Yields of Free Ions Formed in Liquids by Radiation

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Foreword

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The technical scope of NSRDS is indicated by the categories of projects active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

Reliable data on the properties of matter and materials are a major foundation of scientific and technical progress. Such important activities as basic scientific research, industrial quality control, development of new materials for building and other technologies, measuring and correcting environmental pollution depend on quality reference data. In NSRDS, the Bureau's responsibility to support American science, industry, and commerce is vitally fulfilled.

ERNEST AMBLER, *Acting Director*

Preface

This report is one of a series of data publications on radiation chemistry; the aim of the series is to compile, evaluate, and present the numerical results on processes occurring in systems which have been subjected to ionizing radiation. Various kinds of data are important in radiation chemistry. The quantities which were measured first were the observed radiation yields or G values (molecules formed or destroyed per 100 eV). Various indirect methods based on G values have been used to determine yields of transient species and relative rates of reactions. The spectral properties (optical, electron spin resonance) of transients have provided a direct method for their identification, and rates of the very fast reactions of transients which occur in irradiated systems have been measured directly by spectroscopic methods. Conductivity and luminescence methods have also provided a means of measuring properties of transients and their kinetics. Some reactions which occur in irradiated systems have also been studied by other methods, such as photochemistry, electric discharge, ultrasonics, chemical initiation, electron impact, etc. The emphasis in these publications is on the data of radiation chemistry, but where other pertinent data exist, they are included.

The data of radiation chemistry are voluminous; thousands of systems have been investigated. As a result there are certain collections, *e.g.* rate constants of particular types of reactions or certain properties of transients, for which tabulations of the data are considered essential, but for which critical assessment of each value is impossible. On the other hand, certain systems and properties have been studied so extensively that critical examination of these data is desirable and timely. Authors of this series of data publications have been asked to evaluate the extent to which the data can be critically assessed, to describe their criteria for evaluation, and to designate preferred values whenever possible.

IV

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Free ions are those produced by ionizing radiation which escape initial recombination. Yields of free-ion pairs are tabulated for liquid alkanes, alkenes, alkynes, dienes and aromatic hydrocarbons, and other non-polar and polar compounds, including alcohols, ethers, esters, halides, amines, nitriles, etc. Total ion yields for a few liquids are compared with gas phase ion yields. Theoretical treatments of these data are discussed.

Key words: Electrons; free ions; ion yields; liquid; non-polar systems; polar systems; radiation chemistry; radiation physics.

1. Definitions

When X–rays, gamma rays or fast charged particles traverse a *gas*, positive and negative ions are formed in equal numbers, and (in the absence of an applied electric field) become uniformly distributed through the volume by diffusion, and eventually disappear by pairwise *general recombination*. If a D.C. electric field is applied, the ions drift to the electrodes and give up their charge to the external circuit. At ordinary radiation intensities, a relatively modest field strength suffices to collect all the ions. The number of ions of either sign produced by unit energy input is called the *ion yield* and is a characteristic property of each gaseous substance.

In a *liquid* under radiation, the charge collected by an applied field is usually only a small fraction of that produced by the same radiation absorbed in the same amount of the same material in gaseous form. The cause of this difference was correctly described nearly seventy years ago by G. Jaffé [080002][1]. In a gas, ionization knocks out an electron with sufficient momentum to escape from the electric field of the positive ion it leaves behind; but in a liquid, collisions with surrounding molecules rapidly reduce its initial outward momentum so that it has only a small escape probability. Usually the electron rapidly returns to its parent ion and recombines with it. This process is called *initial recombination* or *geminate recombination*. The number of electrons that escape initial recombination, per unit energy input by the radiation, is called the *free-ion yield*. Since an applied electric field tends to pull the electron out of the field of the positive ion, the free—ion yield increases with the applied field. The field strength that a liquid can stand is limited by dielectric breakdown; in most liquids, the free—ion yield at the maximum usable field is still only a small fraction of the ion yield found in the gaseous form of the same substance. Only in monatomic liquids (liquefied rare gases) has complete collection of the ions been reported.

The escaped electron can (1) remain as a *quasi–free electron* in a delocalized state in a conduction band; (2) aggregate solvent molecules about itself to form a *solvated electron*; (3) react with a solvent molecule, or an impurity or solute molecule to form a new negatively charged molecule, or *negative ion*.

[1] Numbers in brackets indicate the literature references at the end of this paper.

The term "negative ion" is however sometimes used to indicate any negatively charged entity, including the electron.

Although attempts are made to extrapolate the free—ion yield to infinite field strength to obtain the *total ion yield*, the zero—field free—ion yield is precisely determinable and has been the focus of much recent work.

The free—ion yield depends strongly on the "radiation quality" or linear energy transfer (LET). At high LET, the positive charges are grouped in columns, the electrons are pulled back by a large group of positive ions instead of by just one or a few, and the escape probability becomes much lower. Most of the data reported here were taken with low LET or near—minimum ionization radiations such as γ rays, 1–2 MeV X—rays or megavolt electron beams, and this condition may be assumed unless otherwise indicated.

The free—ion yield is of practical significance in determining the chemical changes that occur in liquid and amorphous systems under radiation. The scientific significance of free—ion yield measurements lies in the fact that no adequate theory exists for the behavior of electrons in non—crystalline condensed systems, and free—ion yields offer one type of data which may point the way to the development of such a theory.

The purpose of this review is to assemble currently available data on zero—field free—ion yields in pure liquids for the convenience of those who wish to use these quantities. No attempt is made here to assess probable errors or to ascertain probable "best" values. Before this can be done, the many differences in results reported from different laboratories will have to be resolved in the light of independent determinations.

2. Notation and Units

The ion yield in gases is usually expressed as its reciprocal, denoted W, which is always expressed in eV per ion pair. In liquids, the yield is usually given as $G \equiv 100/W$, the number of ions of either sign produced per 100 eV energy input. In this paper, the zero—field free—ion yield in liquids is denoted by G_{fi}^{o}, while the total ion yield is G_{fi}^{∞}. The electron is represented by e^-.

3. Methods of Measurement

3.1. Scavenging

The scavenging method involves adding a substance which reacts directly with the electron (or in some cases with the positive ion or its deprotonated successor radical) to form a chemical product which is determined quantitatively. Examples of scavengers are anthracene, biphenyl, pyrene and the free radical galvinoxyl, which readily add an electron to form a colored radical anion of known optical absorptivity, and N_2O, which reacts with an electron to form O^- and a molecule of nitrogen, which is determined. There are two varieties of the method: (1) the *steady—state* method, in which a permanent chemical product is determined, following an exposure to a continuous source such as γ rays; (2) the *pulse* method, in which the optical absorption of a transient product such as pyrene ion gives a measure of the electron yield.

There are many sources of error. If the scavenger concentration is too high, some of the initially recombining electrons or ions may be counted as well as the free ions; results should always be extrapolated to zero scavenger concentration. A less obvious error occurs if some of the electrons react with the scavenger to form other products, which are not determined; or the electron may also be reacting with impurities, or with free radicals or other radiation products; these errors make the reported yield too low. If, however, the determined product also is formed by the reaction of the scavenger with other free radicals formed by the radiation, the reported yield might be too high. If the radiation dose is too large, the product may begin to compete with the scavenger. It is generally difficult or impossible to estimate the accuracy of a determination of a free—ion yield by the scavenger method except by comparison with results of other methods.

3.2. Conductivity

The specific conductance of a system is proportional to the product of the number of ions formed and their mobility. If the mobility is known, or guessed, then a determination of the conductivity produced by a known intensity of radiation can be used to calculate the free—ion yield. For non—polar liquids, the method is difficult and not too reliable and has been superseded by the charge collection method. Used with a pulse radiolysis system in aqueous and alcoholic media, this method has given valuable results.

3.3. Charge Collection

Charge collection methods comprise steady—state and pulse methods.

In the steady—state method, the current of ions collected by the field is measured with the radiation intensity so low and the field so high that essentially no general ion recombination occurs as the ions are swept out by the field.

In the pulse or "clearing field" method the charge produced by a short pulse of radiation is collected by the field and measured. In one version, the field is turned on immediately after the radiation pulse to give a direct measurement of the zero—field free—ion yield; a ballasting condenser takes care of the charge necessary to bring the electrodes to voltage when the field is switched on directly after the radiation pulse. In another version, the field is maintained during the pulse and the zero—field value obtained by extrapolation.

In all the electrical methods, the collected currents or charges must be kept very small to avoid recombination errors, and it is difficult to avoid systematic errors in the electrical measurement systems. Also, difficulties in measuring the energy put into the liquid may occur at these very low dose rates.

Although careful determinations of G_{fi}° by charge collection should be accurate to ±5%, values reported by different laboratories for the same pure liquid at the same temperature unfortunately often differ by many times this amount.

4. Tabulations of G_{fi}°

Tables 1—4 give values of G_{fi}° for a variety of pure liquids. When values were determined by a particular worker over a series of temperatures, only one value is usually given in the tables; values obtained over a range of temperatures are shown graphically in figures 1—6. For temperature effects in aromatic hydrocarbons, see [741110]. The tables give the name of the liquid, temperature of measurement, dielectric constant of the liquid, method used, reported value of G_{fi}°, and literature reference. The dielectric constants are omitted from the hydrocarbon tables because the values nearly all lie about 1.8—2. When no temperature is reported, "room temperature" may be assumed. Under "Methods" is indicated whether conductivity (condy.), charge collection (charge coll.) or scavenging (scav., followed by the formula or name of the scavenger used) was employed.

Data on mixtures of non—polar compounds are given in [680376] and [700055], but are not reproduced here. In mixtures of hydrocarbons, G_{fi} changes gradually with composition; but addition of a little CCl_4 to neopentane results in an abrupt drop of G_{fi}°. Relative values of G_{fi}° in mixtures of hexane and alcohols are reported in [710464] and [731090], mixtures of benzene and alcohols in [741084], mixtures of ethanol and water in [730143], and mixtures of alcohols and alkanes in [741035].

TABLE 1. Zero-field free-ion yields in saturated hydrocarbon liquids

Compound	Temp.[a,b] K	Method[c]	$G_{fi}^{\bullet}$ [d]	Reference
Methane	140	charge coll.	1.13	741012
Ethane	200	charge coll.	0.158	741012
Propane	238	charge coll.	0.166	741012
	233	charge coll.	0.143	720166
Cyclopropane	234	charge coll.	0.049	741012
Butane	293	charge coll.	0.225	741012
	296	charge coll.	0.193	700055
Isobutane	294	charge coll.	0.31	720166
n−Pentane	296	charge coll.	0.17	731054
	296	charge coll.	0.145	700055
Isopentane	296	charge coll.	0.170	700055
Neopentane	296	condy.	1.1	700090
	296	charge coll.	0.86	700055
	294	charge coll.	1.09	720269
	294	scav., N_2O	0.95	700650
Cyclopentane	296	charge coll.	0.155	700055
n−Hexane	296	condy.	0.10	650216
	297	condy.	0.10	660149
	—	condy.	0.137	680821 recalc. in 720405
	296	condy.	0.11	690240
	296	scav., $(C_6H_5)_3CCl$	0.12	690348
	—	scav., CH_3Br	0.12	700047
	296	charge coll.	0.131	700055
	298	scav., $c-C_6F_{12}$	0.08	700299
	—	condy.	0.13	720405
	292	charge coll.	0.18	731054
	—	scav., C_2H_5OT	0.12	730242
2−Methylpentane	296	charge coll.	0.148	700055
3−Methylpentane	296	charge coll.	0.146	700055
	298	scav., $c-C_6F_{12}$	0.17	700299
2,3−Dimethylbutane	296	charge coll.	0.192	700055
2,2−Dimethylbutane	296	charge coll.	0.304	700055
Cyclohexane	296	charge coll.	0.148	700055
	—	scav., CH_3Br	0.13	700047
	298	scav., $c-C_6F_{12}$	0.14	700299
	296	scav., anthracene	0.17	700360
	296	scav., $(C_6H_5)_3CCl$	0.13	690348
	296	scav., galvinoxyl	0.15	700019
	294	charge coll.	0.19	731054
Methylcyclohexane	293	scav., pyrene	0.122	730124
n−Heptane	296	charge coll.	0.131	700055
2,4−Dimethylpentane	296	charge coll.	0.178	700055
2,2,3−Trimethylbutane	296	charge coll.	0.290	700055
n−Octane	296	charge coll.	0.124	700055
2,3,4−Trimethylpentane	296	charge coll.	0.174	700055
2,2,4−Trimethylpentane	296	charge coll.	0.332	700055
	—	scav., CH_3Br	0.36	700047
	—	scav., $c-C_6F_{12}$	0.37	700299
	296	scav., $(C_6H_5)_3CCl$	0.36	690348
	296	scav., galvinoxyl	0.39	700019
	—	scav., CH_3Br	0.13	720032
	—	scav., C_2H_5OT	0.22	730242
	—	scav., CH_3Br	0.3	740092
2,2,3,3−Tetramethylbutane	379[e]	charge coll.	0.80	720269
n−Nonane	296	charge coll.	0.117	700055
2,2,4,4−Tetramethylpentane	295	charge coll.	0.83	720269
2,2,3,3−Tetramethylpentane	295	charge coll.	0.42	720269
n−Decane	296	charge coll.	0.117	700055

Compound	Temp.[a,b] K	Method[c]	$G_{fi}^{°}$[d]	Reference
2,2,5,5–Tetramethylhexane	293	charge coll.	0.67	720269
2,2,6,6–Tetramethylheptane	293	charge coll.	0.47	720269
2,2,7,7–Tetramethyloctane	316	charge coll.	0.34	720269
n–Tetradecane	296	charge coll.	0.120	700055
Squalane ($C_{30}H_{62}$)	296	charge coll.	0.119	700055

[a] When no temperature is given in the reference, room temperature may be assumed.

[b] When determinations were made at several temperatures on the same compound, only one result is given here; the others are displayed in the accompanying figures.

[c] Abbreviations: condy. = conductivity under irradiation combined with measured or assumed ion mobility values
     charge coll. = charge collection by clearing field,
     scav. = scavenging of the negative or positive charge by the compound indicated.

[d] Free–ion yield in molecule/100 eV.

[e] This octane isomer melts at 374 K.

TABLE 2. Zero-field free-ion yields in unsaturated and aromatic hydrocarbon liquids

Compound	Temp. K	Method	$G_{fi}^{°}$	Reference
Ethylene	170	charge coll.	0.010	741012
Propylene	234	charge coll.	0.042	741012
Butene–1	293	charge coll.	0.093	731054
cis–Butene–2	293	charge coll.	0.23	731054
trans–Butene–2	293	charge coll.	0.080	731054
Isobutene	293	charge coll.	0.25	731054
2–Methylbutene–2	292	charge coll.	0.26	731054
Hexene–1	296	charge coll.	0.062	700055
	293	charge coll.	0.10	731054
Hexene–2[e]	296	charge coll.	0.076	700055
trans–Hexene–2	293	charge coll.	0.092	731054
cis–Hexene–3	293	charge coll.	0.13	731054
trans–Hexene–3	293	charge coll.	0.10	731054
3,3–Dimethylbutene–1	296	charge coll.	0.169	700055
2,3–Dimethylbutene–2	293	charge coll.	0.44	731054
Cyclohexene	296	charge coll.	0.15	700055
	293	charge coll.	0.20	731054
Propadiene(Allene)	282	charge coll.	0.050	731054
Butadiene–1,3	269	charge coll.	0.038	731054
Pentadiene–1,4	293	charge coll.	0.067	731054
Cyclopentadiene	195	scav., NH_3	0.05	652067
Hexadiene–1,5	292	charge coll.	0.066	731054
Heptadiene–1,6	292	charge coll.	0.067	731054
Octadiene–1,7	292	charge coll.	0.065	731054
Acetylene	198	charge coll.	0.02	731054
Propyne	260	charge coll.	0.17	731054
Butyne–2	293	charge coll.	0.32	731054
Hexyne–1	253	charge coll.	0.10	731054
Hexyne–2	293	charge coll.	0.19	731054
Hexyne–3	293	charge coll.	0.21	731054
Benzene	—	scav., tritiated water or alc.	0.077	690650
	—	scav., tritiated water or alc.	0.098	700349
	298	scav., galvinoxyl	0.055	700019
	296	charge coll.	0.053	700055
	292	charge coll.	0.081	741110
Toluene	298	scav., galvinoxyl	0.051	700019
	292	charge coll.	0.093	741110
tert–Butylbenzene	296	charge coll.	0.089	700055
o–Xylene	292	charge coll.	0.094	741110

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Compound	Temp. K	Method	G_{fi}^o	Reference
m–Xylene	292	charge coll.	0.082	741110
p–Xylene	292	charge coll.	0.073	741110
1,2,3–Trimethylbenzene	292	charge coll.	0.12	741110
1,2,4–Trimethylbenzene	292	charge coll.	0.083	741110
1,3,5–Trimethylbenzene	293	charge coll.	0.087	741110
1,2,3,4–Tetramethylbenzene	292	charge coll.	0.11	741110
1,2,4,5–Tetramethylbenzene	358	charge coll.	0.15	741110
Pentamethylbenzene	353	charge coll.	0.25	741110
Hexamethylbenzene	448	charge coll.	0.6	741110
Naphthalene	376	charge coll.	0.11	741110
Anthracene	500	charge coll.	~0.1	741110
Biphenyl	373	pulse radiolysis, ion spectra	<0.35	690431

Cis–trans mixture.

TABLE 3. Zero–field free–ion yields in miscellaneous non–polar liquids

Compound	Temp. K	ϵ	Method	G_{fi}^o	Reference
Tetramethylsilane	296	1.84	charge coll.	0.74	700055
Tetramethyltin	296	2.07	charge coll.	0.62	700055
Carbon disulfide	296	2.63	charge coll.	0.314	700055
	296		scav., $(C_6H_5)_3CCl$	0.26	690348
Triethylamine	296	2.44	charge coll.	0.148	700055
Germanium tetrachloride	296	2.44	charge coll.	0.127	700055
Carbon tetrachloride	296	2.232	charge coll.	0.096	700055
	296		scav., $(C_6H_5)_3CCl$	0.093	690348
	296		condy.	0.068	660148
1,4–Dioxane	295	2.21	condy.	0.05	650216
	296		condy.	0.038	660148
	—		scav., benzophenone	0.1	690521
	296		charge coll.	0.046	700055
	296		scav., anthracene	0.10	700360
	293	2.20	charge coll.	0.08	751047
	335	2.15	charge coll.	0.12	751047
	374	2.08	charge coll.	0.16	751047
Carbon tetrafluoride	143	1.64	charge coll.	0.07	730095
Perfluoro–*n*–pentane	296	1.68	charge coll.	0.035	700055
Perfluoromethylcyclohexane	296	1.85	charge coll.	0.028	700055
Oxygen	87	1.50	charge coll.	0.013	720034

TABLE 4. Zero–field free–ion yields in polar liquids ($\epsilon > 3$)

Compound	Temp. K	ϵ	Method	G_{fi}^o	Reference
Ethers:					
Di–*n*–butyl ether	—	3.1	condy.	0.11	650216
	187	4.50	charge coll.	0.21	751047
	220	3.99	charge coll.	0.23	751047
	255	3.52	charge coll.	0.26	751047
	293	3.14	charge coll.	0.30	751047
	332	2.83	charge coll.	0.36	751047
	373	2.55	charge coll.	0.42	751047
	406	2.35	charge coll.	0.48	751047
	436	2.20	charge coll.	0.54	751047

Compound	Temp. K		Method	G_{fi}°	Reference
Di–n–propyl ether	169	5.64	charge coll.	0.23	751047
	202	4.76	charge coll.	0.25	751047
	254	3.90	charge coll.	0.30	751047
	293	3.43	charge coll.	0.34	751047
	342	2.91	charge coll.	0.38	751047
	376	2.60	charge coll.	0.44	751047
Diisopropyl ether	296	3.9	charge coll.	0.305	700055
Diethyl ether	—	4.3	condy.	0.19	650216
	296		charge coll.	0.35	700055
	—		scav., CH_3Br	0.15	700249
	296		scav., anthracene	0.28	700360
	195	8.0	charge coll.	0.53	751047
	223	6.45	charge coll.	0.50	751047
	252	5.40	charge coll.	0.49	751047
	293	4.39	charge coll.	0.54	751047
	328	3.70	charge coll.	0.57	751047
Dimethyl ether	165	10.7	charge coll.	0.64	751047
	195	9.0	charge coll.	0.73	751047
	226	7.4	charge coll.	0.74	751047
Tetrahydropyran	231	7.28	charge coll.	0.45	751047
	254	6.60	charge coll.	0.48	751047
	293	5.60	charge coll.	0.51	751047
Tetrahydrofuran	296	.7.5	scav., pyrene, anthracene	0.68	700406
	—		scav., benzophenone	0.5	690521
	—		scav., maleic anydride	0.6[a]	701042
	—		pulse radiolysis	0.39[b]	731069
	—		scav., pyrene	0.3	741030
	205	11.6	charge coll.	0.72	751047
2–Methyltetrahydrofuran	296	7.9	scav., anthracene	0.23	700360
Halides:					
n–Butyl bromide	295	6.9	condy.	0.27	650216
n–Butyl chloride	295	7.2	condy.	0.39	650216
Fluoroform	183	21.4	charge coll.	1.1	730095
Methyl fluoride	183	27.9	charge coll.	1.6	730095
Difluoromethane	183	38.9	charge coll.	1.9	730095
Ketones:					
Methyl ethyl ketone	293	18.5	condy.	0.84	720153
Acetone	296	21	scav., anthracene	1.18	700360
	—		scav., anthracene	1.5	710186
	—		scav., stilbene and anthracene	1.1	710189
	—		condy.	1.2	720002
Dimethyl sulfoxide	296	46.6	scav., anthracene	1.62	700360
	—		scav., N_2O	1.8	710215
	—		scav., biphenyl	1.8	720232
	—		scav., anthracene and Br^-	1.2–1.8	731016
Esters:					
Methyl formate	296	8.5	scav., anthracene	0.32	700360
1,2–Propanediol carbonate	296	64.5	scav., anthracene	2.25	700360
Nitriles:					
Benzonitrile	296	25.2	scav., anthracene	1.40	700360
	296		scav., $trans$–stilbene	1.4	741100
Acetonitrile	296	37.5	scav., anthracene	1.55	700360
Pyridine	296	12	scav., anthracene	0.40	700360
Amines:					
Aniline	—	6.9	scav., pyrene	0.95	680227
Tributylamine	293	5.	condy.	0.25	720153
Butylamine	293	5.	condy.	0.27	720153
Diethylamine	—	3.6	scav., pyrene	0.1	741030
Ethylamine	—	6.2	scav., pyrene and $(C_6H_5)_2$	1.8	741094

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Compound	Temp. K	ϵ	Method	G^o_{fi}	Reference
Methylamine	—	9.4	scav., pyrene and $(C_6H_5)_2$	2.2	741094
Ammonia	258	20.	scav., pyrene and $(C_6H_5)_2$	3.3	741094
	296	17.	pulse radiolysis	3.2	741062
	225	25	pulse radiolysis	3.0	740159
	225		scav., Cu^{2+}	2.9	740159
Ethanolamine	—	57.7	scav., anthracene	0.2	731106
Alcohols:					
Neopentyl alcohol	337	8.3	scav., galvinoxyl	0.21	700019
tert–Butyl alcohol	333	7.8	scav., anthracene and pyrene	0.7	720574
	296	12.3	scav., galvinoxyl	0.67	700019
Hexyl alcohol	293	13.3	scav., anthracene and pyrene	1.1	720574
n–Pentyl alcohol	298	14.2	scav., galvinoxyl	0.45	700019
	337		scav., galvinoxyl	0.46	700019
Isopentyl alcohol	293	15.	scav., anthracene and pyrene	0.35	720574
	293		condy.	0.40	720153
n–Butyl alcohol	298	17.1	scav., galvinoxyl	0.63	700019
	298		scav., acetone	0.55	670004
	293		scav., anthracene and pyrene	0.56	720574
	293		condy.	0.58	720153
Isobutyl alcohol	293	17.7	scav., anthracene and pyrene	0.5	720574
Isopropyl alcohol	296	18.3	scav., anthracene	0.92	700360
	—		scav., $(C_6H_5)_2$	1.0	650499
	298		scav., N_2O	1.2	680042
	—		scav., NO_3^-	1.7	690655
	298		condy.	2.2	710064
	291		scav., tetranitromethane	1.2	710564
	293		scav., anthracene and pyrene	1.0	720574
n–Propyl alcohol	—	20.1	scav., $(C_6H_5)_2$	1.0	650499
	298		scav., N_2O	1.2	690387
	298		scav., acetone	0.65	670004
	298		condy.	2.2	710064
	150–298		pulse radiolysis	1.45	751054
Ethyl alcohol	—	24.3	scav., $(C_6H_5)_2$	1.0	640113
	298		scav., N_2O	1.5	680047
	296		scav., galvinoxyl	1.0	700019
	294		scav., anthracene	0.98	700360
	298		condy.	1.95	710064
	290		condy.	3.9^e	710531
	296		scav., acetone, nitrobenzene	1.7	720199
	—		scav., $(C_6H_5)_2$	1.7	700172
Methyl alcohol	—	32.6	scav., $(C_6H_5)_2$	1.1	650499
	298		scav., acetone	1.3	670004
	—		scav., N_2O	2.0	670018
	296		scav., anthracene	1.1	700360
	298		scav., N_2O	2.0	680610
	298		condy.	2.0	710064
	—		condy.	1.9	731086
	296		scav., nitrobenzene and acetone	1.7	730292
Ethylene glycol	—	38.	scav., $(C_6H_5)_2$	1.2	650499
	293		scav., anthracene and pyrene	1.2	720574
Nitro compounds:					
Nitrobenzene	298	34.8	scav., galvinoxyl	0.43	700019
Nitromethane	298	37.8	scav., galvinoxyl	0.31	700019
Amides:					
Hexamethylphosphoramide	—	30	scav., biphenyl and anthracene	2.4	720105
	293		condy.	1.2	720153
	—		scav., anthracene and pyrene	2.3	731091
Dimethylformamide	296	37.	scav., anthracene	2.0	700360
Dimethylacetamide	296	38.	scav., anthracene	1.7	700360

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TABLE 4. Zero-field free-ion yields in polar liquids ($\epsilon > 3$) — Continued

Compound	Temp. K	ϵ	Method	G_{fi}^o	Reference
Formamide	—	109.	scav., N_2O	3.3	700173
N–Methylpropionamide	296	164.	scav., anthracene	2.6	700360
Water^d (H_2O)	—	80	scav., $KMnO_4$	$G(e_{aq}^-) = 2.7$	670311
	—		review	$G(e_{aq}^-) = 2.7$	730418
	—		condy.	$G(OH^-) = 0.7$; $G_{fi}^o = G(H^+) = 3.4$	710138
	—		condy.	$G(OH^-) = 0.8$; $G_{fi}^o = G(H^+) = 3.5$	700243
	—		condy.	$G(OH^-) < 0.3$; $G_{fi}^o = 2.85 \pm 0.15$	720404
(D_2O)	—		scav., $KMnO_4$	$G(e_{aq}^-)(D_2O) = 2.9$	680061

^{a}Much lower values were obtained with high–LET radiations.

^{b}Absorption due to $e^- \cdot Na^+$ ion pair, extrapolated to zero Na^+.

^{c}Yield includes G(anions) = 2.1, in addition to solvated electrons, as deduced from decay kinetics; not observed by other workers.

^{d}Yields change very little with temperature up to 523 K, C.J. Hochanadel, [550048].
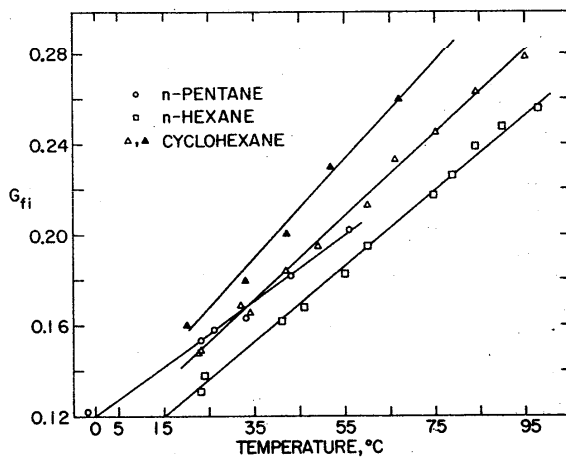
FIGURE 1. G_{fi}^o for n-pentane, n-hexane and cyclohexane.
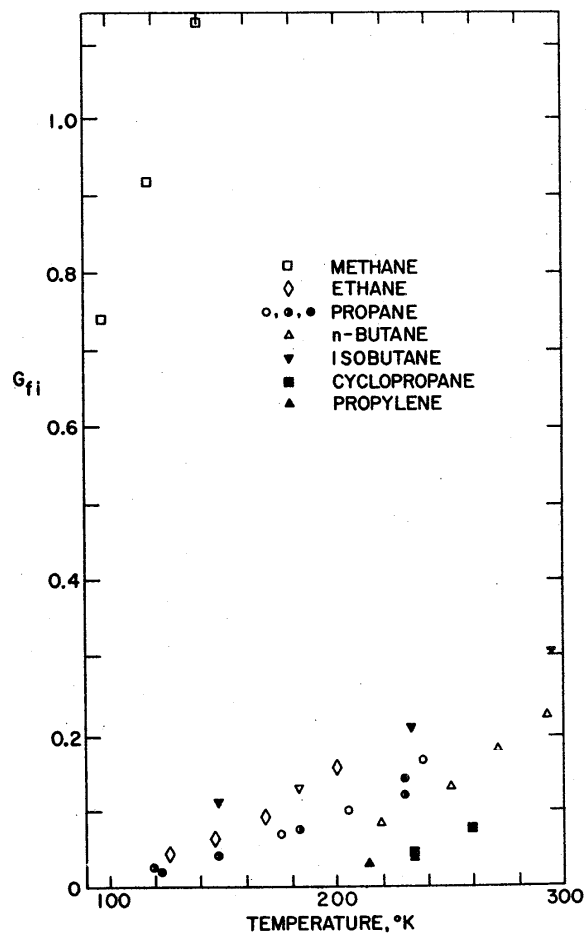Open symbols from [680376]; filled symbols, [720269].

FIGURE 2. G_{fi}^o for low-molecular-weight saturated hydrocarbons.
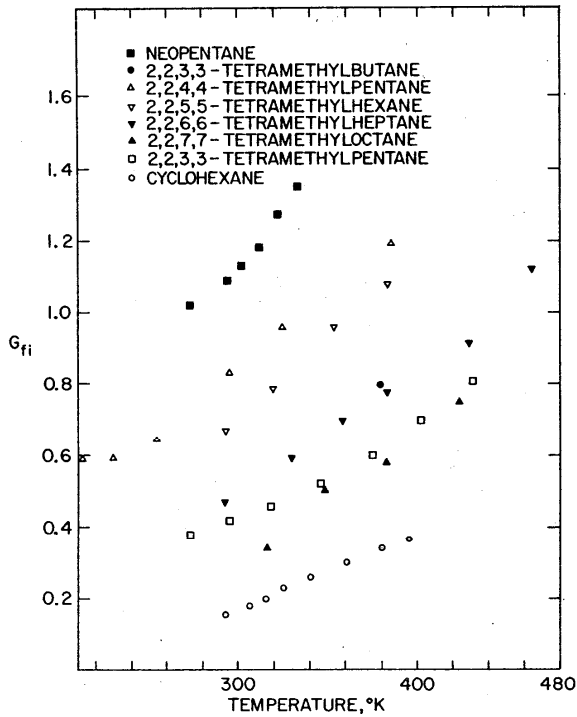Data from [741012, 720034 and 720166].

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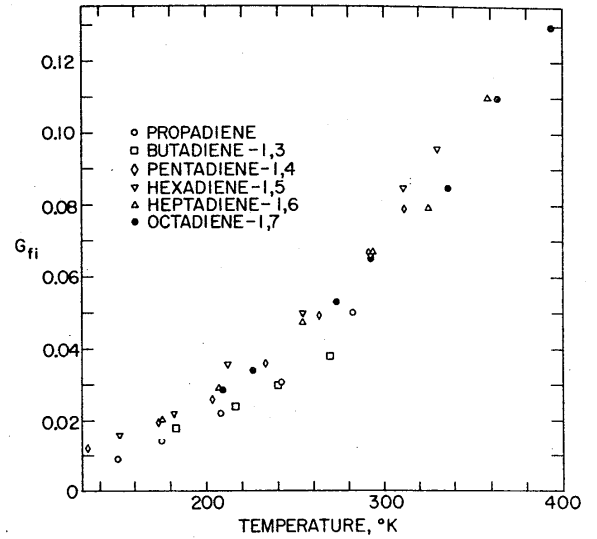FIGURE 3. G_{fi}° for some saturated hydrocarbons, from [720269].

FIGURE 5. G_{fi}° for some dienes, from [731054].
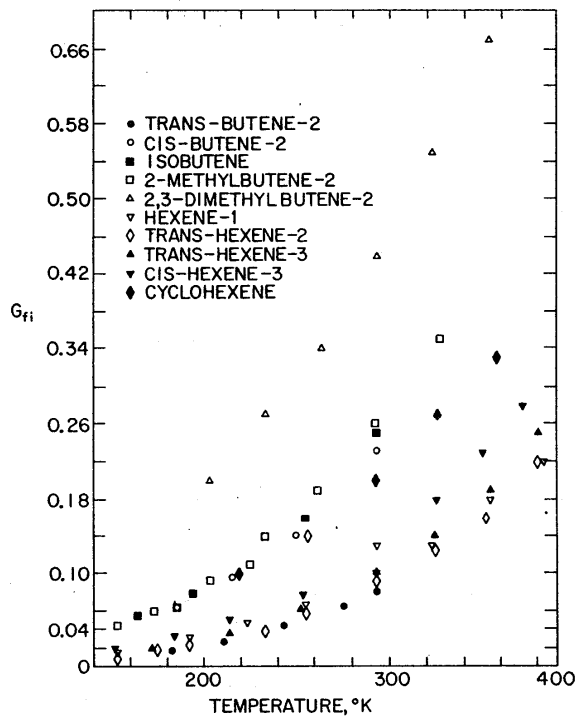

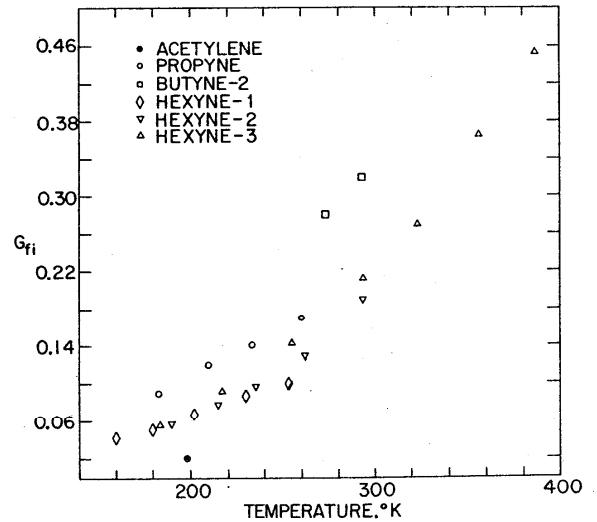FIGURE 4. G_{fi}° for some singly–unsaturated hydrocarbons, from [741012].

FIGURE 6. G_{fi}° for some alkynes, from [731054].

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5. Remarks on G_{fi}° Data

5.1. Hydrocarbons

The chief property determining G_{fi}° in hydrocarbons is molecular shape. By and large, the more nearly spherical the molecules, the bigger G_{fi}°. Despite variations in G_{fi}° by a factor of up to 100, the temperature coefficients are quite comparable. The effect of double and triple bonds is relatively minor, although the difference between *cis*– and *trans*–butene–2 is surprising. Comparing results from the two laboratories responsible for most of the data, we find that the more recent data from Freeman's laboratory are consistently about 30% higher than the data on the same liquids by Schmidt and Allen. Further work is required to settle this and other discrepancies.

5.2 Other Non–polar Compounds

The near–spherical tetramethides have large values of G_{fi}°, but equally spherical carbon tetrachloride has a low value. This is attributed to the reactivity of CCl_4 with e^-, which seems to convert e^- to Cl^- before it emerges from the positive ion field. However, CF_4, which does not ordinarily react readily with electrons [690179], also has a very low G_{fi}°. This seems to be an outstanding anomaly.

5.3. Polar Liquids

The yield of free solvated electrons in water has been the subject of dozens of papers, and only in recent years has agreement been obtained. The two papers cited in table 4 for $G(e_{aq}^-)$ in water contain references to earlier work. For effects of radiation quality (LET) on the yields see [610164] and [690185]. The free–ion yield also includes some OH^- which is shown by pulse conductivity studies; therefore, G_{fi}° is actually larger than G_{e^-}.

There is some controversy about yields of solvated electrons and free ions in methyl and ethyl alcohols. Earlier scavenger studies gave $G(e^-)$ about 1.0, but pulse conductivity gave values near 2. In the light of later work, it now appears that electron reaction with biphenyl and anthracene may have been underestimated because of the short lifetime of the product ions in alcohol, while in other cases too low a scavenger concentration was used. The two conductivity studies differ widely, however, on the total ion pair yield; [710531] found the yield of other anions to be larger than that of solvated electrons while [710064] found the anion yield less than 8% of the electron yield. Another disagreement involves the yield in tetrahydrofuran.

G_{fi}° should increase with increasing dielectric constant, which shortens the range of the Coulomb forces. Table 4 shows a strong tendency in this direction, but with many exceptions. The yield in ammonia, which is much larger than that in liquids of similar dielectric constant, seems connected with the slowness of reaction of the solvated electron with the conjugate acid ion NH_4^+.

6. Total Ion Yields

Only in two polyatomic liquids has G_{fi} been determined to high enough fields to allow a reasonable extrapolation to infinite field. Table 5 shows that the extrapolated total yield for γ rays in neopentane and CS_2 is close to that measured in the gas phase. In the monatomic liquids Ar, Kr and Xe, nearly complete collection of the ions is possible, and the total ion yield in the liquid is found to be greater than in the gas. In the solid forms of these elements, optical absorptions are found by Baldini at longer wave–lengths than in the corresponding gas [629023] and it is believed that the resulting excited states spontaneously ionize, in the liquid as well as the solid state [719437]. If this is true, Baldini's absorptions give the effective ionization potential in the liquid, I_{liq}. Takahashi *et al.* [740153] found reasons for assuming that the ratio of W to I should be the same in the liquid and gas, and obtained the following calculated values for W_{liq}: Ar, 24.0; Kr, 20.1; Xe, 16.7. These calculated values agree with their measured values within the experimental error (3 to 8%).

TABLE 5. Total ion yields reported for selected liquids

Compound	Temp. K	Radiation Source	% satn. obtained	G_{fi}^∞	W_{liq} (eV)	G_{liq}/G_{gas}	Reference
Carbon disulfide	Room	γ rays from Ra	80	3.8	26	~1	340008
Neopentane	296	^{60}Co γ rays	84	4.03	24.8	0.94	700090[a]
Argon	87	20–kV or 50–kV X rays	95–100	3.9	26 ± 3	~1	660847
	87	Internal conversion e^-, from ^{207}Bi	~100	4.2	23.6	1.11	740029
	87	^{63}Ni β–rays	98	4.22	23.7	1.11	740153
	87	^{60}Co γ rays	100	4.5	22.5	1.18	690429
	87	1.7 MeV X–rays	100	7.3	13.7	1.9	730059
Krypton	148	1.7 MeV X–rays	98	13.0	7.7	3.2	730059
	120	^{63}Ni β–rays	91	4.9	20.5	1.17	740153
Xenon	183	1.7 MeV X–rays	~100	13.7	7.3	3.0	730059
	183	Po α–rays		5.8	17.3	1.27	730735
	166	^{63}Ni β–rays	90	6.1	16.4	1.33	740153

[a]G_{gas} from 710122.

7. Theoretical Treatments

No good quantitative theory exists of the free–ion yield. Jaffé's theory [080002] was based on a columnar model which is unrealistic for low LET radiations and has not proved useful quantitatively. Recent treatments start with Onsager's formula for the probability $P(r)$ of escape by thermal agitation of a pair of ions separated by a distance r:

$$P(r) = (1 + f(E))\exp(-r_c/r)$$

where $r_c = e^2/\epsilon kT$, e is electronic charge, ϵ dielectric constant, k Boltzmann's constant, T the absolute temperature, and $f(E)$ is a function of the applied field expressed as a double summation of terms again involving ϵ and T. The model for hydrocarbons assumes that an electron very quickly loses energy to electronic and vibronic modes and attains a level of energy which is less than that of molecular vibrations but still greater than thermal. It then loses energy much more slowly by elastic collisions, and how far it travels before it is thermalized depends on how smooth a potential surface it finds, which in turn depends on how nearly spherical the liquid molecules are. Eventually it attains thermal energy at a distance r from the positive ion, which of course is not the same for all electrons. Some distribution function $D(r)$ must exist which gives the probability of the electron becoming thermalized at r, and the escape probability is then $\int D(r)P(r)dr$. If this model holds, the same function should determine both the field dependence and the temperature dependence of G_{fi}. Every worker who has in recent years seriously considered G_{fi} has expressed his results in terms of an assumed $D(r)$, which usually includes two parameters, the total yield G_{fi}^∞ and a "mean penetration range" called b or r_o. Both the temperature coefficient of the zero–field free–ion yield and the field effect on the yield may be used to obtain the best value of the range r_o defined by an assumed $D(r)$. Mozumder [748021] fitted experimental data on G_{fi} for 19 hydrocarbons and other organic liquids with five different assumed forms of $D(r)$ to obtain values of the range r_o. For any particular liquid, the five values of r_o ranged over a factor of 1.6 to 1.8. But all the calculated "mean" ranges are many times longer than anyone would have supposed prior to the analysis of the free–ion yields. Thus, the smallest r_o values in Mozumder's results were obtained from a "truncated power law" $D(r) = (2.7/4\pi r_o^3)$ $(r/r_o)^{-5.7}$ and ranged from 28Å for 1,4–dioxane to 133Å for neopentane. The majority of electrons formed in the ionization of liquids by α, β, γ or X–rays have initial energies below 100 eV. Extrapolation of the usual "electron ranges" obtained by experiments on kilovolt electrons suggests maximum ranges <1 Å for 100–eV electrons in hydrocarbons [660148]. The usual "electron range" determination consists in finding how thick a foil must be inserted in an electron beam to prevent ionization in air beyond the foil; the foil is thus only sufficient to reduce the electron energy below the ionization threshold (15–20 eV). The extra distance traveled in liquids is required to reduce the electron energy from a few eV to thermal levels. This distance depends strongly on the shape of the molecules.

The ranges in dielectric liquids deduced from free–ion yields agree in order of magnitude with values obtained by photoionization of solute molecules [710638] and metal surfaces [720439]. Recent work on electron scattering in metals has shown similar effects; the "mean free path" in the metal, which decreases with decreasing energy at higher energies, shows a sharp upturn at electron energies below 40 eV [749139].

The trouble with the Onsager model is that it does not conform well with physical reality, for only about 40% of the ions are formed in isolated pairs. The remainder occur in groups, usually known as "spurs", which contain from 2 to 50 or more ionizations, located close together. The electrons formed by ionization in such a group are attracted back by the collective charge of all the ions in the group, partially shielded by the charge on all the other electrons. Obviously the Onsager formula cannot apply to such a vague and complex situation. When the field is not too high and the escape probability from a spur remains low, the parameter r_o may be rationalized as the mean distance between the positive and negative charges in the last pair to remain in a spur at the moment that all the other pairs have recombined. When the field is high enough so that an appreciable number of spurs contribute more than one free–ion pair, the use of the Onsager formula cannot be justified. Dodelet and Freeman [758020] have proposed a model of the spur which, together with an assumed $D(r)$, gives a reasonable fit to the data on field effects in such diverse liquids as xenon and water. The values obtained for the parameters G_{fi}^{∞} and r_o are not however very different from those obtained (much more simply) by not taking the spurs into account. The physical significance of such values remains doubtful as long as $D(r)$ is taken arbitrarily, which it must be until the process of electron slowing–down in the low energy range is better understood.

We do not include any quoted values of the "penetration range" in our tables of data, because the numbers have no precise quantitative significance. Nevertheless, the r_o values listed in any paper on free–ion yields, have great qualitative meaning. It is clear that electrons of somewhat superthermal energy must lose their momentum more slowly, in passing through a liquid, the more nearly isotropic are the molecules of the liquid. The same behavior of thermal electrons is indicated by mobility measurements of thermal electrons in hydrocarbon liquids, although quantitative correlation between G_{fi} and mobility has not yet been made. A great deal of information remains to be extracted from G_{fi} data.

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