PROGRESS IN
INORGANIC CHEMISTRY

EDITED BY
STEPHEN J. LIPPARD
DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
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PROGRESS IN
INORGANIC CHEMISTRY

Volume 12

Dimethyl Sulfoxide in Inorganic Chemistry

By Warren L. Reynolds

University of Minnesota, Minneapolis, Minnesota

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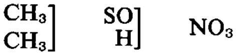
Part I. Chemical and Physical Properties of DMSO

I. INTRODUCTION

Dimethyl sulfoxide was first synthesized by Alexander Saytzeff (1) more than one hundred years ago by oxidation of dimethyl sulfide (DMS) with nitric acid. Solid DMSO·HNO_3, written as



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right] \quad \left.\begin{matrix}SO\\H\end{matrix}\right] \quad NO_3$$

was isolated, analyzed for C, H, S, and N, then treated with a carbonate to liberate DMSO which was analyzed in turn. During most of the century since its discovery DMSO was of interest to chemists mainly as the first member of the homologous series of sulfoxides and its oxidation–reduction reactions, bond energies, entropies, and enthalpies of fusion and formation, dipole moment, parachor, infrared, ultraviolet, and visible spectra were studied. In the late 1950's interest grew slowly in DMSO as a reagent, ligand, solvent, and biologically useful compound. By 1960 the number of publications on inorganic and organic applications of DMSO increased very sharply, partly as a result of commercial availability of the solvent. In 1964 Jacob, Bischel, and Herschler (2) reported on a number of promising medical uses of DMSO in addition to its proven use in low-temperature preservations of living tissues and organisms; these were: (*1*) penetrant carrier, (*2*) local analgesic agent, (*3*) anti-inflammatory adjunct, (*4*) bacteriostatic agent, (*5*) diuretic, (*6*) tranquilizer, and (*7*) potentiator of other drugs or compounds used in medical treatments. At this point the number of publications involving DMSO reached near-flood proportions. Of approximately 1500 papers utilizing DMSO in some way between 1867 and the end of 1967, the majority are post 1964. In this chapter literature of interest to inorganic chemists will be reviewed comprehensively.

II. PHYSICAL PROPERTIES

There is some disagreement among reported values of many of the physical properties of DMSO which may result from lack of proper purification, from decomposition at elevated temperatures and from the tendency of DMSO to undergo oxidation–reduction reactions. Reported values are listed in Table I.

TABLE I
Various Physical Properties of DMSO

Property	Values	Refs.
Boiling point[a]	189.0 ± 0.2°, 190°	2,3
Freezing point	18.42°, 18.45°, 18.55 ± 0.02°, 18.50°, 18.52°[b], 19.5°	2–7
Freezing point constant	4.09, 4.36, 4.4 deg/molal 4.8 deg/molar	2,8,9,10
Density	1.0950 g/ml at 25°	11
Viscosity	1.96, 1.99, 2.000, 2.003, 2.19 centipose at 25°	3,11–14
Surface tension	46.2, 43.54 dyne/cm at 20°	3,15
Parachor	184.4, 182.7	3,15
Surface free energy	42.41 erg/cm^2	15
Surface entropy	0.115 erg/deg cm^2	15
Surface enthalpy	77.1 erg/cm^2	15
Surface latent heat	34.7 erg/cm	15
Refractive index	1.4740 to 1.4773 at 25°	3,11,14, 16,17
Molar refraction	20.12, 20.13, 20.14	3,11,14
Polarizability	8×10^{-24} cm^3	3
Dipole moment	3.9, 3.96 ± 0.04, 4.1, 4.3 D; 3.94 ± 0.06 D (DMSO-d_6)	3,16–18 18
Dielectric constant	46.36, 46.4 at 25°	17,19,20
Enthalpy of vaporization	12.64 kcal/mole at 25°; 13.67 kcal/mole at 189°	4 3
Trouton constant	29.5 cal/deg mole	3
Enthalpy of fusion	1.56, 3.03, 3.23, 3.43 kcal/mole	3,8,9,21
Entropy of fusion	10.4 cal/deg mole	9
Moments of inertia	61.9, 127.6, 334.8 $\times 10^{-40}$ g cm^2 (principal moments); 5.079 $\times 10^{-40}$ g cm^2 (methyl group rotation)	22

[a] These values are probably more accurate than the value of 192° calculated by Douglas (4) from a pressure–temperature equation.

[b] Thermometer checked against highly purified *tert*-butyl alcohol which melted at 25.59°.

The freezing points of binary mixtures of water and DMSO (23,24), acetic acid and DMSO (25), benzene and DMSO (9), and sucrose and DMSO (26) have been determined.

Molecular weight determinations in DMSO by the freezing point depression method have been made (10,27–30) but mainly for organic compounds.

Activity coefficients of alkali metal halides have been estimated from freezing point depressions (see Sec. I in Part II on Group IA elements).

Variation of density has been studied for pure DMSO over a range of temperatures (3,15) or for mixtures of DMSO with a second component either at one temperature (6,11,31) or at several temperatures (5,13,14,19, 32–34). The second component in the mixture has been variously water (6,11,13,14,19), benzene (13,31), sugar (5), methanol (32), ethanol (32), propanol (32), toluene (33), benzaldehyde (33), chlorobenzene (33), nitrobenzene (33), aniline (33), phenol (33), guaiacol (33), acetic acid (13), chloroform (13), 1,2,3-propanetriol (34), 1,2-ethanediol (34), or 2-methoxyethanol (34).

Wolford (19) expressed the density of DMSO–water mixtures as a function of composition and temperature with the equation:

$$\rho = b_0 - b_1 \cdot 10^{-3} \cdot t - b_2 \cdot 10^{-6} \cdot t^2$$

for the temperature range $0^\circ \leqslant t \leqslant 75^\circ$ and conveniently listed the values of the b parameters to be used for various compositions in a table.

Schläfer and Schaffernicht (3) measured the viscosity, η, at 10° intervals over the range 20–130° and, assuming that η was given by $\eta = A \exp(B/RT)$, found that the plot of $\log \eta$ vs. $1/T$ was concave upward. In the temperature range 20–50°, B was approximately equal to 3.7 kcal mole^{-1}, whereas in the range 90–130°, B was approximately equal to 2.5 kcal mole^{-1}.

From a plot of molar volume versus $1/\eta$ Schläfer and Schaffernicht (3) determined free volumes for DMSO; these ranged from 2.8 cm^3 mole^{-1} at 20° to 6.4 cm^3 mole^{-1} at 80°.

LeBel and Goring (11) and Cowie and Toporowski (14) determined viscosities over the complete range of water:DMSO ratios at 25° and found that the plot of η vs. composition had a maximum at approximately 0.65 mole fraction of water, i.e., at approximately a 2:1 water:DMSO ratio. The minimum in the plot of freezing point vs. composition also occurred at this composition (23). Lindberg and Lauren (13) obtained similar results for water, acetic acid, chloroform, and benzene added to DMSO indicating that a 2:1 complex was formed between the added component and DMSO. On the other hand, Hastbacka and Lindberg (34) found that a 1:1 complex was indicated for the same reasons between 1,2,3-propanetriol, 1,2-ethanediol, or 2-methoxyethanol and DMSO.

The parachor was not independent of temperature but increased somewhat with increasing temperature (15). As a function of temperature the surface tension was given by (15)

$$\sigma = 45.78 - 0.1145t$$

for $20° \leqslant t \leqslant 60°$.

Refractive indices of DSMO–water (11,14), DMSO–benzene (17), and DMSO–alcohol (35) mixtures have been determined.

Dielectric constants at temperatures other than 25° were listed by Schläfer and Schaffernicht (3) and Wolford (19). Dielectric constants of binary mixtures of DMSO with water (19,20), benzene (17), alcohols (35), and sulfamic acid (36) are also available. In DMSO–water mixtures the measured dielectric constants showed a positive deviation from the value calculated by the simple expression, $x_1\epsilon_1 + x_2\epsilon_2$, involving the mole fractions of the two components and their dieletric constants.

A. Crystal and Molecular Structure

DMSO crystallized in the monoclinic system with four molecules per unit cell. At −60° the *a*, *b*, *c* unit cell dimensions were (37) 11.496, 6.742, and 5.234 Å, respectively, and the β angle was 95.37°; at 5° they were 11.693 ± 0.010, 6.829 ± 0.003, 5.303 ± 0.005 Å, and 94°30′ ± 15′, respectively (38).

The molecular interatomic distances and angles found for gaseous and solid DMSO are listed in Table II.

TABLE II

Molecular Interatomic Distances and Angles for DMSO

State	r(S—O), Å	r(C—S), Å	r(C—H), Å	∠CSC	∠CSO	∠SCH	Ref.
Gaseous	1.47	1.82	1.08	100 ± 5°	107 ± 5°	—	39
	1.477	1.810	1.095	96°23′	106°43′	107°31′	40
Solid[a]	1.471	1.812	—	97.86°	107.04°	—	37
		1.801	—	—	107.43°	—	37
	1.531	1.798	—	97.4°	106.7°	—	38

[a] The values found in reference 38 were not corrected for thermal motion and the values found in reference 37 were corrected for thermal motion.

B. Thermal Expansion Coefficients

Thermal expansion coefficients have been determined over the temperature range 0–50° for DMSO–water (41) and DMSO–alcohol (42) mixtures and over the temperature range 20–50° for the DMSO–benzene (43) mixture.

C. Vapor Pressure and Activity Coefficients

From vapor pressure measurements of pure DMSO over the range 20–50° Douglas (4) proposed the equation

$$\log p = 26.49558 - (3539.32/T) - 6.00000 \log T$$

which accurately predicted (44) the vapor pressure at 70.00°. These measurements have been extended for a few temperatures above 70° (3); at 98.0° the measured vapor pressure was 32.1 torr but the calculated value is 34.9 torr so that disagreement is serious at this temperature.

Vapor pressures of DMSO mixtures with water at 70° (44), benzene at various temperatures (45), methanol, dioxane, and carbon tetrachloride at 20° and 40° (46) have been measured and used to calculate activities or activity coefficients (44–47) of the components over the complete range of compositions.

D. Heat Capacity

The equation for the heat capacity at constant pressure of DMSO as a function of temperature has been given as (6)

$$C_p^t = C_p^{25} + a(t - 25)$$

where $C_p^\circ = 35.6$ cal deg^{-1} mole^{-1} and $a = 0.070$. The values predicted by this simple relation do not agree well with the values of 37.7 and 40.6 cal deg^{-1} mole^{-1} listed (21) for 96.0° and 149.0°, respectively.

Heat capacities of DMSO–water (6) and DMSO–benzene (31) mixtures over the full range of concentrations have been given also.

Mackle and O'Hare (22) have proposed the relation:

$$C_p^\circ(T\,^\circ\mathrm{K}) = 6.94 + 5.6 \times 10^{-2}T - 2.27 \times 10^{-5}T^2$$

for the gas in the ideal state.

E. Enthalpy and Entropy of Formation

The enthalpy of formation of liquid DMSO at 18° from rhombic sulfur and beta-graphite carbon was given as −47.7 kcal mole^{-1} by

Douglas (4), that of gaseous DMSO at 298.16°K using the same standard states (48) as -35.3 kcal mole^{-1}, and that of gaseous DMSO at 298.16°K using $S_2(g)$ as the standard state of sulfur as -49.99 kcal mole^{-1} (22). The free energies of formation at 298.16°K from S(rhombic) and $S_2(g)$ were -18.9 (48) and -27.65 (22) kcal mole^{-1}, respectively. The entropy of DMSO(g) at 298.16°K was 73.20 cal deg^{-1} mole^{-1} (22). The $H_0°$ values at 298.16°K were (48) -30.3 and -46.1 kcal mole^{-1} for S(rhombic) and $S_2(g)$ standard states. The values of these and other thermodynamic functions were given for the temperature range 298.16–1000°K (22,48).

The enthalpies for the subtraction and addition of an oxygen atom at 18° were

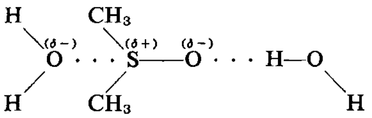
$$(CH_3)_2SO(l) = (CH_3)_2S(l) + \tfrac{1}{2}O_2(g);$$
$$\Delta H = 33.26 \pm 0.1 \text{ kcal mole}^{-1}$$
$$(CH_3)_2SO(l) + \tfrac{1}{2}O_2(g) = (CH_3)_2SO_2(c);$$
$$\Delta H = -59.00 \pm 0.2 \text{ kcal mole}^{-1}$$

F. Enthalpy of Mixing

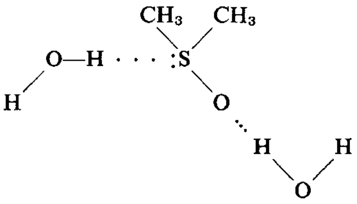
Mixing of DMSO with water was accompanied by an exothermic reaction (6,14,44) the magnitude of which depends upon the composition and, to a lesser extent, upon the temperature of the mixture. Kenttämaa and Lindberg (6) expressed the enthalpy of mixing, ΔH_m^t, by the equation:

$$\Delta H_m^t = \Delta H_n^{25} + \alpha(t - 25) + \beta(t - 25)^2$$

and listed values of ΔH_m^{25}, α and β for various mole fractions of DMSO. There is disagreement between these values of ΔH_m^{25} and those given by Cowie and Toporowski (14) although both sets of values show a maximum evolution of heat at a water:DMSO mole ratio of approximately 2:1. In the mixing process water–water hydrogen bonds and DMSO–DMSO dipole–dipole bonds are broken and water–DMSO bonds are formed with a considerable evolution of heat indicative of the strength of the new bonds formed. It is this strong interaction between DMSO and water which lowers the activity of the water to such an extent that the presence of small amounts of water do not appreciably interfere with preparations of anhydrous salts, electrode reactions, rates of reaction, or positions of chemical equilibria in DMSO. At the 2:1 mole ratio of water:DMSO where properties such as density, viscosity, freezing point, and heat of mixing have an extremum it would appear that some complex, perhaps of the structure of **1** or **2**



or



(1) **(2)**

is formed.

Enthalpies of mixing of DMSO with acetic acid, alcohols (49), acetone (15), benzene (31), chloroform (50), and carbon tetrachloride (50) have also been measured.

G. Bond Energies

For the reaction

$$R_1R_2SO(g) = R_1R_2S(g) + O(g) \qquad \Delta H = D(R_1R_2S—O)$$

Mackle and O'Hare (51) calculated the value of 89 to 90 kcal mole^{-1} for the dissociation energy of the sulfoxide bond of a number of sulfoxides. Although DMSO was not explicitly treated there is little doubt that the energy would not be the same in DMSO. In sulfones the mean dissociation energy for loss of the oxygen atoms was 100–103 kcal mole^{-1} each. The stronger S—O bond of sulfones is associated with a greater double bond character and a smaller basicity of the oxygen atoms so that complexes with metal ions are much less readily formed than with sulfoxides.

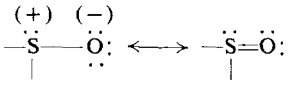
The dissociation energy of the C—S bond in the reaction (state of SO not specified):

$$R_1R_2SO(g) = R_1(g) + R_2(g) + SO(g)$$

was 50.3 kcal per bond (51) for DMSO and was essentially constant for a series of symmetrical sulfoxides.

H. Infrared Spectra

The vibrational frequencies used by Mackle and O'Hare (22) were those assigned by Horrocks and Cotton (52) from a study of the infrared spectrum of liquid and gaseous DMSO (53) and DMSO-d_6. Many studies of infrared and raman spectra of sulfoxides and sulfones have been made since such spectra were first reported in 1949 (54); most of these have been very qualitative and incomplete. The S—O stretching frequency, ν(SO), has been of great importance in the study of the bonding and complexing of DMSO by other chemical species. The sulfur–oxygen bond has been frequently regarded as having considerable double bond character (55), i.e., as being a resonance hybrid of structures **3** and **4**:



(3) **(4)**

Bonding of a metal ion (16,53) *to the oxygen atom of coordinated DMSO stabilizes electronic structure* **3**, *lowers the bond order of the* S—O *bond and decreases* ν(SO); *bonding of a metal ion to the sulfur atom of coordinated DMSO stabilizes electronic structure* **4**, *increases the* S—O *bond order and increases* ν(SO). Likewise, replacement of the methyl groups of DMSO by increasingly electronegative groups increases ν(SO) (62).

The values of ν(SO) which have been determined for gaseous and liquid phases and in various solvents are given in Table III.

TABLE III

Sulfur–Oxygen Stretching Frequencies of DMSO in Gaseous, Liquid, and Solution Phases

State or solvent	ν(SO), cm^{-1}	Ref.
Vapor	1102, 1103	53,56
(cf. SO	1124	54)
Liquid	1055	53
	1057	57
	1056	58
	1046	59
	1043 (raman)	60
	1042 (raman)	61
Hexane	1085	57
Tetrachloroethylene	1075	57
Carbon tetrachloride	1072	57
Carbon disulfide	1071	57
Acetonitrile	1061	57
Pyridine	1060	57
Chloroform	1055	57

In solution ν(SO) varies with the nature of the solvent. The data of Cairns, Eglinton, and Gibson (57), given in Table III, are illustrative of the change of ν(SO) with solvent. But it should be pointed out that because of the tendency of DMSO to associate, the shifts in ν(SO) are usually concentration dependent. Not even the data obtained at a constant concentration of DMSO in a series of solvents are strictly comparable since the state of aggregation of DMSO may vary from solvent to solvent. Few values of ν(SO) are available at infinite dilution. An exception is the value of ν(SO) for DMSO in water. Lindberg and Majani (59) found that ν(SO) was a linear function of the dielectric constant of the solution over the range of concentrations from pure DMSO to nearly pure water at 25°; the extrapolated value of ν(SO) at infinite dilution was 1010 cm^{-1}. Raman spectra of acetic acid–DMSO mixtures (25) showed a continuous change from a predominance of symmetrical acetic acid dimers in pure acetic acid to a hydrogen bonded network of acetic acid and DMSO molecules where ν(SO) was approximately equal to 1010 cm^{-1}. Other reports on ν(SO) in solutions exist (58,60,63).

Quantitative treatments of vibrational frequencies (52,64), centrifugal expansion (65) and the internal rotation barrier (66) have been made; the latter had a value of approximately 3 kcal $mole^{-1}$. The force constant obtained for the S—O stretch was (52) 6.54×10^5 dyne cm^{-1}, for the C—S stretch, 3.03×10^5 dyne cm^{-1}, for the C—S—O bend, 0.502×10^5 dyne cm^{-1}, and for the C—S—C bend, 0.459×10^5 dyne cm^{-1}. The force constant for the S—O stretch in DMSO may be compared with those of Br_2SO, Cl_2SO, and F_2SO which are 7.80×10^5, 9.69×10^5, and 11.0×10^5 dyne cm^{-1} (67), respectively. Other force constants which have been given for the S—O bond are 7.0×10^5 (68) and 6.95×10^5 dyne cm^{-1} (54) in DMSO and 9.4×10^5 and 10.8×10^5 dyne cm^{-1} (54) for Cl_2SO and F_2SO, respectively.

As a medium in which to record the infrared spectra of other substances, DMSO is useful between 1.0 and 1.67 and between 1.78 and 2.14 μ (69).

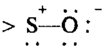
I. Ultraviolet, Visible, and Near-Infrared Spectra

The vacuum ultraviolet spectrum of gaseous DMSO showed one absorption at 190 nm and a second, more intense absorption from 175 to 155.5 nm (70). Below 135 nm continuous absorption occurred. Contrary to this, saturated dialkyl sulfones were transparent to wavelengths down to at least 180 nm (71).

In ethanol the absorption maximum for various dialkyl sulfides, disulfides, and sulfoxides occurred at approximately 201 nm (72); presumably DMSO would absorb at the same wavelength but DMSO was not among the compounds examined. The fact that dialkyl sulfones did not absorb in this region led the authors (72) to the conclusion that the transition involved the lone-pair electrons on the sulfur. Furthermore, the lack of dependence of the position of the maximum absorption on the alkyl groups attached to sulfur in the sulfides and sulfoxides led the authors (72) to suggest that the electron transition was to a sulfur 3*d* orbital rather than to a σ antibonding carbon–sulfur orbital.

The DMSO absorption maximum occurred at 210 nm in heptane (73) and at 210 nm, with a molar extinction efficient, ϵ, of $889M^{-1}\,\text{cm}^{-1}$, in water (74). Change of solvent has been noted to markedly change the extinction coefficients of dialkyl sulfides, which absorb in essentially the same region as the sulfoxides, but to have only a small effect on λ_{max} (72). For example, the extinction coefficients of dialkyl sulfides incyclo hexane are approximately twice those in ethanol but λ_{max} is not significantly changed (72). On the other hand, change of solvent significantly affected ν(SO) (see Sec. II-H in part I on Infrared Spectra). Hence it would seem that the lone pair of electrons on the sulfur atoms of sulfides and sulfoxides is not significantly involved in the solvent–solvent interaction whereas the oxygen atom of the sulfoxide is. If the lone-pair electrons on sulfur are not involved in solvent–solvent interaction then structures such as **2** in Sec. II-F in Part I may be eliminated.

Addition of a proton to DMSO blue-shifted the absorption at 210 nm (74) so that the protonated form of DMSO had only a small absorption at 210 nm. Because addition of a proton to the oxygen of DMSO would increase the positive charge on the sulfur by stabilizing the structure



$$> \overset{+}{\underset{\cdot\cdot}{S}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{-}$$

the lone-pair electrons on sulfur would be drawn in closer to the sulfur and the absorption blue-shifted if the lone-pair electrons on sulfur are involved in the excitation. Of course, the absorption for this lone pair of electrons would be blue-shifted if the proton bonded to the DMSO through the lone pair but this is less likely than the proton bonding to the oxygen atom.

Throughout the visible region DMSO is transparent. In the near infrared region absorption peaks at 1100, 1350, 1650, 1700, 2250, 2300, 2450, 2500, and 2800 nm (3) have been reported.

Oxygen dissolved in liquid DMSO markedly enhanced the ultraviolet absorption of DMSO from 400 to 260 nm (75). A charge-transfer interaction with oxygen as electron acceptor and DMSO as electron donor apparently occurred. If this interpretation is correct the wave number ν of the oxygen-induced absorption band can be calculated to be 35,800

cm^{-1}, taking the vertical ionization potential of DMSO to be 8.85 ± 0.05 eV (76), in good agreement with the observed value of 36,600 cm^{-1} (75). From the position (36,800 cm^{-1}) of the absorption band for the I_2–DMSO charge-transfer complex (see Sec. XII-E in Part II), Klaeboe (73) has estimated the ionization potential of DMSO to be 9.6 eV, which agrees within 10% with the value of Vilesov and Kurbatov (76).

The anion of DMSO, methyl sulfinyl carbanion, $CH_3COCH_2^-$, in DMSO showed a strong absorption at approximately 272 nm with an ϵ_{max} of $\sim 4 \times 10^4 M^{-1}$ cm^{-1} (77).

J. Mass Spectrum

The main peaks in the mass spectrum of DMSO were due to CH_3SO^+, HCS^+, $(CH_3)_2SO^+$, $CH_3SCH_2^+$, and CH_3^+ (78). The potential at which O^+ appeared in the spectrum corresponded to a dissociation energy of 30 kcal $mole^{-1}$ (3).

K. Nuclear Magnetic Resonance Spectrum

The chemical shift of the main proton resonance in liquid DMSO of normal isotope composition has been reported as +4.98 ppm (79) relative to a benzene external standard, as −2.5 ppm (80) and −152.5 Hz (81) relative to TMS and DDS (disodium 3-(trimethylsilyl)-1-propane sulfonate), respectively. The ^{13}C, present in natural abundance, gave rise to two satellite peaks, one on each side of the main DMSO peak. The $^{13}C—^1H$ coupling constant has been reported as 138 (80,82) and 137.6 Hz (83), cf. 138 for CH_3SH, 138 for $(CH_3)_2S$, and 140 Hz for $(CH_3)_2SO_2$ (84). The coupling constant of 138 Hz for $^{13}C—^1H$ was used to calculate a value of 2.65 for the Huggins' electronegativity of S bonded to C in DMSO (85). This coupling constant was affected by solvent, a mole fraction of 0.35 DMSO in carbon tetrachloride, water, and phenol giving values of 137.6, 139.2, and 138.9 Hz, respectively (83).

The ^{13}C satellites are actually quartets due to the coupling of the protons on one methyl group with the protons on the other, with a $^1H—^1H$ coupling constant of 0.45 Hz (80,83). This coupling constant appeared to be independent of solvent (83).

The rate constants for the exchange of hydrogen between DMSO and $Na^+CH_3SOCH_2^-$ and between DMSO and $Li^+CH_3SOCH_2^-$ in DMSO at 37° were $12M^{-1}$ sec^{-1} and $7M^{-1}$ sec^{-1} determined from the broadening of the ^{13}C satellites at various concentrations of the base (80).

The motion of the methyl groups in solid DMSO was examined from 95°K to the melting point (86). At temperatures greater than 150°K there was rapid reorientation of the methyl groups about their three-fold axis.

Partly because of its simple spectrum and good solvent properties, DMSO is very useful as a medium in which to study the NMR spectra of other species. Also DMSO-d_6 can be prepared by a relatively inexpensive, simple and rapid method (87,88).

L. Instability of DMSO in Certain Systems

Addition of concentrated perchloric acid to DMSO, even cooled and solidified DMSO, results in an explosive reaction. Solid metal perchlorates containing DMSO are also highly explosive. Drying of DMSO with magnesium perchlorate has resulted in an explosion (89), as has reacting sodium hydride with DMSO containing isoquinoline (90). Various chlorides such as cyanuric, acetyl, benzoyl, benzenesulfonyl, thionyl and phosphoryl chlorides, and phosphorus trichloride also react vigorously and exothermally with DMSO (91).

III. ACID-BASE PROPERTIES

The DMSO molecule is more basic than acetone or dimethyl sulfone molecules with respect to hydrogen ion, metal ions, neutral acids such as BF_3, and hydrogen bond formation with acidic protons. Kolthoff and Reddy (92) obtained a value of 2.2 mole liter^{-1} for the equilibrium constant of the reaction

$$H_3O^+ + DMSO = H_2O + DMSO \cdot H^+$$

in DMSO at room temperature; Reynolds and Lampe (74) obtained a pK_a for DMSO·H$^+$ dissociation in aqueous perchloric acid media of -2.01 ± 0.15 at 21°. The value of 5×10^{-18} (92) for the autoprotolysis constant of DMSO in DMSO is not in agreement with the pK_a values of 31 to 33 (93–95) for DMSO in DMSO.

Perchloric, sulfuric, and hydrochloric acids were strong monoprotic acids in DMSO (96). The limiting ionic conductance of the proton in DMSO was approximately 17 at 30° (96) as compared to 16 for Cs$^+$ (see Table V). This value for the proton showed that a Grotthuss type of conduction was absent for the hydrogen ion in DMSO and that it diffused in the solution much as any other ion with a unit positive charge. The diffusion coefficient of the proton was 4.4×10^{-6} cm^2 sec^{-1} (96).

Solutions of methanesulfonic acid in DMSO do not show conventional OH bands in the infrared spectrum (97). It has been postulated that the proton from the completely ionized acid jumps back and forth between two DMSO molecules in a strong, nearly symmetrical, hydrogen bond with a frequency of approximately 10^{-14} sec^{-1} (97). Similar spectra have been reported by Hadzi (98,99). However, the infrared spectra of HCl solutions in highly purified DMSO show a strong wide band in the region 3000–3500 cm^{-1} (100) where the OH frequency may be expected.

The Hammett acidity function H_- for the DMSO–water–0.011*M* $(CH_3)_4NOH$ system ranges from 12 in purely aqueous media to 26.2 at 99.6 mole % DMSO (101–104); H_{2-} values have also been reported (105) over the range from zero to 96.9 mole % DMSO. The H_{2-} values are only slightly less than the H_- values at all concentrations of DMSO greater than zero. The availability of a wide range of very basic media, which are rather good solvents in addition, may be expected to stimulate considerable research in metal–OH^- complexes or in metal–anion complexes where the anion is derived from a very weak acid, i.e., the anion is very basic.

The basicity of DMSO towards Lewis acids such as metal ions or BF_3 has been well proven and will not be discussed here; the complexes formed will be discussed in the sections devoted to the particular elements involved.

The basicity of DMSO is also demonstrated by its readiness to form hydrogen bonds with water, alcohols, phenols, oximes, carboxylic acids, C—H and N—H bonds, nucleosides, and carbohydrates. The extensive literature in this area is beyond the scope of this article to review.

DMSO has been titrated with perchloric acid in glacial acetic acid (106–108) and weak acids have been titrated with dimsylsodium, $Na^+CH_3SOCH_2^-$ (109), with dimsylpotassium, $K^+CH_3SOCH_2^-$ (110), alkoxide bases (111–113), or with substituted ammonium hydroxides (114) in DMSO.

Equilibrium constants for the reaction of methylsulfinyl carbanion, $CH_3SOCH_2^-$, with triphenylmethane, *tert*-butanol and *n*-propanol were determined (115); the equilibria lay far to the right in favor of undissociated DMSO.

IV. SOLVENT PROPERTIES

Solvent activity coefficients, ${}^0\gamma_i{}^s$, which relate the concentration equilibrium constant in a solvent *S* to the activity equilibrium constant in a reference solvent, have been determined by Parker and co-workers (116,117) for DMSO relative to methanol for the cations Na^+, K^+, Ag^+, and Ph_4As^+ and for the anions Cl^-, Br^-, I^-, N_3^-, SCN^-, ClO_4^-,

BPh_4^-, $AgCl_2^-$, $AgBr_2^-$, AgI_2^-, and acetate ion from solubility and stability constant measurements. The equation defining the ${}^0\gamma_i{}^s$ is

$$\bar{\mu}_i{}^s - \bar{\mu}_i{}^0 = RT \ln {}^0\gamma_i{}^s$$

where the $\bar{\mu}_i$ are the partial molar free energies of ion *i* in solvent *S* and the reference solvent; by reference to this equation it is seen that a positive value of log ${}^0\gamma_i{}^s$ means that ion *i* is less solvated in solvent *S* than in the reference solvent, whereas a negative value means that ion *i* is more solvated in *S* than in the reference solvent. The Cl^-, Br^-, I^-, N_3^-, SCN^-, and acetate ions were less solvated in aprotic DMSO than in the protic solvent methanol whereas the remainder were more solvated by DMSO.

Less quantitative studies of solubilities have been made of various inorganic salts (3,118–121), sodium hydroxide and sodium methoxide (122), acetylene (2,123,124), sulfur dioxide (125), helium, neon, and hydrogen (126).

The cyanides (120) of sodium, potassium, Cu(I), Ni(II), Zn(II), and Co(II) were insoluble but the cyanides of Hg(II) and Cd(II) were soluble. However, mixtures of KCN and Hg(II), Cu(I), Ni(II), Zn(II), or Co(II) cyanides did dissolve, probably with formation of cyano complexes of the nonalkali metal ions. The soluble Cd(II) cyanide did not dissolve KCN.

General discussions of solubilities and factors affecting solubilities have been given by Parker (127), Ranky and Nelson (24), Miller and Parker (128), and Agami (129). For dipolar, aprotic solvents Miller and Parker (128) gave the order

$$\text{picrate} > I^- > SCN^- > Br^- > N_3^- > Cl^- \gg F^-$$

for the order of decreasing solvation of anions with F^- showing a very high activity due to very poor solvation. As a general rule, the small anions are very poorly solvated and have high activities in dipolar, aprotic solvents as compared to protic solvents since the anions can form hydrogen bonds in the latter solvents. Even alkoxide ions were much more basic in DMSO than in alcoholic media (110) as a result of the lack of stabilizing hydrogen bond formation in DMSO and alcohols appeared to be intrinsically much weaker acids in DMSO than in alcoholic media.

For dipolar, aprotic solvents the order of decreasing ability to solvate cations has been given as (127)

$$\text{DMSO} > \text{DMF} > \text{acetone} \gg \text{acetonitrile.}$$

This order for the solvents differs from the order which would be assigned on the basis of Kosower's *Z*-value (130). The order of decreasing *Z*-value is:

$$\text{acetonitrile, DMSO} > \text{DMF} > \text{acetone.}$$

However, the *Z*-value is a measure of the ionizing power of the medium rather than the solvating ability so that the two orders need not be identical.

Prue and Sherrington (131) calculated Stokes' radii for anions and cations from limiting equivalent ionic conductances in DMSO as well as DMF and DMA solutions and compared them with crystallographic radii. The Stokes' radii of Na^+, K^+, Br^-, and I^-, for example, were 3.2, 3.0, 1.7, and 1.7 Å, respectively, whereas the crystallographic radii were 0.95, 1.33, 1.95, and 2.16 Å, respectively. They concluded that the cations carried a solvation shell with them but the anions did not. The radii given by Bolzan, Giordano, and Arvia (132) for the alkali metal ions were 3.8, 3.1, 2.9, 2.8, and 2.6 Å for Li^+ to Cs^+, respectively, and were in good agreement with those of Prue and Sherrington.

V. BIOLOGICAL STUDIES

The effect of DMSO on plant and animal systems and tissues was being investigated to some extent prior to the 1964 report of Jacob, Bischel, and Herschler (133), particularly in the areas of cold-storage preservation (134–147), reduction of radiation damage (148–151), and toxicology (152). After the preliminary report by Jacob, Bischel, and Herschler the number of studies in biological areas increased tremendously. In November, 1965, the Federal Food and Drug Administration suspended clinical testing of DMSO on humans after lens changes were observed in canines fed large doses of DMSO daily for many weeks, but in December 1966, limited clinical testing on humans was restored.

There is much of interest to inorganic chemists in the biological studies being conducted with DMSO such as chemical and phase equilibria, membrane permeability, surface chemistry, diffusion and reaction rates, hot-atom chemistry, hydrogen bonding, electrochemistry, and biological effects of metal complexes transported across membranes by DMSO.

A. Cancer

DMSO administered along with intraperitoneal tumor cell implantation in rabbits did not give a higher cancer rate in the DMSO-treated group as compared to the control group (153) even though DMSO penetrates most tissues rather readily and could presumably aid tumor cell implantation in this case. The penetration and carrying properties of DMSO were shown (154) by the effect of DMSO on dimethylbenzanthracene-induced carcinogenesis in the right cheek pouch of the hamster. When DMSO was used as a "vehicle" for the compound, the compound was apparently carried through the cheek so that it gained contact with the left cheek pouch where tumors also developed. When mineral oil was used as the vehicle for the compound a transport of tumor from the right to left cheek did not occur. Also, it was observed in this study that DMSO reduced the latent period for tumor production although DMSO did not otherwise appear to affect the tumors. Somewhat contradictory results have also been found (155). DMSO administered in rather small quantities in drinking water had no statistically significant effect on breast cancer induced by dimethylbenzanthracene in rats (156) but it apparently caused regression or retardation when applied with decadron to carcinoma lesions (157).

DSMO has been reported to be more toxic toward lymphocytes from leukemia patients than toward lymphocytes from normal persons and thus able to differentiate, at least *in vitro*, between two kinds of blood (158). The reasons for the toxic effects are unknown as yet. When DMSO penetrates the cell membranes it may exert its effect because of the substance it carries into or out of the cell. It may make the cell membrane more permeable to salts and in this way alter the salt concentration difference between inside and outside of the cell or in this way introduce metal ions into the cell which would be more poisonous to the abnormal than to the normal cells. Or the DMSO penetrating the cell may unfavorably change protein configurations because of changes in hydrogen bonding resulting from the altered solvent medium.

B. Radiology

For therapeutic utility in reducing or preventing radiation damage in living systems exposed to dangerous or lethal levels of radiation a compound should be effective at nontoxic dosages, have nontoxic metabolic products, be metabollically stable for periods sufficiently long to give protection for a satisfactory period of time after administration of the dose, be effective against various kinds of radiation, and be effective when administered after irradiation. DMSO has shown some promise in this application, at least for use in patients who may have to undergo radiation treatments regularly for medical purposes.

It has been found (see Sec. V-E of Part I) that DMSO is relatively nontoxic and this implies that the metabolic products of DMSO in the amount produced are relatively nontoxic. Metabolism of DMSO has received some study in man and animals. In man, DMSO administered orally, cutaneously, or intravenously was excreted partially unchanged in the urine (159–163) but there is disagreement as to the fraction excreted and as to the half-life for excretion. At present it would appear that the major fraction of the DMSO was excreted unchanged. Some dimethyl sulfone ($DMSO_2$) was also excreted in the urine of man and animals but usually in much smaller amounts than DMSO and with a longer half-life (159–161,164–166). A small fraction of the administered DMSO appeared as dimethyl sulfide (DMS) in the exhaled breath of man and animals in a very short time (162,163,167,168).

Ashwood-Smith (148,169) has reported a 70% survival rate at 30 days for a group of mice given a lethal dose of irradiation compared to 100% fatalities for the control group. The protective action of DMSO was not due to $DMSO_2$ or DMS metabolites. Radioprotective action has also been observed by others for mice (150,170–173), for rats (174,175), for bacteria (176), for enzymes (177,178), and for tissue cells (151).

The mechanisms for the radioprotective effects of DMSO in the various systems are not known. Indeed, the radiation chemistry of DMSO itself in simple systems has not been investigated. The protective action may arise from the early reaction of DMSO with free radicals formed in the system so as to prevent more extensive free radical processes, from the interaction of DMSO itself with the radiation, from the interaction of radiation with a substance whose concentration is increased by the presence of DMSO, or from other mechanisms. Certainly it is known that DMSO readily becomes widely distributed in the bodies of experimental rats (162,179) so that it can provide protective action when the whole body is subjected to radiation.

C. Permeability

There is no doubt that DMSO applied to the skin is quickly transported in part to the bloodstream because DMS is rapidly detected in the breath (see Sec. V-B on radiology) both by odor and by gas chromatography. However, there is disagreement concerning the efficacy of DMSO as a penetrant carrier of substances dissolved in DMSO or in DMSO–water mixtures. Some investigators (180,181) have found little evidence for penetrant carrier claims for DMSO whereas others have evidence for such claims. Hydrocortisone and fluocinoline acetonide in DMSO quickly established a protected reservoir in the *stratum corneum* which did not wash off with soap and water or with ethanol (182–184) when applied topically. Dimethyl formamide (DMF) and *N*,*N*′-dimethyl acetamide (DMA) were also very useful (185) but DMSO was stated to be the most useful. The penetration of radio-labeled hydrocortisone and testosterone increased markedly when applied to human skin in DMSO as judged by the quantity of radioactivity appearing in the urine over a five-day period (186). Cortisone acetate and 17-β-estradiol administered to female rats either subcutaneously in aqueous suspension or topically in DMSO gave comparable results in both groups indicating effective administration by the topical route (187). In 5% DMSO solutions several strains of *Escherichia coli* grew on lactose whereas they normally do not (188). Apparently the bacterial cells were made permeable to sugar in presence of DMSO. A somewhat similar observation has been made that DMSO aided sugar transport through the intestine (189). The drug P2S (1-methyl-2-hydroxyiminomethylpyridiniummethane sulfonate), when applied in DMSO to the clipped skins of guinea pigs or rabbits, gave effective protection against sarin, an anticholinesterase, and no deaths occurred even when seven LD_{50} doses of sarin were given two hours after the P2S–DMSO application (190).

Although some study has been made of the change in permeability of membranes toward some selected inorganic and organic compounds and of change in electrical potential across a membrane (191) when DMSO was added to a solution on one side of the membrane, there has been little study of a quantitative nature and the reasons for the changes may be said to be largely unknown. One suggestion (192) was that DMSO caused a change from a *cis* to a *trans* configuration about the double bonds in the lipids forming the membranes. However, the mechanism of the effect of DMSO upon the membrane and for the transport of substances through the membrane is certainly much more complicated than this. Electrochemical, hydrogen-bonding, calorimetric, and kinetic studies are indicated in addition to change-of-structure studies.

D. Preservative

The usefulness of DMSO has already been proven in preservations of blood, cells, and tissues. Glycol has been, and is, being used also but DMSO, in many instances, is as good as, or superior to, glycol. For example, bovine red blood corpuscles, which are not permeable to glycol and suffer hemolysis during freezing and thawing, can be preserved at −79° using DMSO (134,142). Human blood has been preserved with DMSO at −85°, used and found to have normal *in vivo* survival (138,139); the method used was stated to be simple, effective, and inexpensive. The maximum length of time which blood can be stored in this way has not been determined but it is likely to be much longer than the 21-day limit for storage of blood at 4° and hence stockpiling to eliminate shortages can be conveniently accomplished. Blood platelets have also been preserved at low temperatures in DMSO-containing media (135,140).

Dilute solutions of DMSO apparently inhibit the postmortem degradation of hyaluronic acid, a polysaccharide, in the vitreous humour of the eye (193). This degradation is thought to have a free-radical mechanism and if the role of DMSO is to scavenge free-radicals then the function of DMSO here may be similar to its function as a radioprotective agent. Very little is known about the reactions of free-radicals with DMSO. For low-temperature preservations DMSO was superior to glycerol (147,194) and the enormous wastage occurring with storage at 4° has, at least, been partially eliminated.

The wide-ranging possibilities for DMSO as a preservative are illustrated by its use for preserving mouse skin which has been successfuly transplanted (195), human spermatozoa (196,197), bone marrow (134,143, 145,146), mitochondria (137,198), and various living cells (136,144,199, 200, 201).

E. Toxicity

Highly purified DMSO has a rather low toxicity when administered orally, cutaneously, subcutaneously, intravenously, or intraperitoneally (152,202–211). However, DMSO can affect the toxicity of other substances such as ethanol (212,213), carbon tetrachloride (214), benzene (215), quaternary ammonium salts (216), and the metal complexes of octamethylpyrophosphoramide, an organophosphorus poison which acts by inhibiting the activity of acetylcholinesterases (217). Furthermore, DMSO readily penetrates skin and certain types of rubber and surgical gloves (218,219) and it may carry carcenogenic or toxic compounds with it so that great care should be used in handling such DMSO solutions.

Part II. Metal–DMSO Interactions

I. GROUP IA ELEMENTS AND AMMONIUM ION

Information on the solvation and Stokes' radii of alkali metal ions in DMSO has already been given in Sec. IV of Part I. Precipitation of common alkali metal salts from DMSO solutions results in the formation of solvates in some cases; the salts examined and the number of moles of DMSO per formula weight of salt are given in Table IV.

TABLE IV

The Number of Moles of DMSO per Formula Weight of Salt[a]

Cation/Anion	F^-	Cl^-	Br^-	I^-	ClO_4^-	SO_4^{2-}	CO_3^{2-}
Li^+	0	1[b]	3	3	3.5	0.5	0
Na^+	0	0	2	3	3	0.66	0
K^+	0	0.66	0	2	0	0	0

[a] Reference 118.

[b] Reference 3.

The melting points (118) of the solvates were low; the sulfate solvates and the KCl solvate melted with decomposition, but decomposition, violent or otherwise, was not noted for the two perchlorate solvates.

Solutions of NH_4^+ and alkali metal salts in DMSO showed infrared bands that have been attributed to cation–solvent interaction (220) and which are similar to those observed in tetrahydrofuran, THF (221). For a particular cation the frequency was essentially independent of anions such as Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, SCN^-, and BPh_4^-. The observed frequencies for Li^+, NH_4^+, Na^+, K^+, Rb^+, and Cs^+ were 429, 214, 200, 153, 125, and 118 cm^{-1}, respectively (221).

The reactions of lithium, sodium, and potassium metals with DMSO have been studied (77,222). Lithium did not react at temperatures up to 80°. Sodium reacted smoothly evolving a gas that has been variously identified as a mixture of hydrogen and DMS (77) and as methane and DMS (222). The mechanism of the reaction involved breaking of some C—S bonds in addition to S—O bonds and did not simply consist of the release of hydrogen by the alkali metal although some methylsulfinyl carbanion, $CH_3SOCH_2^-$, was formed.

Potassium metal reacted violently with DMSO.

Solutions of the sodium and potassium salts of methylsulfinyl carbanion (frequently referred to as dimsylsodium and dimsylpotassium, respectively, but more correctly as (methylsulfinyl)methylsodium and (methylsulfinyl)methylpotassium, respectively) in DMSO are very basic and their use in titration of very weak acids has been referred to in Section III of Part I. The preparation of dimsylpotassium was not described (110) but the preparation of dimsylsodium usually follows the method described by Corey and Chaykovsky (223) and involves the reaction

$$NaH + CH_3SOCH_3 \longrightarrow CH_3SOCH_2^-Na^+ + H_2$$

in an inert atmosphere (N_2) and heating to 65–70°. The preparation of dimsyllithium (224) is analogous to that of dimsylsodium.

Alkali metal acetylides were conveniently prepared from dimsylmetal and the substituted acetylene according to the reaction (224,225)

$$RC{\equiv}CH + M^+DMSO^- \longrightarrow RC{\equiv}CM + DMSO.$$

The viscosities, freezing points, conductances, and NMR spectra of DMSO solutions of LiCl (226), CsI (227), and RbI (228) have been studied in some detail by Gasser and co-workers. The freezing points were used to evaluate mean molal activity coefficients at various concentrations. The proton resonances in CsI and RbI solutions were shifted downfield as a result of deshielding of the methyl protons through solvent–ion interaction. The ^{87}Rb and ^{133}Cs resonances shifted to lower fields with increasing salt concentrations. The viscosities of the solutions of CsI and RbI obeyed the equation (229)

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc + Dc^2$$

where η and η_0 are the viscosities of the solution and the pure solvent at a given temperature, A is a quantity which depends on ion–ion interaction (230) and may be calculated, B and D are curve-fitting parameters but B is related to the ion–solvent interaction and is approximately the sum of the B_{ion} values of the individual ions in the salt. Since the conductivities of the solutions did not indicate extensive ion pairing or incomplete dissociation (although the conductivity measurements were not sensitive to this type of behavior because of the increase of viscosity with increasing salt concentration) and since DMSO has a dielectric constant of $\sim$46.5 (see Table I) and is a good solvent for these salts it may be assumed that the salts were completely ionized at concentrations below 0.5 molal. If the salts were completely ionized then only the cation and anion contribute to the B-value determined. The B-values determined for RbI and CsI were +0.70 and +0.68, respectively; the values for aqueous solutions are (229) −0.099 and −0.114, respectively. The B-values are large and positive in DMSO and negative in water, indicating that in DMSO the net effect of the salts is structure-making whereas in water it is structure-breaking. Individual B_{ion} values have not been determined in DMSO as they have in water (229). The net structure-making effect of these salts in DMSO is somewhat surprising in view of the highly associated structure expected (3,9,17, 231) for pure, liquid DMSO. The decrease of the S—O stretching frequency from 1102 cm^{-1} in the gas phase to approximately 1055 cm^{-1} (see Sec. II-H of Part I) in the liquid phase is indicative of strong association between DMSO molecules in the liquid state. This decrease is as large as that observed in many cases when DMSO molecules in the liquid phase become coordinated to multivalent metal ions.

Dissociation constants of complexes between formate ion and Li^+, Na^+, and K^+ have been determined in DMSO–water mixtures containing 0.409 and 0.800 mole fraction DMSO at 20.7° (232); the values ranged from 0.070*M* for Li^+ and Na^+ in 0.800 DMSO to 0.45*M* for K^+ in 0.409 DMSO.

Limiting ionic conductances obtained for a number of alkali metal and tetraalkylammonium salts are given in Table V.

TABLE V

Limiting Ionic Conductances of Alkali Metal and Substituted Ammonium Ions

Ion	Λ_0 ohm^{-1} cm^2 mole^{-1}	Ref.
Li^+	11.1	233
	11.4	226
Na^+	13.8	12
	13.4	233
K^+	14.4	12
	14.5	233
Rb^+	14.8	233
	15.3	228
Cs^+	15.9	233
	16.1	227
$(t\text{-Bu})_4N^+$ [a]	11.2	12
Me_3PhN^+ [b]	14.1	12
Me_3OctdN^+ [c]	10.0	12

[a] Tetra-*t*-butylammonium ion.
[b] Trimethylphenylammonium ion.
[c] Trimethyl-*n*-octadecylammonium ion.

Morel (234) measured conductances of solutions of HCl, KCl, NaCl, and sodium acetate in DMSO–water mixtures but did not calculate ionic contributions. When the values of 17 (96), 14.4 (12), and 23.9 (226) are used for H^+, K^+, and Cl^-, respectively, in DMSO solution, excellent agreement is obtained with the limiting equivalent conductances of Morel for DMSO solution. The limiting equivalent conductances decreased as the DMSO mole fraction in the solvent increased; for HCl and KCl they passed through a minimum. The minimum for HCl occurred at ~0.35 mole fraction DMSO where many physical properties of DMSO–water mixtures show an extremum (see Sec. II, Part I).

The electrode

$$Li(2\text{ mole }\%\text{ in Hg})/Li^+$$

in LiCl–DMSO solutions obeyed the Tafel equation with a transfer coefficient, α, of 0.05 over a large range of current densities (235). In combination with a Tl(Hg)/TlCl(s) electrode the Nernst equation was obeyed over a range of LiCl concentrations.

The half-wave potentials vs. aqueous saturated calomel electrode (SCE) for the alkali metal ions and ammonium ion in DMSO vary from -2.45 V for Li^+ to -2.03 V for Cs^+ (96,236). For Li^+, Na^+, K^+, and $NH_4{}^+$ ions half-wave potentials have also been reported with respect to a reference electrode containing a saturated solution of $Zn(ClO_4)_2 \cdot 4DMSO$ in DMSO in contact with a saturated zinc amalgam (237). The algebraic order of the $E_{1/2}$ values was $Li^+ < K^+ < Na^+$ in DMSO as in aqueous solutions (236,237). The $E_{1/2}$ values of Li^+ and Rb^+ vs. aqueous SCE were slightly more negative in DMSO than in water, whereas the values for Na^+, K^+, and Cs^+ were slightly more positive in DMSO than in water.

Reduction of Na^+ to the metal (238) at a platinum electrode resulted in the evolution of H_2, CH_4, C_2H_4, and C_2H_6, the composition of the evolved gas depending on the current density. (See the discussion of the reaction of sodium metal with DMSO on page 22.) (See also the effect of Li^+, Na^+, and K^+ on the electroreduction of oxygen in Sec. X-A in Part II.)

Potassium ion activates the enzyme pyruvic kinase (239) and hence plays an important role in cell metabolism. When DMSO diffuses across cell membranes and affects enzyme activity (240–243) it is not known whether the DMSO affects the enzyme directly or whether the DMSO affects the enzyme activity because of the effect of DMSO on the K^+ ion activity.

II. GROUP IB ELEMENTS

A. Copper(I)

Copper(I) chloride was soluble in DMSO (244); it reacted with CCl_4 in DMSO solution to give copper(II), chloride ion, DMS, and a mixture of CO and CO_2. In the course of this work it was observed that DMSO oxidized CO to CO_2 (however, see reference 278 in the discussion of organomercury compounds). It was also noted that copper(I) reacted with phosgene, $COCl_2$, in DMSO so that it was possible that phosgene may have been an intermediate in the copper(I)–CCl_4 reaction.

Copper(I) cyanide was insoluble in DMSO (120) but it dissolved in the presence of KCN (also insoluble in DMSO). When CuCN(s) was present in excess presumably $K[Cu(CN)_2]$ was formed in solution with an enthalpy of -15.3 kcal per mole of CuCN(s) (120). When KCN(s) was present in excess presumably $K_3[Cu(CN)_4]$ was formed in solution with an enthalpy of -25.3 kcal per mole of CuCN(s) (120).

B. Copper(II)

The copper(II) compounds containing DMSO which have been prepared are listed in Table VI.

TABLE VI

Copper(II) DMSO Compounds

Formula	Color	Mp, °C	ν(SO), cm^{-1}	Ref.
$Cu(ClO_4)_2 \cdot 9DMSO$				245
$Cu(ClO_4)_2 \cdot 4DMSO$	Aqua	exploded	940, 986	53,246
$CuCl_2 \cdot 2DMSO$	Green	153–155	923, 980, 987	53,246,247
$CuCl_2 \cdot DMSO$	Orange	125 d	987	246
$CuBr_2 \cdot 3DMSO$	Lime green			16,245
$CuBr_2 \cdot 2DMSO$	Orange	115 d	911, 989, 988	16,53,246, 247,248
$Cu(NO_3)_2 \cdot 3DMSO$	Blue			249
$Cu(NO_3)_2 \cdot 2DMSO$	Blue			16
$CuSO_4 \cdot 2DMSO$	Green			16
$Cu(OAc)_2 \cdot DMSO$	Blue-green			8
$Cu[C(CN)_3]_2 \cdot 6DMSO$	Light green	57		250
$Cu[C(CN)_3]_2 \cdot DMSO$	Light brown			250
$Cu[N(CN)_2]_2 \cdot 2DMSO$	Blue-green	99–100		250
$Cu(C_5H_5NO)(DMSO)Cl_2$				251
$Cu(CH_3C_5H_4NO)(DMSO)Br_2$				252[a]

[a] $\mu_{eff} = 0.97$ BM assuming a monomer for the calculation of the molecular weight.

Green $CuCl_2 \cdot 2DMSO$ formed orthorhombic crystals (253), space group *Pnam*, $a = 8.093$, $b = 11.400$, $c = 11.562$ Å, four molecules per unit cell, calculated density $= 1.827$ g ml^{-1}. From the single-line X-band ESR spectra the *g*-values along the crystallographic axes were determined (253). The corrected paramagnetic susceptibility was 1742×10^{-6} at 299°K (16) from which the magnetic moment of 2.04 BM may be calculated assuming the Curie law to hold. The diamagnetic susceptibility was

-152×10^{-6} (16). Conductances of solutions in DMSO were determined (8); the plots of Λ versus $c^{1/2}$ were not linear and the Shedlovsky equation

$$\Lambda_0' = (\Lambda + \beta c^{1/2})/(\Lambda - \alpha c^{1/2}) = \Lambda_0 + Bc$$

was used with $\alpha = 0.502$ and $\beta = 35.7$ (12). A plot of Λ_0' versus c extrapolated to zero concentration gave $\Lambda_0 = 42.5$ which was consistent with the values of Λ_0 obtained for other 1:2 salts such as $CaCl_2$, $NiCl_2 \cdot 3DMSO$, $CoCl_2 \cdot 3DMSO$, and $Co(NO_3)_2 \cdot 4DMSO$. Differential thermal analysis was only partially successful (8,245) in detecting stepwise loss of DMSO.

If, as has been discussed by Cotton and Francis (53), the DMSO molecule bonds to a metal ion through the oxygen atom the stretching frequency of the S—O bond is expected to decrease. There is general agreement that DMSO bonds through the oxygen to copper(II) in the salts whose infrared spectra have been studied because of the observed decrease in ν(SO). However, there has not been complete agreement on the magnitude of the decrease since different assignments of infrared bands have been made (53,247,254).

Selbin, Bull, and Holmes (246) suggested that $CuCl_2 \cdot 2DMSO$ should be written as $[Cu(DMSO)_2Cl_2]$ whereas Drago and co-workers (247,254) suggested that the compound was $[Cu(DMSO)_4][CuCl_4]$. The preliminary crystal structure analysis (253) has indicated that two chlorine and two oxygen atoms are coordinated to each copper(II) ion, a result in line with the formulation of Selbin, Bull, and Holmes. Holah and Fackler (248) investigated the solution, reflectance, and infrared spectra and the x-ray powder patterns of this and related compounds in an attempt to answer the question of its structure in the solid state and in nitromethane solution and concluded that the formulation $[Cu(DMSO)_4][CuCl_4]$ did not correctly represent the structure of the solid or of the ions produced when the solid was dissolved in nitromethane. However, the copper(II) chloride in nitromethane readily formed the tetrahedral $CuCl_4^{2-}$ ion when quaternary ammonium chloride was added (248). Thus, in nitromethane $CuCl_2 \cdot 2DMSO$ had an absorption at 11,900 cm^{-1} with $\epsilon_{max} = 100 M^{-1}$ cm^{-1} which moved to 8,300 cm^{-1} with $\epsilon_{max} = 105 M^{-1}$ cm^{-1} when excess chloride ion was added. In DMSO and in ethanol solutions the compound had absorption maxima at 10,650 and 11,000 cm^{-1}, respectively, with $\epsilon = 82$ and $70 M^{-1}$ cm^{-1}, respectively. Contrary to its behavior in nitromethane Gutmann and Hüber (255) reported that $CuCl_4^{2-}$ was not formed in DMSO solution in presence of chloride ion. Furthermore, the copper(II) chloride did not form complexes in DMSO solution with chlorides such as $SbCl_5$, $SnCl_4$, and $TiCl_4$ (256).

One molecule of DMSO was readily lost from $CuBr_2 \cdot 3DMSO$ at temperatures below 50° (16,245). The infrared spectrum showed two types of DMSO in this salt; one kind of DMSO molecule, the one with the highest SO frequency, was lost when the salt was converted to the disolvate (16). The powder pattern of the trivolvate was similar to that of the disolvate but the complexes were not isomorphous (248). As in the case of $CuCl_2 \cdot 2DMSO$, two formulations $[Cu(DMSO)_2Br_2]$ (246) and $[Cu(DMSO)_4][CuBr_4]$ (247,254), were suggested for the disolvate. Holah and Fackler (248) concluded that the former formulation was correct since the powder pattern showed the disolvate to be isomorphous with the analogous chloride and since the latter formulation had been shown to be incorrect for $CuCl_2 \cdot 2DMSO$ as discussed above.

In nitromethane solution $CuBr_2 \cdot 2DMSO$ was straw yellow, had an absorption maximum at 11,900 cm^{-1} with $\epsilon = 320M^{-1}\,cm^{-1}$, and was readily converted by excess bromide ion to the deep violet, tetrahedral $CuBr_4{}^{2-}$ ion with an absorption maximum at 8300 cm^{-1} and $\epsilon = 120M^{-1}\,cm^{-1}$ (248).

$Cu(ClO_4)_2 \cdot 9DMSO$ was converted to the pentasolvate at 50° and to the tetrasolvate at 75° which remained stable to 100° (245). Solutions of this salt in DMSO were used to determine extinction coefficients from 350 to 1000 nm and the *Dq* value of 1190 cm^{-1} for DMSO and copper(II) (257). The suggested formulation of the tetrasolvate was (53,246) $[Cu(DMSO)_4](ClO_4)_2$; the compound showed strong absorptions (258) in the 500–265 cm^{-1} region where other metal–oxygen bonds have been found. By comparison of the bands for Cu(II), Ni(II), Co(II), and Mn(II) the order Cu(II) > Ni(II) > Co(II) > Mn(II) was assigned for the bond strengths in agreement with the Irving and Williams order for the stability of complexes.

When $Cu(NO_3)_2 \cdot 3DMSO$ was dissolved (249) in DMSO, the nitrate ligands remained partly coordinated and a charge-transfer band appeared in the spectrum at ~290 nm. The charge-transfer, $d \leftarrow \pi$ transition may be expected because of the availability of the +1 oxidation state of copper (249). (See also the discussion of the spectrum of $NO_3{}^-$ in DMSO in Sec. VIII-A.) Infrared spectra of the solid showed coordinated nitrate groups (249). Reflectance spectra showed the intense absorption attributed to charge transfer and coordinated nitrate groups. It was suggested that the trisolvate might contain tetranitrato anions of the metal (249).

In DMSO solution $Cu(OAc)_2 \cdot DMSO$ was a nonelectrolyte and was considered to be dimeric (8).

Azido complexes of copper(II), $Cu(N_3)_x{}^{2-x}$, $x = 1, 2, 4$, have been proposed (259).

Copper(II) gave two, essentially reversible, one-electron reduction waves in DMSO with half-wave potentials of +1.084 and +0.960 V vs. a $Zn^{2+}/Zn(ClO_4)_2 \cdot 4DMSO/Zn(Hg)$ reference electrode (237).

C. Silver(I)

Studies of the solubility products of silver halides, of the activity coefficient of Ag^+ and of the stability constants of the dihalosilver(I) complexes were referred to in Section IV on solvent properties. The pK values of the solubility products (pK_s) and of the overall formation constants of the dihalosilver(I) complexes are given in Table VII.

TABLE VII

pK_s and pβ_2 Values

Salt	pK_s	Ref.	Complex	pβ_2	Ref.
AgCl	10.4[a]	116	$AgCl_2^-$	11.7[a]	116
	10.4[b]	260		12.0[b]	260
	9.7[c]	261		10.6[c]	261
AgBr	10.6[a]	116	$AgBr_2^-$	11.4[a]	116
	10.6[b]	260		11.9[b]	260
	10.0[c]	261		10.6[c]	261
AgI	11.4[a]	116	AgI_2^-	12.5[a]	116
	12.0[b]	260		13.1[b]	260
	11.5[c]	261	$Ag_2I_3^-$	23.95[c]	261
AgN_3	6.5[d]	116	$Ag(N_3)_2^-$	7.0[a,d]	116
AgSCN	7.1[d]	116	$Ag(SCN)_2^-$	7.4[a,d]	116
AgOAc	4.4[d]	116	$Ag(OAc)_2^-$	5.8[a,d]	116
$AgBPh_4$	4.6[e]	116			

[a] $\mu = 0.005\text{–}0.01M$, 25°.

[b] In 0.100 F $(C_2H_5)_4NCl$, 23°.

[c] In 0.1M NH_4NO_3, 25°.

[d] $\mu = 0.05\text{–}0.10M$, 25°.

[e] At μ corresponding to the solubility of the tetraphenyl borate salt.

Solid silver(I) cyanide reacted with solid KCN to give a 1:1 mole ratio of the cyanides in DMSO solution (120); presumably $Ag(CN)_2^-$ was formed. The enthalpy of the reaction was −8.5 kcal per mole of silver(I) cyanide.

A complex $AgBF_4 \cdot DMSO$ which lost DMSO between 200–300° has been reported (262).

The suitability of Ag/Ag^+ or of Ag/AgCl electrodes for use in DMSO has been examined (263–265). In the case of the latter electrode, formation of $AgCl_2^-$ occurred but the electrode gave reproducible results.

III. GROUP IIA ELEMENTS

Relatively little work has been reported on the chemistry or properties of alkaline earth ions or compounds in DMSO. The solvates $Be(ClO_4)_2 \cdot 4DMSO$ (266) and $Mg(NO_3)_2 \cdot 6DMSO$ (249) have been reported.

In DMSO solution, colorless $Mg(NO_3)_2 \cdot 6DMSO$ and anhydrous $Be(NO_3)_2$ were completely ionized (249); the $\pi^* \leftarrow n$ transition of the nitrate ions occurred at 312.5 nm as it did for numerous other ionic nitrates dissolved in DMSO. In the reflectance spectrum of the solid solvate the transition occurred at 315 nm indicating ionic nitrate ions (249). The assigned infrared bands for the ionic nitrate groups in the solid DMSO solvate were (249) $\nu_2 = 832$ and $\nu_3 = 1350\ cm^{-1}$ (cf. 819 and 1369 cm^{-1} for $Mg(NO_3)_2 \cdot 6H_2O$).

Weaver and Keim (8) reported a limiting equivalent conductance of 45.7 for $CaCl_2$ in DMSO solution, consistent with the value for a 1:2 electrolyte. However, the van't Hoff *i*-factor of a 0.03 molal solution of the same salt indicated incomplete dissociation.

Magnesium nitrate and chloride were titrated as acids with sodium methoxide in DSMO (267).

The dissociation constant of a Ba^{2+}-formate ion complex in water–DMSO mixtures was equal to 0.081*M* in 0.409 mole fraction DMSO and 0.015*M* in 0.800 mole fraction DMSO at 20.7° (232).

The electroreductions of Be(II) (266), Mg(II) (236,268), Ca(II) (236), Sr(II) (236,237), and Ba(II) (236,237) have been studied in water-free DMSO; the half-wave potentials of the last four in DMSO vs. aqueous SCE were in the algebraic order Ca(II) < Mg(II) < Sr(II) < Ba(II), the order of the first two being reversed as compared to water. (See also the effect of alkaline earth ions on the electroreduction of oxygen in Sec. X-A.)

IV. GROUP IIB ELEMENTS

The group IIB compounds containing DMSO which have been prepared are listed in Table VIII.