can obtain glass-electrode pH values, for reduced blood and other body fluids, that agree within ± 0.01 unit with pH numbers obtained by means of the hydrogen electrode [1].¹ The high degree of stability in these biological systems and in the measuring apparatus suggests that blood pH measurements with a precision of 0.005 unit (or even 0.001 unit) could profitably be made. Meaningful comparisons of highly precise results of different laboratories could then be made, provided that a suitable reference standard were available.

Unfortunately, useful comparisons of pH data, quoted to 0.001 unit, from different sources have in general been impossible. The difficulty can be attributed to the fact that in all of the major conventions defining pH [2], a nonthermodynamic convention concerning single-ion activity coefficients is by necessity adopted. At the present time no single convention for defining an ionic activity is widely accepted. Although the conventions used heretofore to estimate single-ion activity coefficients are "reasonable" and yield pH numbers consistent

with each other to within 0.01 unit, they all lack the exactness required for assignment of values to 0.001 unit.

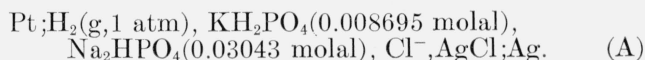
Bates and Guggenheim [3], in a recent report to the International Union of Pure and Applied Chemistry, have proposed a very simple and precise way of defining the single-ion activity for the establishment of pH standards. By means of the convention they have set forth, pH values precise to within 0.001 unit may be assigned to selected standards in a restricted sector of the pH range.

Errors due to the faulty response of the glass electrode are minimized if the pH of the standard is close to that of the unknown. The availability of a precise pH standard in the physiological range would assist materially in the exact comparison of pH measurements made on biological systems in different laboratories.

It is the purpose of this paper to propose, as a physiological pH standard, a phosphate buffer mixture with a pH of about 7.4 and to assign pH values to this standard. The proposed standard has the following composition: KH_2PO_4 (0.008695 molal), Na_2HPO_4 (0.03043 molal).

2. Method of Defining pH_s

In order to avoid the theoretical and practical difficulties inherent in the estimation of liquid junction potentials, standard pH values have been based upon measurements of cells without liquid junction. In this work, hydrogen and silver-silver chloride electrodes were used, measurements being made of the electromotive force of the cell:



The electromotive force, E , of cell (A) is related to the standard electrode potential (E°) of the silver-

¹ Figures in brackets indicate the literature references at the end of this paper

silver-chloride electrode [4] and to the activities of the hydrogen and chloride ions in the solution by the relation

$$E = E^\circ - \frac{RT}{F} \ln (\mathbf{a}_H \mathbf{a}_{Cl}), \quad (1)$$

where \mathbf{a} is the activity (molal basis) of the ionic species designated by the subscript. Rearrangement, conversion to decadic logarithms, and substitution of $m_{Cl} \gamma_{Cl}$ for \mathbf{a}_{Cl} yields a thermodynamic acidity function, $-\log(\gamma_H \gamma_{Cl} m_H)$:

$$-\log(\gamma_H \gamma_{Cl} m_H) = (E - E^\circ)F / (2.3026RT) + \log m_{Cl}. \quad (2)$$

In eq (2), m is the molality and γ is the activity coefficient, on the molal scale, of the ions designated by the subscripts.

For satisfactory reproducibility and constancy of the electromotive force, a finite amount of chloride must be present in the buffer solution. Nevertheless, it is the acidity function of the chloride-free buffer solution that is desired. The value of $-\log(\gamma_H \gamma_{Cl} m_H)$ was therefore measured at each of three low chloride concentrations, namely 0.005 m , 0.010 m , and 0.015 m and $-\log(\gamma_H \gamma_{Cl} m_H)^\circ$, the limit of $-\log(\gamma_H \gamma_{Cl} m_H)$ as m_{Cl} approaches zero, was obtained by extrapolation.

If the standard pH (denoted pH_s) is defined formally as $-\log \mathbf{a}_H$ or $-\log m_H \gamma_H$, then

$$pH_s = -\log(\gamma_H \gamma_{Cl} m_H)^\circ + \log \gamma_{Cl}^\circ. \quad (3)$$

It will be observed that, according to eq (2), $-\log(\gamma_H \gamma_{Cl} m_H)$ is a measurable quantity. On the contrary, γ_{Cl} in eq (3) is the activity coefficient of a single ion, a quantity that is not measurable. To obtain pH_s , therefore, some assumption must be made, or convention adopted, to evaluate γ_{Cl} .

For the purposes of assigning standard pH values to the standard buffers already proposed by the National Bureau of Standards, various assumptions have been used to estimate γ_{Cl} [5,6,7]. If the ionic strength does not exceed 0.1, the numerical values of γ_{Cl}° (obtained from the above assumptions) can all be closely represented by the following form of the Debye-Hückel equation:

$$-\log \gamma_{Cl}^\circ = \frac{A\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}}, \quad (4)$$

where μ is the ionic strength, a_i is an adjustable "ion-size parameter", and A and B are constants dependent upon temperature and solvent.² In the last analysis, therefore, the differences among the conventions themselves can be expressed as differences in a_i . Fortunately, all "reasonable" conventions for the definition of γ_{Cl}° lead to substantially equivalent values for the pH_s of the standard phosphate buffer ($\mu=0.1$) [10]. All of these values fall within ± 0.01 unit of the assigned NBS standard values for this buffer solution. The agreement at lower ionic strengths is even more satisfactory.

² Tabulations of A and B are to be found in references [8] and [9].

Since there is really no apparent basis for choice among these assumptions, any one of them may be selected to represent γ_{Cl}° . Bates and Guggenheim have proposed, in their report to the Analytical Chemistry and Physical Chemistry Sections of the International Union of Pure and Applied Chemistry, a value of $Ba_i=1.5 \text{ mole}^{-1/2} \text{ kg}^{1/2}$ [3]. The pH values given in the present work are based upon eqs (3) and (4) and this convention of Bates and Guggenheim.

3. Experimental Procedures and Results

The cells used for the measurements have been described in detail in a previous article [6]. Briefly, each cell consists of two electrode compartments and a chamber in which incoming hydrogen is saturated with the vapor over the buffer solution. The chamber terminates in a tube which leads to the jet in the hydrogen electrode compartment of the cell. Hydrogen gas escapes from the top of the hydrogen electrode compartment. The silver-silver chloride electrode compartment is connected to the hydrogen electrode compartment by a broad tube filled with the cell solution.

The standard buffer solution selected was 0.008695 molal in potassium dihydrogen phosphate (molecular weight, 136.092) and 0.03043 molal in disodium hydrogen phosphate (molecular weight, 141.982).³ These proportions were chosen with the intention of producing a solution of pH about 7.4 at 25 °C and with an ionic strength of 0.1.

The solvent used in this study was ammonia-free distilled water of conductivity no greater than $0.8 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. The phosphate salts were specimens of NBS Standard Sample 186Ib (KH_2PO_4) and 186IIb (Na_2HPO_4), dried for an hour in an oven at 110 °C and used without further treatment. The potassium chloride was taken from a highly purified sample whose manner of preparation and purification has been described elsewhere [11].

Twenty cells containing the phosphate buffer with low concentrations of chloride (0.005 m , 0.010 m , or 0.015 m) were made up. The emf of 13 of these cells was measured over the temperature range 0 to 50 °C; five cells were studied over the range, 25 to 50°, one cell over the range 0 to 40°, and one cell at only three temperatures.

After the emf had been corrected to the standard partial pressure of hydrogen (760 mm), the acidity function $-\log(\gamma_H \gamma_{Cl} m_H)$ for each cell was calculated by means of eq (2). Values of $-\log(\gamma_H \gamma_{Cl} m_H)$ are listed in table 1. For these calculations, R was taken as 8.3147 j mole⁻¹ deg⁻¹ and F as 96,495.4 coul equiv⁻¹ [12].

4. Assignment of pH_s Values

The $-\log(\gamma_H \gamma_{Cl} m_H)$ was found to be a linear function of m_{Cl} , and the limiting value, $-\log(\gamma_H \gamma_{Cl} m_H)^\circ$ (at $m_{Cl}=0$), was evaluated by the method of least

³ The density at 25 °C of this solution is 1.0020 g/ml. A solution of this composition may be made by dissolving 1.179 g (air weight) KH_2PO_4 and 4.303 g (air weight) Na_2HPO_4 in water and diluting to 1 liter at 25 °C.

TABLE 1. Electromotive force of cell (A) containing the phosphate buffer solution: 0.008695 m KH_2PO_4 , 0.03043 m Na_2HPO_4 with three molalities of added KCl

Temperature °C

KCl, molality	0	5	10	15	20	25	30	35	38	40	45	50
0.005	0.77510	0.78078	0.78631	0.79187	0.79754	0.80324	0.80897	0.81457	0.81800	0.82018	0.82577	0.83149
.005	.77481	.78037				.80308						
.005	.77502	.78045	.78807	.79168	.79745	.80322	.80888	.81451	.81796	.82018	.82586	.83145
.005	.77484	.78042	.78612	.79177	.79756	.80296	.80893	.81434	.81791	.82021	.82606	.83180
.005	.77537	.78080	.78650	.79198	.79771	.80336	.80902	.81469	.81810	.82048		
.005	.77531	.78063	.78612	.79149	.79722	.80326	.80884	.81450	.81794	.82025	.82578	.83142
.005						.80330	.80884	.81435	.81798	.82025	.82565	.83122
.005						.80322	.80886	.81450	.81798	.82036	.82612	.83151
.010	.75857	.76392	.76912	.77442	.77970	.78512	.79047	.79584	.79916	.80124	.80672	.81222
.010	.75835	.76380	.76899	.77424	.77958	.78508	.79070	.79588	.79909	.80115	.80663	.81200
.010	.75862	.76374	.76903	.77421	.77946	.78506	.79044	.79568	.79903	.80136	.80667	.81188
.010	.75869	.76384	.76915	.77445	.77989	.78506	.79056	.79588	.79911	.80133	.80678	.81224
.010	.75869	.76379	.76920	.77438	.77979	.78500	.79048	.79587	.79906	.80129	.80662	.81222
.010	.75868	.76381	.76922	.77435	.77970	.78517	.79054	.79596	.79921	.80143	.80671	.81235
.010						.78497	.79026	.79563	.79887	.80107	.80659	.81195
.010						.78527	.79048	.79585	.79920	.80135	.80673	.81195
.015	.74873	.75392	.75900	.76406	.76923	.77427	.77966	.78478	.78800	.78993	.79513	.80036
.015	.74859	.75360	.75875	.76383	.76895	.77421	.77949	.78443	.78768	.78966	.79501	.80042
.015	.74895	.75373	.75895	.76394	.76918	.77449	.77947	.78476	.78779	.78999	.79521	.80067
.015						.77446	.77978	.78498	.78803	.79017	.79546	.80049

squares. Figure 1 shows the array of $-\log(\alpha_{\text{H}}\gamma_{\text{Cl}})$ or $-\log(\gamma_{\text{H}}\gamma_{\text{Cl}}m_{\text{H}})$ values at two temperatures. Values of $-\log(\gamma_{\text{H}}\gamma_{\text{Cl}}m_{\text{H}})^{\circ}$ and the standard deviation (σ_i) of the intercept are given in table 2. The quantities $-\log\gamma_{\text{Cl}}^{\circ}$ computed from eq (4) are also listed. The standard $p\text{H}_s$ values were derived from $-\log(\gamma_{\text{H}}\gamma_{\text{Cl}}m_{\text{H}})^{\circ}$ by eq (3). They are listed in the last column of table 2 and are represented graphically as a function of temperature in figure 2.

The standard solution proposed here has an ionic strength of 0.1 and a buffer ratio of 3.5. The difference in $p\text{H}$ resulting from small variations in the concentration of one or both phosphates is given with sufficient accuracy by the following expression, based on the mass law:

$$p\text{H}_s - p\text{H}_x = 0.544 - \log \frac{m_{\text{HPO}_4^-}}{m_{\text{H}_2\text{PO}_4}} + 3\{\log \gamma_{\text{Cl}}^{\circ}(\text{s}) - \log \gamma_{\text{Cl}}^{\circ}(\text{x})\}, \quad (5)$$

where x designates the solution of buffer ratio slightly different from 3.5, and/or ionic strength slightly different from 0.1, and where s designates the standard

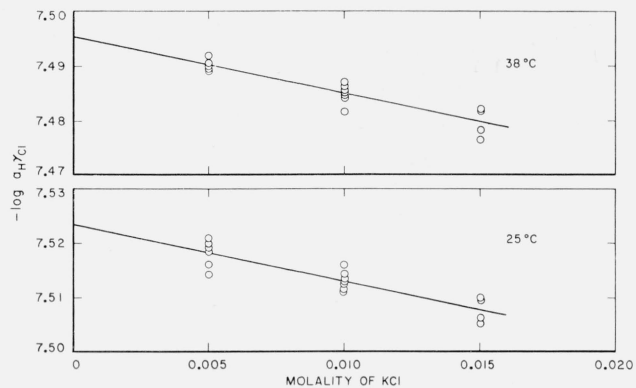


FIGURE 1. $-\log(\gamma_{\text{H}}\gamma_{\text{Cl}}m_{\text{H}})$ of a solution 0.008695m in KH_2PO_4 and 0.03043 m in Na_2HPO_4 as a function of molality of added chloride.

solution proposed here. Also assumed in the derivation of eq 5 was the approximation

$$\gamma_{\text{HPO}_4^-} = (\gamma_{\text{Cl}^-}^{\circ})^4 = (\gamma_{\text{H}_2\text{PO}_4}^{\circ})^4.$$

It should be noted that neither of these phosphate salts is a strong enough acid or base to react appreciably with water. Hydrolysis corrections are therefore unnecessary, and the ratio of the concentrations of the phosphate ions is the same as the stoichiometric ratio of the molalities of the two salts. The first term within the braces in eq (5) is given in table 2. The second quantity inside the braces may be calculated from eq (4) with $Ba_i = 1.5 \text{ mole}^{-1/2}\text{kg}^{1/2}$. For buffer solutions composed of potassium hydrogen phosphate (m_1) and disodium hydrogen phosphate (m_2), $\mu = m_1 + 3m_2$.

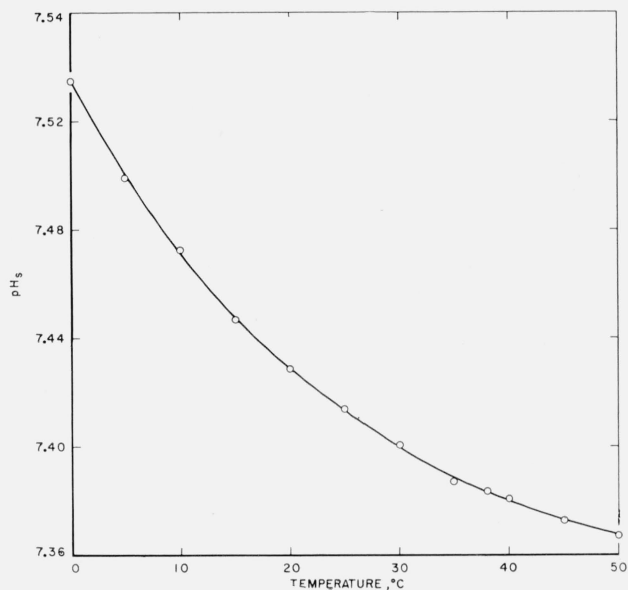


FIGURE 2. $p\text{H}_s$ of a solution 0.008695m in KH_2PO_4 and 0.03043 m in Na_2HPO_4 as a function of temperature.

TABLE 2. pH_s and $-\log(\gamma_H\gamma_{Cl}m_H)^\circ$ for the solution 0.008695 *m* in KH_2PO_4 and 0.03043 *m* in Na_2HPO_4

$t^\circ C$	$-\log(\gamma_H\gamma_{Cl}m_H)^\circ$	σ_i	$-\log \gamma_{Cl}^0$	pH_s (experimental)
0	7.6400	0.0023	0.1055	7.534
5	7.6052	.0018	.1062	7.499
10	7.5793	.0018	.1070	7.472
15	7.5547	.0017	.1078	7.447
20	7.5374	.0019	.1087	7.429
25	7.5234	.0011	.1095	7.414
30	7.5109	.0011	.1104	7.400
35	7.4985	.0014	.1114	7.387
38	7.4955	.0011	.1121	7.383
40	7.4934	.0013	.1125	7.381
45	7.4863	.0016	.1135	7.373
50	7.4816	.0018	.1146	7.367

TABLE 3. Recommended values of pH_s at specified temperatures
(values calculated from eq (6))

t	pH_s	t	pH_s
0	7.531	30	7.399
5	7.501	35	7.387
10	7.474	38	7.382
15	7.450	40	7.379
20	7.430	45	7.373
25	7.413	50	7.369

The "experimental" values of pH_s listed in table 2 were smoothed with respect to the temperature (T) in $^\circ K$ by the method of least squares, with the following result:

$$pH_s = \frac{1592.07}{T} - 2.3392 + 0.014798T. \quad (6)$$

Recommended values of pH_s , calculated at specified temperatures from eq (6), are given in table 3.

5. Internal Consistency of the Standard pH Scale

It was considered desirable to test the operational consistency of the pH_s values defined in this paper with those defined some years ago by Bates and Acree for the equimolar 0.025 *m* phosphate buffer (0.025 *m* KH_2PO_4 , 0.025 *m* Na_2HPO_4) [6]. To this end, emf measurements were made with a symmetric cell [13] consisting of two hydrogen electrode compartments connected by a bridge of saturated potassium chloride.

The standard equimolar phosphate buffer solution was placed in one of the hydrogen electrode compartments and the solution of buffer ratio 3.5 in the other. The emf between the two hydrogen electrodes yields the operational pH difference (ΔpH), which can then be compared with the difference of assigned pH_s (ΔpH_s). The assignment of pH_s is made by eq (3), where $\log \gamma_{Cl}^0$ is defined by the Bates-Guggenheim convention (and therefore constant for a given value of the ionic strength).⁴ The difference in pH_s is therefore equal to the difference between the values of $-\log(\gamma_H\gamma_{Cl}m_H)^\circ$ for the two solutions, namely 7.523–6.972 or 0.551 at 25 $^\circ C$ and 7.496–6.952 or 0.544 at 38 $^\circ C$.

Measurements of the symmetrical cell with liquid junction were made at 25 and 38 $^\circ C$. The experimental values of ΔpH at the two temperatures were,

⁴ The earlier assignment of pH_s to the phosphate buffer solution was based on a more complex formula for estimating γ_{Cl}^0 [6]. The two procedures lead to values of pH_s for the equimolar phosphate standard that differ by only 0.003 unit at 25 $^\circ C$.

respectively, 0.550 and 0.546 pH unit. These values are in good agreement with the values of ΔpH_s given above, which were, of course, derived from the emf of cells without liquid junction.

The internal consistency of the practical scale to a few thousandths of a unit in the physiological range therefore seems to have been demonstrated. By a similar series of measurements at 25 $^\circ C$, it has already been shown that the standard phthalate (pH 4.006), phosphate (pH 6.863), and borax (pH 9.183) buffer solutions are consistent among themselves to about ± 0.003 unit [14]. In the authors' opinion, these intercomparisons constitute an experimental justification for the assignment of a third decimal to the pH_s for the primary standards of intermediate pH .

6. References

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(Paper 65A3-110)

Publications of the National Bureau of Standards

(Including papers in outside journals)

Selected Abstracts

Irrational power series, M. Newman, *Proc. Am. Math. Soc.* **11**, 699–702 (Oct. 1960).

It is shown that if α is a real number, g a non-constant polynomial, then

$$\sum_{n=0}^{\infty} g([n\alpha])x^n$$

is a rational function of x if and only if α is a rational number. The same statement is proved for the function

$$\sum_{n=0}^{\infty} x^{[n\alpha]}.$$

Ensemble method in the theory of irreversibility, R. Zwanzig, *J. Chem. Phys.* **33**, No. 5, 1338–1341 (Nov. 1960).

We describe a new formulation of methods introduced in the theory of irreversibility by Van Hove and Prigogine, with the purpose of making their ideas easier to understand and to apply. The main tool in this reformulation is the use of projection operators in the Hilbert space of Gibbsian ensemble densities. Projection operators are used to separate an ensemble density into a “relevant” part, needed for the calculation of mean values of specified observables, and the remaining “irrelevant” part. The relevant part is shown to satisfy a kinetic equation which is a generalization of Van Hove’s “master equation to general order.” Diagram summation methods are not used. The formalism is illustrated by a new derivation of the Prigogine-Brout master equation for a classical weakly interacting system.

On the theory of the critical point of a simple fluid, M. S. Green, *J. Chem. Phys.* **33**, No. 5, 1403–1409 (Nov. 1960).

The consequences of a new system of integral equations for the theory of the critical point are discussed. Reasons are given for believing that the fundamental assumption of the Ornstein-Zernicke theory about the direct correlation function is incorrect.

Topological derivation of the Mayer density series for the pressure of an imperfect gas, M. S. Green, *J. Math. Phys.* **1**, No. 5, 391–394 (Sept.–Oct. 1960).

A new derivation of Mayer’s classical density expansion for the pressure of an imperfect gas based on a classification of cluster graphs according to topological criteria is presented. The classification is a generalization of the classification of simple trees into trees with centers and trees with bicenters.

Collection of ions produced by alpha particles in air, Z. Bay and H. H. Seliger, *Phys. Rev.* **120**, No. 1, 141–143 (Oct. 1, 1960).

In the measurement of the ionization caused by alpha particles in air recombination effects between slowly moving positive and negative ions (the latter formed by electron attachment to oxygen) have to be considered. The usual procedure in such measurements is to determine the saturation current (by extrapolation of reciprocal current versus reciprocal voltage curves to infinite field strength) according to the Jaffé theory. A paper by Wingate, Gross and Failla has cast doubt on the validity of this extrapolation technique, in that the authors propose a field-independent part of the recombination amounting to 3.3 percent at atmospheric pressure in air. This proposal implied that all previous measurements of W_a for air were in error by this amount and

that this error is a possible cause for the reported difference (3 to 4 percent) between W values for alpha and beta particles in air. In view of our own W measurements we felt compelled to reexamine this supposedly field-independent part of the recombination. Approximating the experimental conditions of Wingate, Gross and Failla we have not been able to reproduce their effect and our experiments demonstrate the validity of the usual extrapolation techniques.

Megaroentgen dosimetry employing photographic film without processing, W. L. McLaughlin, *Radiation Research* **13**, No. 4, 594–609 (Oct. 1960).

The new photographic method of high-level dosimetry of X- and gamma radiation involves two steps: (1) Large radiation exposures are given, resulting in the formation of print-out image in the silver halide emulsion layers of ordinary commercial X-ray films, without requiring photographic processing for the evaluation; (2) The unknown exposure is measured by means of a special densitometric procedure, the exposure being related to the net density of the print-out darkening on a characteristic curve obtained with known exposures. The density readings are made with a narrow band of red light, obtained by placing a suitable band-pass filter between the densitometer light source and the film.

Gamma radiation exposures from 2×10^4 to 10^8 roentgens can be read with a precision limit of ± 5 percent, under appropriate conditions of dosimetry. The response is rate independent and the print-out image is stable. The chief limitations in the method are a considerable dependence of response upon radiation energy below 0.3 Mev, and the requirement of controlling the temperature during exposure to within ± 10 degrees Celsius for accurate readings.

Vibration-rotation bands of N_2O , E. D. Tidwell and E. K. Plyler, *J. Opt. Soc. Am.* **50**, No. 12, 717–720 (Dec. 1960).

About 40 bands of nitrous oxide have been measured with a high resolution grating spectrometer in the region from 2395 to 3510 cm^{-1} . Many first and second hot bands were observed and it was possible to obtain accurate-type doubling constants. By the use of bands observed in this work in conjunction with previous work a fairly complete set of vibrational levels for N_2O has been determined. A number of interactions have been observed and the interaction constants calculated. The observed spectra are shown in nine figures. The ground state rotational constants and the vibrational constants have been calculated. Several bands have been identified as arising from isotopic molecules.

Microwave spectrum structure, and dipole moment of propane, D. R. Lide, Jr., *J. Chem. Phys.* **33**, No. 5, 1514–1518 (Nov. 1960).

The microwave spectrum of ordinary propane and five isotopic species has been measured and analysed. The rotational constants of C_3H_8 are 29207.36, 8446.07, and 7458.98 Mc, and the dipole moment is 0.083 ± 0.001 D. In its equilibrium configuration the molecule has C_{2v} symmetry with both CH_3 groups staggered with respect to the CH_2 group. The complete structure has been determined by the substitution method. Important parameters are: $r(CC) = 1.526 \pm 0.002$ Å, $CCC = 112.4^\circ \pm 0.2^\circ$; in the CH_2 group, $r(CH) = 1.096 \pm 0.002$ Å, $HCH = 106.1^\circ \pm 0.2^\circ$; in the CH_3 groups, $r(CH) = 1.091 \pm 0.010$ Å, $HCH = 107.7^\circ \pm 1.0^\circ$. The influence of zero-point effects on the structure determination is discussed; these are found to be particularly bad for the CH_3 group, probably because of its large vibrational amplitude.

Structure of the isobutane molecule; change of dipole moment on isotopic substitution, D. R. Lide, Jr., *J. Chem. Phys.* **33**, No. 5, 1519-1522 (Nov. 1960).

The microwave spectra of 5 isotopic species of isobutane have been measured and analyzed. The isobutane molecule is shown to belong to point group C_{3v} . The structural parameters determined by the substitution method are: $r(CC) = 1.525$ A, $CCC = 111.15^\circ$, $r(CH) = 1.108$ A (tertiary), $r(CH) = 1.09-1.10$ A (methyl), $HCH = 107.5^\circ$. The structure is compared with that of other hydrocarbons, and it is suggested that a small systematic difference exists between CC distances determined by microwave and electron diffraction methods. Accurate Stark measurements show that the dipole moment of $(CH_3)_3CD$ is $6.5\% \pm 0.9\%$ higher than that of $(CH_3)_3CH$.

Spatial distribution of energy dissipated by fallout-rays, A. E. Boyd and E. E. Morris, *Health Phys.* **2**, 321-325 (1959). Calculations are described of the spatial distribution of energy dissipated in air by the delayed beta rays from products of slow neutron U^{235} fission. Results are given for both plane isotropic and point isotropic sources for times after fission of 1.12 and 23.8 hr.

Mismatch errors in microwave phase shift measurements, G. E. Schafer, *IRE Trans. Microwave Theory and Tech. MTT-8*, No. 6, 617-622 (Nov. 1960).

Mismatch errors in microwave phase shift measurements are analyzed. The results are applied to two measurement techniques. Graphs are presented to estimate the limits of mismatch error when measuring or producing changes in phase of the emergent wave amplitude with a microwave phase shifter or attenuator. The limits of mismatch error for a typical microwave phase shifter in a system with equivalent generator and detector voltage standing wave ratios of 1.05, or less, are estimated to be $\pm 0.90^\circ$.

The rotational constants of hydrogen chloride, E. K. Plyler and E. D. Tidwell, *Z. Elektrochem.* **64**, No. 5, 717-720 (Feb. 1960). The fundamental absorption band of hydrogen chloride has been measured on a high resolution spectrometer. Twenty-nine lines of HCl^{35} and twenty-eight lines of HCl^{37} have been measured to a high precision by the use of the fringe system of a Fabry-Perot interferometer.

The average deviation of the observed from the calculated values is ± 0.003 cm^{-1} . The rotational constants for each isotopic species have been calculated. The rotational constants have been used to predict the positions of the pure rotational spectra of HCl^{35} and HCl^{37} . The equilibrium separation of the atoms has been calculated to be 1.2746 A.

Dipole moments of hydrocarbons, D. R. Lide, Jr., *J. Chem. Phys.* **33**, No. 6, 1879 (Dec. 1960).

The dipole moments of several hydrocarbons are considered in terms of hyperconjugation and a bond-moment model. It is shown that hyperconjugation affords a better explanation of both the orientation and magnitude of the observed moments.

Nonresonant microwave absorption and relaxation frequency at elevated pressures, A. A. Maryott and G. Birnbaum, *J. Phys. Chem.* **64**, No. 11, 1778-1780 (Nov. 1960).

The microwave absorption in $CClF_3$ has been measured at pressures up to 30 atmospheres at 1190 Mc. Below 10 atm, the absorption due to the pure rotational transitions appears to be negligible compared to the nonresonant contribution. The nonresonant relaxation frequency is found to increase essentially in proportion to the density over the entire range, and, at the highest density, is of the same order as in the liquid state.

Spectrum of ReF_6 , J. C. Eisenstein, *J. Chem. Phys.* **33**, No. 5, 1530-1531 (Nov. 1960).

The theoretical interpretation of the optical absorption spectrum of ReF_6 is discussed. It is pointed out that the value of the spin-orbit coupling constant required to fit the experimental data is appreciably reduced if a small field of axial symmetry about a threefold axis of the molecule is present.

Nuclear magnetic resonance in tantalum metal, J. I. Budnick and L. H. Bennett, *J. Phys. Chem. Solids* **16**, No. 1/2, 37-38 (Jan. 12, 1960).

The nuclear magnetic resonance of Ta^{181} has been observed in tantalum metal. The sample was a stack of high purity foil which was degassed and annealed. No resonance was observed in tantalum metal powder.

Magnetic resonance determination of the nuclear moment of tantalum-181 in $KTaO_3$, L. H. Bennett and J. I. Budnick, *Phys. Rev.* **120**, No. 5, 1812-1815 (Dec. 1960).

The nuclear magnetic moment of Ta^{181} is found from the nuclear magnetic resonance of Ta^{181} in $KTaO_3$. The uncorrected value of the moment is 2.340 ± 0.001 nm. Consideration of diamagnetic shielding effects and a possible second order paramagnetic correction leads to the estimated value of $\mu = 2.35 \pm 0.01$ nm.

Green and purple sulfur: Electron-spin resonance studies, H. E. Radford and F. O. Rice, *J. Chem. Phys.* **33**, No. 3, 774-776 (Sept. 1960).

Electron spin resonance absorption has been found in the colored deposits formed by condensing heated sulphur vapor on cold surfaces. Complexities in the resonance spectrum give evidence for the existence in the cold deposits of at least two types of trapped sulphur radicals with differing degrees of internal magnetic anisotropy. Measurements of the intensity and stability of the resonance absorption yield information on the radical trapping process.

Effect of structure on the spectra emitted by solid nitrogen during electron bombardment, L. J. Schoen and H. P. Broida, *J. Mol. Spectroscopy* **5**, No. 5, 416-419 (Nov. 1960).

Spectra emitted from solids subjected to electron bombardment at low temperature have been found to exhibit a dependence on deposition flow rate. It is shown that the observed changes may be ascribed to the effect of deposition temperature on the structure of the solid.

Chemical reactions to free radicals at low temperatures, R. A. Ruehrwein, J. S. Hashman and J. W. Edwards, *J. Phys. Chem.* **64**, 1317-1322 (1960).

Free radicals generated by subjecting gases to an electrodeless discharge were condensed in a trap cooled to liquid helium temperature. The nature of the radical reactions which had taken place upon condensation and upon warming the solid deposits was indicated by the analyses of the products obtained. The gases discharged (and the principal products) were $O_2(O_3)$, $HO_2(H_2O_2, H_2)$, N_2 , $NO_2(N_2O_3)$, H_2 , $NH_3(N_2, H_2)$, $CO(CO_2)$, $CO_2(CO, O_3)$, $SO_2(O_2, S)$, and some mixtures thereof. Also the reactions of O, OH, H, N and HO_2 radicals with O_2 , H_2O , NO, NO_2 , CO_2 , SO_2 , CH_4 , C_2H_4 , $i-C_4H_8$, CO and CH_3COCH_3 were investigated by blending in the latter downstream from the discharge and ahead of the liquid helium trap. In some of the systems it was apparent that considerable radical reaction occurred before condensation. However most of the experimental results can be interpreted on the basis that at very low temperature the free radicals react by random recombination, by addition to molecules with unpaired electrons, and by addition to carbon-carbon double bonds. It was found that molecular oxygen is loosely bound in several solids such as hydrogen peroxide, water, nitrogen dioxide and probably others. The bound or trapped oxygen is evolved from the solid at temperatures well above the boiling point of oxygen.

The reaction of hydrogen atoms with solid propene at low temperatures, R. Klein, M. D. Scheer and J. G. Waller, *J. Phys. Chem.* **64**, 1247-1250 (1960).

The reaction of hydrogen atoms with solid films of propene has been studied below 100 °K. The hydrogen atoms diffuse through and react with the propene films to form propane and 2,3-dimethylbutane. A one dimensional diffusion equation containing a chemical reaction term is used to describe the kinetics of this process. A value of 5×10^7 cc/mole sec is obtained for the specific rate constant at 77 °K for the reaction $H + CH_3 - CH = CH_2 \rightarrow CH_3 - CH - CH_2$. The ratio of propane to 2,3-dimethylbutane is about 9 and does not change as the concentration of propene is varied over two

orders of magnitude. The propane as well as the 2,3-dimethylbutane must therefore be formed by a process which is second order with respect to the isopropyl radical concentration.

Preparation and thermal stability of tetrakis-(pentafluorophenyl)-silane and tris-(pentafluorophenyl)-phosphine, L. A. Wall, R. E. Donadio, and W. J. Pummer, *J. Am. Chem. Soc.* **82**, No. 18, 4846-4852 (Sept. 1960).

The completely fluorinated organo-metalloid compounds, tetrakis(pentafluorophenyl) silane, tris(pentafluorophenyl)-phosphine, and tris(pentafluorophenyl)phosphine oxide have been prepared from pentafluorophenyl magnesium bromide and the appropriate metalloid chloride. The thermal stabilities of these compounds have been compared with those of other aromatic substances. It was found in the case of the phosphine, where coordinating electrons exist on the metalloid atoms, that complete fluorine substitution increases its thermal stability and resistance to oxidation. On the other hand, complete fluorination decreases the thermal stability of the silane.

Rate of reaction of nitrogen atoms with ethylene, J. T. Herron, *J. Chem. Phys.* **33**, No. 4, 1273-1274 (Oct. 1960).

A mass spectrometric study has been made of the rate of the reaction of nitrogen atoms with ethylene. The average value of the second order rate constant over the temperature interval 200 °C to 330 °C was 5.8×10^{10} cm.³mole⁻¹sec⁻¹.

Surface area determination of kaolinite using glycerol adsorption, K. H. Woodside and W. C. Ormsby, *J. Am. Ceram. Soc.* **43**, No. 12, 671-672 (Dec. 1960).

Some work has already been done on the application of the so-called glycerol retention method in the determination of surface areas of clays, including kaolinites, as well as well as other solid adsorbents. The present investigation compares the surface areas of a series of controlled particle-size fractions of a domestic kaolinite using this rapid method with the more conventional but more laborious nitrogen adsorption method. Results showing good agreement confirm the work of earlier investigators and demonstrate the utility of the method when applied to kaolin-type clays.

The heat of combustion of dicyanoacetylene, G. T. Armstrong and S. Marantz, *J. Phys. Chem.* **64**, 1776-1777 (1960).

The heat of combustion of liquid dicyanoacetylene (C₄N₂) in oxygen to form carbon dioxide and nitrogen has been measured to be 2078.5 ± 0.7 kJ mole⁻¹ (496.8 ± 0.2 kcal mole⁻¹), the indicated uncertainty being the standard error of the preceding mean. The standard heat of formation, $\Delta H^\circ_{f,298}$ [C₄N₂(l)], is calculated to be 120.6 kcal mole⁻¹. The binding energy at 298 °K of the C₄N₂ molecule is calculated to be 783.6 kcal mole⁻¹.

Electrodeless passage of direct current through an electrolyte, A. Brenner, *J. Electrochem. Soc.* **107**, No. 12, 968-973 (Dec. 1960).

An experimental setup is described for directly observing the electrical migration of a dye in a conducting system without electrodes. Direct current was produced in a continuous circuit of electrolyte, which included the dye solution, by means of a transformer and a mechanical commutator.

Condensation coefficient of arsenic trioxide glass, A. B. Bestul and D. H. Blackburn, *J. Chem. Phys.* **33**, No. 4, 1274-1275 (Oct. 1960).

The maximum rate of vaporization from arsenic trioxide glass at 194 °C has been determined by measurement of weight loss in vacuum. The results lead to a condensation coefficient of 2.2×10^{-6} . It has been shown that undetected surface cooling due to the absorption of latent heat of vaporization cannot account for the major part of the deviation of this value from unity.

The compound BaTiGe₃O₉, C. R. Robbins, *J. Am. Ceram. Soc.* **43**, No. 11, 610 (Nov. 1960).

BaTiGe₃O₉ is stable from 1132° ± 10 °C to 1235° ± 10 °C. The room temperature X-ray powder diffractometer pattern was indexed on the basis of a hexagonal unit cell with $a = 11.73\text{Å}$, $c = 10.02\text{Å}$ and $c/a = 0.8542$. The theoretical density

is 4.54 and $Z = 6$. The description of BaTiGe₃O₉ in the literature apparently describes a solid solution of titania in barium tetragermanate. At room temperature, BaTiGe₃O₉ is structurally similar to, but not isostructural with BaTiSi₃O₉. Within its temperature stability range, BaTiGe₃O₉ is apparently isostructural with BaTiSi₃O₉, with $a \cong 6.8\text{Å}$ and $c \cong 10.04\text{Å}$.

Other NBS Publications

Journal of Research, Section 65C, No. 2, April-June 1961. 75 cents.

An experimental study concerning the pressurization and stratification of liquid hydrogen, A. F. Schmidt, J. R. Purcell, W. A. Wilson, and R. V. Smith.

Temperature dependence of elastic constants of some cermet specimens, S. Spinner.

Analog simulation of zone melting, H. L. Mason.

Residual losses in a guard-ring micrometer-electrode holder for solid-disk dielectric specimens, A. H. Scott and William P. Harris.

A bolometer mount efficiency measurement technique, G. F. Engen.

Telescope for measurement of optic angle of mica, S. Ruthberg.

An automatic fringe counting interferometer for use in the calibration of line scales, H. D. Cook and L. A. Marzetta.

Journal of Research, Section 65D, No. 3, May-June 1961. 70 cents.

Propagation studies using direction-finding techniques, E. C. Hayden.

Diversity effects in long distance high frequency radio pulse propagation, S. A. Bowhill.

Influence of ionospheric conditions on the accuracy of high frequency direction finding, P. J. D. Gething.

Phase difference observations at spaced aerials and their application to direction finding, W. C. Bain.

Research at the National Bureau of Standards applicable to long-distance location and direction-finding problems, R. Silberstein.

Design for spinning goniometer automatic direction finding, W. J. Lindsay and D. S. Heim.

Resolution characteristics of correlation arrays, I. W. Linder.

Instrumentation for propagation and direction-finding measurements, E. C. Hayden.

Brooke variance classification system for DF bearings, E. M. L. Beale.

Estimation of variances of position lines from fixes with unknown target positions, E. M. L. Beale.

Statistics of a radio wave diffracted by a random ionosphere, S. A. Bowhill.

Space analysis of radio signals, J. B. Smyth.

Effect of receiver bandwidth on the amplitude distribution of VLF atmospheric noise, F. F. Fulton, Jr.

Excitation of VLF and ELF radio waves by a horizontal magnetic dipole, J. Galejs.

Climatic charts and data of the radio refractive index for the United States and world, B. R. Bean, J. D. Horn, and A. M. Ozanich, Jr., NBS Mono. **22** (1960) \$2.

Units of weight and measure (United States customary and metric) definitions and tables of equivalents, NBS Misc. Publ. **233** (1960) 40 cents.

Report of the 45th national conference on weights and measures 1960, NBS Misc. Publ. **235** (1960) 75 cents.

Standard frequencies and time signals from NBS stations WWV and WWVH, NBS Misc. Publ. **236** (1960) 10 cents.

Research highlights of the National Bureau of Standards, Annual Report, fiscal year 1960, NBS Misc. Publ. **237** (1960) 65 cents.

Report of the International Commission on radiological units and measurements (ICRU) 1959, NBS Handb. H78 (1961) 65 cents.

Supplementary world maps of F2 critical frequencies and maximum usable frequency factors, D. H. Zacharisen, NBS TN2-2 (PB151361-2) (1960) \$3.50.

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- Quarterly radio noise data—June, July, August 1960, W. Q. Crichlow, R. D. Disney, and M. A. Jenkins, NBS TN18-7 (PB151377-7) (1960) \$1.75.
- VHF radio propagation data for Cedar Rapids-Sterling, Anchorage-Barrow, and Fargo-Churchill test paths April 1951 through June 1958, G. R. Sugar and K. W. Sullivan, NBS TN79 (PB161580) (1960) \$4.00.
- Bibliography of tropospheric radio wave scattering, R. L. Abbott, NBS TN80 (PB161581) (1960) \$2.25.
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- A theoretical study of sporadic-E structure in the light of radio measurements, K. Tao, NBS TN87 (PB161588) (1961) \$1.25.
- Flexural strength of specimens prepared from several uranium dioxide powders; its dependency on porosity and grain size and the influence of additions of titania, F. P. Knudsen, N. S. Parker, and M. D. Burdick, *J. Am. Ceram. Soc.* **43**, No. 12, 641-647 (Dec. 1960).
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