

Group contribution method for predicting the lower and the upper flammable limits of vapors in air

William H. Seaton

1329 Belmeade Drive, Kingsport, TN 37664 (U.S.A.)

(Received August 2, 1990; accepted in revised form January 18, 1991)

Abstract

A mathematical model has been derived from Le Chatelier's law to estimate the flammable limits of vapors in air. The parameters of the model are obtained by a group contribution procedure which is based on the second order structural groups of the kind defined by Benson and Buss (*J. Chem. Phys.*, 29 (1958) 546). Both the lower and the upper flammable limits can be estimated from nothing more than the chemical structure of a compound. Although there are some outstanding exceptions, the model predicts most lower flammable limit values to within 10% of published values. Likewise, the model predicts most upper flammable limit values to within 20% of published values. Data are presented to suggest that better results could be obtainable when more measured values become available from standardized and accurate methods.

Introduction

The lower and upper limits of flammability are the concentrations of a combustible vapor in air below which and above which a flame will not propagate. Vapor/air concentrations which fall between the lower and the upper flammable limits have the potential to burn and thus to increase the volume of the vapor/air mixture and its combustion products. The sudden release of pressure by such a process is termed an explosion. Even if the composition is only capable of causing a relatively weak and mild explosion it may make newspaper headlines if large volumes are confined within buildings. Furthermore, it is current thinking that almost any flammable mixture of a vapor with air will detonate if it is ignited under the proper conditions [2]. Detonations are a type of explosion wherein the reaction zone progresses very rapidly through the combustible composition and the resulting shock waves are potentially very damaging. Clearly, it is important to know when vapors mixed with air are within the lower and the upper flammable concentration limits so that such mixtures can be avoided or handled safely. Process engineers have two problems with such mixtures at this point in time. The first problem is that conflicting data are often found in the literature. This is probably because most of

the data were measured before reliable and standardized methods of measurement were developed. The second problem is that there are also no reliable methods for the estimation of these concentrations which apply to broad spectrums of compounds. It can be expected that highly accurate estimation methods must await the accumulation of a body of accurate experimental data from which the parameters of the model can be derived. Nevertheless, the purpose of this publication is to propose a mathematical model which can be used to correlate and to estimate the lower and the upper flammable limits of vapors in air.

ASTM Committee E-27 and computer program CHETAH

Commercial laboratories have long made measurements of impact sensitivities, flash points, autoignition temperatures, dust explosibility indices, and the like, in their efforts to evaluate the energy hazard potential of chemicals and mixtures. Historically, the wide variety of test methods made it difficult to communicate useful information between test laboratories. In the early 1960's it was recognized that there was a need for some agency to develop standardized techniques for the evaluation of chemical hazards. In response to this need, ASTM Committee E-27, On Chemical Hazards, was formed to promote the development and standardization of physical and chemical test methods, nomenclature, and the promotion of knowledge and stimulation of research bearing on the hazard potential of chemicals. The hazard potential was defined as the degree of susceptibility to ignition or release of energy under varying environmental conditions. Subcommittee E-27.07 of this committee was charged with the development and standardization of computational methods for estimating the energy hazard potential of chemicals arising during their manufacture, transport, storage or use. For this purpose, computer program CHETAH was developed to predict the energy release potential and to provide an overall assessment of the hazard potential of a chemical or mixture. The program requires as input information, nothing more than chemical structures, so it can be used in advance of the actual synthesis of the chemical or mixture [3]. Version 6 of this computer program is currently being developed.

As indicated above, any flammable vapor/air mixture should be regarded as a potentially explosive mixture. For this reason, the members of Subcommittee E-27.07 have been searching for several years for a method that can be used in program CHETAH to predict when a vapor/air mixture is flammable. Two earlier methods have been found to be reasonably accurate [4,5]; however, all of the earlier methods are judged to be too limited in scope and/or incompatible with the coding scheme of program CHETAH. Therefore, the objective of this project is to develop and evaluate a new method that is based on the second order groups that are used to code chemical structures for program CHETAH [1,3,6]. A second order group is defined as a central group or atom plus all of

its singly attached ligands, at least one of which must be polyvalent. Interested readers who are unfamiliar with the nature of second order groups can find complete descriptions in references [1] and [6]. The limited sets of second order groups in Tables 1 and 2 use the widely accepted notation wherein the central atom or group is shown on the left of the hyphen while the attached ligands are shown on the right of the hyphen.

The mathematical model

Le Chatelier published eq. (1) to connect the lower flammable limits of two gases in air with the lower flammable limit of any mixture [7]. His equation can be derived from the assumption that the minimum amount of heat which must be generated in order for the mixture to be flammable is approximately constant for all gases and gas mixtures.

$$p_1/L_1 + p_2/L_2 = 1 \quad (1)$$

where p is the concentration of a gas, in vol.%, in any lower-flammable-limit mixture of the two gases, and L is the concentration of a gas, in vol.%, at its lower flammable limit in air. Subscripts 1 and 2 refer to the two gases.

The equation of Le Chatelier has been generalized by subsequent workers to the form shown here as eq. (2). As Bartknecht states, the validity of eq. (2) has been proven many times for predicting both the lower and upper limits of mixtures of flammable gases [8].

$$F_m = \Sigma p_i / \Sigma (p_i / F_i) \quad (2)$$

where F_m denotes the concentration of mixture in air at either the lower or the upper flammable limit, p_i the concentration of gas i in the air-free mixture, and F_i the concentration of component i at its lower or upper flammable limit in air. All concentrations are given in vol.%.

Imagine a vapor which is composed of pseudomolecules that are really just clusters of a single kind of second order group. Let us define f_i as the reciprocal of the number of groups of this type that it takes to make a pseudomolecule of just this one kind of second order group. (The reciprocal is used here as a mathematical device to avoid divisions by zero in the iteration procedure that is used to determine the values of f_i .) Let us define the concentration of this vapor at its flammable limit to be g_i . We usually cannot make an experimental determination of the value of g_i because we cannot have real molecules that are made of only one kind of second order group. Now imagine that a mole of a real molecule is a mixture of our pseudomolecules such that the total number of second order groups in the mixture is correct for the real molecule. Let us now define n_i as the number of second order groups of the i th kind in a molecule of the real compound. The product $n_i f_i$ thus represents the number of moles of pseudomolecule i in the mixture of pseudomolecules that has the same num-

ber of second order groups as one mole of the real molecule. We may now apply eq. (2), in the form of eq. (3), to correlate flammability data for gases. The denominator of eq. (3) no longer sums to unity as it does in eq. (2) but that does not matter because the numerator of eq. (3) differs from that of eq. (2), for any particular molecule, by the same factor. Inherent in this derivation is the assumption that the amount of heat which is yielded by the combustion of our mixture of pseudomolecules is the same as that which is yielded by the combustion of one mole of the real molecule. This assumption is consistent with Benson's second order group method for computing heats of combustion, since the oxidation products are the same in both cases and since the same number and kind of second order groups are used to construct the reactant(s) in both cases. It is this factor that ties the flammable limit of our mixture to that of the real molecule.

$$F = \Sigma(n_i f_i) / \Sigma(n_i f_i / g_i) \quad (3)$$

where F denotes the concentration, in vol.%, of a real gas in air at its lower or upper flammable limit, n_i the number of times that group i appears in the molecule, f_i the empirical parameter associated with group i , and g_i the empirical parameter associated with group i .

Experimental work

Now that the form of the equation is defined, let us not be limited by any notions that the equation is based on a rigorously correct theory. In other words, the parameters f_i and g_i will be determined empirically by the best fit of available data and not by what we think the theory suggests.

The two parameters for each second order group have been determined by a non-linear regression procedure. For two reasons, this work was done piecemeal with small sets of compounds. Each set of compounds was selected such that all of the involved second order groups were used in at least four different compounds. The first reason is that, in the judgment of the author, the data for hydrocarbons are probably more accurate than the data for most of the other types of compounds, and it is felt that better values would be obtained, where feasible, by using only data for hydrocarbons. The process was started with the data for paraffins and went from there to data for olefins, aromatic hydrocarbons, etc. The second reason for using small sets of compounds is that some of the determined parameters are dependent on the initial estimates, and this makes it desirable to keep the number of parameters in each iteration as low as possible. Even with limited numbers of parameters, it was necessary to make each determination many times, using different initial values. The entire process was automated. The selected parameters are those which gave the smallest value for the objective function after many trials, although there is no proof that a better set could not have been obtained with additional trials.

TABLE 1

Equation (3) parameters for the estimation of lower flammable limit data

2nd Order group	Parameters of eq. (3)		2nd Order group	Parameters of eq. (3)	
	<i>f</i>	<i>g</i>		<i>f</i>	<i>g</i>
C-(C)(C _B)(H) ₂	0.18308	0.01344	C _B -(N)	26.25975	1.27710
C-(C)(CO)(H) ₂	0.02613	0.00980	C _B -(O)	74.99764	25.99844
C-(C)(H) ₂ (Cl)	11.55786	6.21312	C _d -(C)(H)	0.05835	142.79900
C-(C)(H) ₂ (O)	0.00242	0.00322	C _d -(CO)(H)	6.88905	1.88402
C-(C)(H) ₃	12.50732	3.12420	C _d -(H)(Cl)	2.31750	5.42088
C-(C) ₂ (C _B)(H)	0.09440	0.00323	C _d -(H) ₂	1.31449	2.61055
C-(C) ₂ (CO)(H)	0.49969	0.02893	CO-(C)(H)	12.05977	4.68871
C-(C) ₂ (H)(O)	0.02488	0.00298	CO-(C)(O)	0.00100	51.59168
C-(C) ₂ (H) ₂	0.15461	0.04492	CO-(C) ₂	0.31889	0.10826
C-(C) ₃ (H)	0.01656	0.00103	CO-(C _d)(O)	0.00215	0.02738
C-(C) ₄	0.33819	0.01178	N-(C _B)(H) ₂	6.91310	3.89132
C-(C _B)(H) ₃	18.80642	1.33971	O-(C)(CO)	0.03929	0.01247
C-(C _d)(H) ₂ (Cl)	1.01650	5.14586	O-(C)(H)	10.62441	5.12929
C-(C _d)(H) ₃	0.15532	1.32511	O-(C) ₂	0.21850	0.04338
C-(CO)(H) ₃	11.57657	3.81915	O-(C _B)(H)	74.99712	0.61106
C-(H) ₃ (O)	13.10617	9.23645	O-(CO) ₂	0.01228	0.00441
C _B -(C)	0.18524	0.03750	Cyclopentane ring	28.97878	6.47494
C _B -(C _B)	0.07821	0.00270	Cyclohexane ring	17.33727	-3.48684
C _B -(H)	6.01743	1.28777	Gauche interaction	-5.04752	0.92017

TABLE 2

Equation (3) parameters for the estimation of upper flammable limit data

2nd Order group	Parameters of eq. (3)		2nd Order group	Parameters of eq. (3)	
	<i>f</i>	<i>g</i>		<i>f</i>	<i>g</i>
C-(C)(C _B)(H) ₂	3.28264	0.37109	C _d -(C)(H)	0.00000	100.00000
C-(C)(C _d)(H) ₂	0.00000	100.00000	C _d -(C) ₂	0.25125	1.26758
C-(C)(CO)(H) ₂	0.09181	0.14551	C _d -(CO)(H)	0.00015	883.90840
C-(C)(H) ₂ (Cl)	65.79851	15.89991	C _d -(H)(Cl)	0.00002	12.80000
C-(C)(H) ₂ (N)	8.11656	20.66602	C _d -(H) ₂	0.00007	28.60000
C-(C)(H) ₂ (O)	32.23775	11.16797	CO-(C)(C _d)	0.03769	4.81641
C-(C)(H) ₃	65.69279	12.23829	CO-(C)(H)	43.57364	54.90230
C-(C) ₂ (CO)(H)	0.00000	100.00000	CO-(C)(O)	0.01264	2.61768
C-(C) ₂ (H)(O)	2.54507	0.39893	CO-(C) ₂	90.85265	8.71534
C-(C) ₂ (H) ₂	3.66985	1.55859	CO-(C _d)(O)	0.00059	5.99268
C-(C) ₃ (H)	1.08653	39737.61000	CO-(H)(O)	0.87166	57.00002
C-(C) ₄	99.99675	2.95898	N-(C)(H) ₂	31.57786	13.35889
C-(C _d)(H) ₂ (Cl)	1.44890	12.48047	O-(C)(CO)	0.27914	2.82715
C-(C _d)(H) ₃	2.61722	11.96680	O-(C)(H)	63.42825	35.71059
C-(CO)(H) ₃	0.08697	492.86670	O-(C) ₂	24.26403	15.71485
C-(H) ₃ (O)	3.01463	43.39455	O-(CO)(H)	0.00000	100.00000
C _B -(C)	12.19265	15392.84000	O-(CO) ₂	0.00127	0.13476
C _B -(H)	22.40435	7.14000	Cyclohexane ring	99.99770	8.58692
C _D -(C)(CO)	0.00725	0.08740	Gauche interaction	-0.71020	-0.18164

TABLE 3

Experimental and estimated data on the lower flammable limit of vapors in air. (All data are from the sources listed in references [10-21])

Compound	Lower flammable limit		Error (%)
	Est'd (vol.%)	Expt'l (vol.%)	
Ethane	3.12	3.00	4.14
Propane	2.20	2.20	-0.07
n-Butane	1.70	1.80	-5.52
n-Pentane	1.39	1.40	-0.72
n-Hexane	1.18	1.18	-0.23
n-Heptane	1.02	1.00	2.27
n-Octane	0.91	0.95	-4.71
n-Nonane	0.81	0.80	1.63
n-Decane	0.74	0.75	-1.51
Isobutane	1.93	1.80	7.31
Isopentane	1.26	1.30	-3.44
Neopentane	1.32	1.38	-3.99
2,3-Dimethylpentane	1.00	1.10	-9.11
2,2,3-Trimethylbutane	1.01	1.00	0.85
Ethylcyclopentane	1.01	1.10	-7.90
n-Propylcyclopentane	0.94	0.95	-1.12
2,2,3,3-Tetramethylpentane	0.88	0.80	10.19
2,3-Dimethylbutane	1.14	1.20	-4.82
2-Methylpentane	1.16	1.20	-3.49
2,2-Dimethylbutane	1.12	1.20	-7.00
Methylcyclohexane	0.95	1.10	-13.73
2-Methylhexane	1.02	1.00	1.83
2,2,4-Trimethylpentane (isooctane)	0.93	0.95	-2.56
Cyclopentane	1.37	1.40	-1.99
Methylcyclopentane	1.10	1.00	10.02
Cyclohexane	1.17	1.26	-7.54
Ethylcyclohexane	0.86	0.90	-4.23
<i>trans</i> -Decahydronaphthalene	0.72	0.74	-2.21
<i>cis</i> -Decahydronaphthalene	0.72	0.70	3.38
Dimethyl decalin	0.70	0.67	5.01
Diethylcyclohexane	0.78	0.80	-2.91
Bicyclohexyl	0.64	0.65	-1.38
Benzene	1.29	1.30	-0.94
Toluene	1.16	1.20	-3.41
<i>m</i> -Xylene	1.10	1.10	-0.41
<i>p</i> -Xylene	1.10	1.10	-0.41
Ethylbenzene	0.94	1.00	-6.45
Cumene	0.83	0.88	-5.43
Propylbenzene	0.87	0.80	9.17
n-Butylbenzene	0.82	0.82	-0.07
<i>sec</i> -Butylbenzene	0.80	0.80	-0.61
Isobutylbenzene	0.83	0.82	0.65

Compound	Lower flammable limit		Error (%)
	Est'd (vol.%)	Expt'l (vol.%)	
<i>p</i> -Cymene	0.86	0.85	0.69
<i>p</i> -Diethylbenzene	0.78	0.80	-2.41
Biphenyl	0.58	0.60	-4.00
2-Isopropylbiphenyl	0.53	0.53	-0.10
Ethylene	2.61	2.70	-3.31
<i>trans</i> -2-Butene	1.82	1.80	0.92
Propylene	2.46	2.40	2.51
Dimethyl ether	3.36	3.40	-1.28
Methyl ethyl ether	2.30	2.20	4.74
Diethyl ether	1.73	1.85	-6.24
Ethyl propyl ether	1.41	1.70	-16.98
Dipropyl ether	1.19	1.30	-8.31
Diisopropyl ether	1.33	1.40	-4.88
<i>n</i> -Amyl ether	0.74	0.70	6.19
<i>n</i> -Hexyl ether	0.63	0.60	4.85
Acetaldehyde	4.22	4.10	2.89
<i>n</i> -Propionaldehyde	2.66	2.60	2.35
<i>n</i> -Butyraldehyde	1.95	1.90	2.69
Isobutyraldehyde	1.63	1.60	1.73
2-Ethylbutanal	1.09	1.20	-9.12
2-Ethylhexanal	0.92	0.85	7.96
Acetone	2.61	2.60	0.22
Methyl ethyl ketone	1.93	1.90	1.67
2-Pentanone	1.53	1.55	-1.42
Diethyl ketone	1.56	1.60	-2.57
Methyl isobutyl ketone	1.24	1.40	-11.68
Diisobutyl ketone	0.89	0.80	11.83
2-Hexanone	1.27	1.30	-2.56
2-Heptanone	1.08	1.10	-1.49
5-Methyl-2-hexanone	1.07	1.00	7.36
Methyl acetate	3.25	3.20	1.64
Ethyl acetate	2.21	2.20	0.25
<i>n</i> -Propyl acetate	1.69	1.77	-4.61
Isopropyl acetate	1.63	1.70	-4.38
Methyl propionate	2.28	2.40	-4.81
Ethyl propionate	1.72	1.80	-4.41
<i>n</i> -Butyl acetate	1.37	1.39	-1.36
Isobutyl acetate	1.33	1.30	2.07
<i>sec</i> -Butyl acetate	1.42	1.70	-16.69
1-Methoxy-2-propyl acetate	1.46	1.50	-2.99
Isopentyl acetate	1.10	1.10	-0.24
Amyl acetate (1-pentanol acetate)	1.16	1.10	5.13
Cyclohexyl acetate	1.11	1.00	11.10
<i>n</i> -Amyl propionate	1.03	1.00	2.59

TABLE 3 (continued)

Compound	Lower flammable limit		Error (%)
	Est'd (vol.%)	Expt'l (vol.%)	
2-Ethylhexyl acetate	0.83	0.80	4.10
Isobutyl isobutyrate	0.97	0.96	1.19
Methyl acrylate	2.42	2.80	-13.44
Ethyl acrylate	1.71	1.40	22.05
n-Butyl acrylate	1.11	1.50	-26.21
2-Ethylhexyl acrylate	0.74	0.70	5.37
Acetic anhydride	2.62	2.70	-3.01
Propionic anhydride	1.56	1.48	5.10
Butyric anhydride	1.10	1.09	1.25
Isobutyric anhydride	0.98	1.00	-1.76
Methanol	6.80	6.70	1.48
Ethanol	3.39	3.30	2.67
n-Propanol	2.27	2.20	3.08
Isopropanol	1.93	2.00	-3.29
n-Butanol	1.71	1.70	0.58
sec-Butanol	1.64	1.70	-3.70
Isobutanol	1.61	1.70	-5.43
2-Methyl-1-butanol	1.33	1.40	-5.03
3-Methyl-1-butanol	1.33	1.40	-5.03
1-Pentanol	1.38	1.40	-1.73
3-Pentanol	1.42	1.20	18.39
4-Methyl-2-pentanol	1.24	1.20	2.97
n-Hexanol	1.15	1.20	-3.89
Cyclohexanol	1.27	1.20	5.73
2-Ethyl-1-hexanol	0.89	0.88	1.44
2-Octanol	1.02	0.80	27.77
Diisobutylcarbinol	0.94	0.82	14.55
Ethyl chloride	4.10	4.00	2.60
1,2-Dichloroethane	6.21	6.20	0.21
2-Chloroethanol	4.74	4.90	-3.35
1-Chloropropane	2.60	2.60	0.11
n-Butyl chloride	1.91	1.80	6.23
Isobutyl chloride	1.77	1.80	-1.46
1-Chloropentane	1.52	1.60	-5.30
1-Chlorobutene-2	4.08	4.20	-2.78
1,3-Dichloropropene	5.42	5.30	2.34
1-Chloropropene-1	4.64	4.50	3.18
3-Chloropropene-1	3.41	3.30	3.22
trans-1,2-Dichloroethylene	5.42	5.60	-3.20
Vinyl chloride	3.90	4.00	-2.48
p-Cresol	1.18	1.10	7.48
m-Cresol	1.18	1.10	7.48
Nonylphenol	0.98	1.00	-1.54
Aniline	1.38	1.30	6.48

Compound	Lower flammable limit		Error (%)
	Est'd (vol.%)	Expt'l (vol.%)	
<i>o</i> -Aminobiphenyl	0.71	0.66	8.29
2-Biphenylamine	0.71	0.70	2.10
Diethylene glycol ethyl ether	1.02	0.98	4.37
2-Methoxyethanol	2.39	2.30	3.80
2-Ethoxyethanol	1.75	1.70	2.76
Diethylene glycol monobutyl ether	0.89	0.85	4.89
1,3-Butandiol	1.64	1.90	-13.71
2-(2-Methoxyethoxy)ethanol	1.46	1.38	5.69
Ethylene glycol diacetate	1.68	1.60	4.70
2-Butoxyethanol	1.17	1.10	6.23
2-(2-Ethoxyethoxy)ethanol	1.18	1.20	-1.32
Diethylene glycol monoisobutyl ether	0.90	0.98	-8.44
Glyceryl triacetate	0.97	1.00	-3.39
2-Methoxyethyl acetate	1.76	1.70	3.75
2-Ethoxyethyl acetate	1.39	1.70	-18.07
Diethylene glycol monobutyl ether acetate	0.81	0.76	5.93
Dibutyl sebacate	0.48	0.44	9.20
Ethylene glycol	3.76	3.50	7.50
1,2-Propylene glycol	1.96	2.60	-24.72
1,3-Propylene glycol	2.36	2.60	-9.42
1,3-Benzenediol	1.20	1.40	-14.25
<i>o</i> -Phenylenediamine	1.43	1.50	-4.88

The parameters of eq. (3) have been determined using lower flammable limit data and then again using upper flammable limit data. The resulting two sets of parameters are presented in Tables 1 and 2.

The ability of the parameters in Table 1 to correlate lower flammable limit data is displayed by the error data in Table 3. In Table 3, 95% of the estimated data are within 10% of published values. The ability of the parameters in Table 2 to correlate upper flammable limit data is displayed by the error data in Table 4. In Table 4, 90% of the estimated data are within 20% of published values.

Discussion

In chapter 3 of his book [6], Benson describes the *gauche* interaction, which is a structural correction that must be made when enthalpy of formation data are being estimated by a second order group contribution method. The *gauche* interaction is primarily due to the repulsion of too-close methyl or methylene groups. Benson describes a method for computing the number of *gauche* inter-

TABLE 4

Experimental and estimated data on the upper flammable limit of vapors in air. (All data are taken from the sources listed in references [10-21])

Compound	Upper flammable limit		Error (%)
	Est'd (vol.%)	Expt'l (vol.%)	
Ethane	12.24	12.40	-1.30
Propane	10.32	9.50	8.60
n-Butane	8.98	9.00	-0.20
n-Pentane	8.00	8.00	0.00
n-Hexane	7.25	7.40	-2.06
n-Heptane	6.65	6.70	-0.71
n-Octane	6.17	6.00	2.83
n-Nonane	5.77	5.60	3.05
n-Decane	5.44	5.40	0.66
Isobutane	7.04	8.40	-16.15
Isopentane	7.63	7.60	0.35
Neopentane	5.08	7.50	-32.32
2-2-Dimethylbutane	5.25	7.00	-24.95
2,3-Dimethylbutane	7.06	7.00	0.90
2-Methylpentane	7.13	7.00	1.82
2-Methylhexane	6.70	6.00	11.74
2,3-Dimethylpentane	7.49	6.75	11.03
Cyclohexane	4.73	7.75	-38.91
Methylcyclohexane	6.43	6.70	-4.01
Ethylcyclohexane	6.06	6.60	-8.14
Diethylcyclohexane	7.00	6.00	16.67
2,4,4-Trimethyl-1-pentene	4.80	4.80	0.00
3,3-Diethylpentane	5.84	5.70	2.37
2,2,3,3-Tetramethylpentane	4.88	4.90	-0.35
Bicyclohexyl	5.10	5.10	0.00
2-Isopropyl bicyclohexyl	5.83	4.10	42.13
Benzene	7.14	7.10	0.56
Ethylbenzene	6.46	6.70	-3.58
Propylbenzene	6.10	6.00	1.71
n-Butylbenzene	5.79	5.80	0.11
Isobutylbenzene	6.00	6.00	0.00
p-Diethylbenzene	6.15	6.10	0.79
Ethylene	28.60	28.60	0.00
1-Butene	12.24	10.00	22.38
trans-2-Butene	11.97	9.70	23.37
1-Pentene	8.98	8.70	3.24
Dimethyl ether	18.00	18.00	0.00
Methyl ethyl ether	12.69	10.10	25.63
Diethyl ether	12.19	24.00	-49.19
Ethyl propyl ether	10.97	9.00	21.85
Dipropyl ether	9.99	7.00	42.76
Diisopropyl ether	8.17	7.90	3.36
Di-n-butyl ether	8.55	7.60	12.46

Compound	Upper flammable limit		Error (%)
	Est'd (vol.%)	Expt'l (vol.%)	
Acetaldehyde	55.00	55.00	0.00
n-Butyraldehyde	12.36	12.50	-1.15
Isobutyraldehyde	8.97	10.60	-15.39
2-Ethylbutanal	11.23	7.70	45.80
2-Ethylhexanal	9.05	7.20	25.74
Acetone	8.73	11.00	-20.62
Methyl vinyl ketone	15.60	15.60	0.00
Methyl ethyl ketone	9.54	9.50	0.45
2-Pentanone	8.54	8.20	4.17
Diethyl ketone	9.92	8.00	24.00
Methyl isopropenyl ketone	8.88	9.00	-1.35
3-Hexanone	9.13	8.00	14.07
Methyl isobutyl ketone	7.50	7.50	0.00
2-Hexanone	7.76	7.60	2.15
4-Methylpentanone-2	7.50	7.50	0.00
2-Heptanone	7.14	7.90	-9.60
5-Methyl-2-hexanone	7.06	8.20	-13.87
Isophorone	4.36	3.80	14.79
Diisobutyl ketone	7.24	7.10	1.93
Methyl formate	22.70	22.70	0.00
Ethyl formate	11.84	13.50	-12.30
n-Butyl formate	8.14	8.20	-0.76
Isobutyl formate	7.63	8.00	-4.64
Methyl acetate	19.59	16.00	22.44
Ethyl acetate	11.76	11.40	3.18
n-Propyl acetate	9.52	8.00	18.99
Isopropyl acetate	7.80	7.80	0.00
2-Methoxyethyl acetate	12.30	12.30	0.00
n-Butyl acetate	8.08	8.00	1.06
Isobutyl acetate	7.60	10.50	-27.65
Amyl acetate (1-pentanol acetate)	7.09	7.10	-0.16
Isopentyl acetate	7.00	7.00	0.02
2-Ethylhexyl acetate	7.77	8.10	-4.11
Methyl propionate	11.19	13.00	-13.89
Ethyl propionate	11.42	11.00	3.85
Isobutyl isobutyrate	7.32	7.59	-3.56
Methyl methacrylate	12.49	12.50	-0.04
n-Butyl methacrylate	8.09	8.00	1.18
Methyl acrylate	19.57	25.00	-21.70
Ethyl acrylate	11.76	14.00	-16.02
n-Butyl acrylate	8.08	9.90	-18.38
2-Ethylhexyl acrylate	7.76	8.20	-5.31
Acetaldehyde	55.00	55.00	0.00
n-Propionaldehyde	16.10	16.10	0.00

TABLE 4 (continued)

Compound	Upper flammable limit		Error (%)
	Est'd (vol.%)	Expt'l (vol.%)	
n-Butyraldehyde	12.36	12.50	-1.15
<i>trans</i> -Crotonaldehyde	16.24	15.50	4.74
Isobutyraldehyde	8.97	10.60	-15.39
Acetic anhydride	10.30	10.30	0.00
Propionic anhydride	10.95	11.90	-7.97
Butyric anhydride	8.31	7.60	9.30
Isobutyric anhydride	7.00	6.20	12.92
Methanol	36.00	36.00	0.00
Ethanol	16.09	18.95	-15.11
n-Propanol	13.32	13.50	-1.30
Isopropanol	10.45	11.80	-11.47
n-Butanol	11.45	11.25	1.73
<i>sec</i> -Butanol	9.46	9.80	-3.45
Isobutanol	9.76	10.90	-10.42
<i>tert</i> -Butanol	8.68	9.00	-3.55
2-Buten-1-ol (crotonyl alcohol)	32.22	35.30	-8.74
3-Buten-1-ol	20.52	34.00	-39.66
2-Methyl-1-butanol	9.01	9.00	0.01
3-Methyl-1-butanol	9.01	9.00	0.10
1-Pentanol	10.08	10.00	0.83
3-Pentanol	8.67	9.00	-3.63
4-Methyl-2-pentanol	7.74	5.50	40.66
2-Ethyl-1-hexanol	9.78	9.70	0.87
Diisobutylcarbinol	6.71	6.10	10.03
Ethyl chloride	13.83	14.70	-5.90
Vinyl chloride	21.70	21.70	0.00
<i>trans</i> -1,2-Dichloroethylene	12.80	12.80	0.00
1,1-Dichloroethane	12.21	11.40	7.07
1,2-Dichloroethane	15.90	15.90	0.00
1,1-Difluoroethane	12.21	18.00	-32.19
Acetic acid	19.90	19.90	0.00
Propionic acid	10.96	12.10	-9.42
n-Butyric acid	8.31	10.00	-16.89
Isobutyric acid	8.92	9.20	-3.04
2-Ethylhexoic acid	6.04	6.00	0.66
Methacrylic acid	8.70	8.70	0.00
<i>trans</i> -Crotonic acid	11.96	15.10	-20.76
Acrylic acid	7.99	8.00	-0.12
Ethylamine	12.97	14.00	-7.34
n-Propylamine	10.41	10.40	0.07
n-Butylamine	8.78	9.80	-10.37
Amyl amine (pentyl amine)	7.66	22.00	-65.17
Hexamethylenediamine	6.30	6.30	0.00
2-Methoxyethanol	16.94	19.80	-14.47
2-Ethoxyethanol	14.42	14.00	2.98

Compound	Upper flammable limit		Error (%)
	Est'd (vol.%)	Expt'l (vol.%)	
2-(2-Methoxyethoxy)ethanol	14.80	22.70	-34.80
2-(2-Ethoxyethoxy)ethanol	13.74	23.50	-41.54
Diethylene glycol ethyl ether	11.99	19.40	-38.17
Diethylene glycol monobutyl ether	11.79	10.60	11.18
Diethylene glycol monoisobutyl ether	10.68	10.70	-0.20
1-Methoxy-2-propyl acetate	7.84	7.00	11.95
Diethylene glycol monobutyl ether acetate	10.22	10.70	-4.48
2-Ethoxyethyl acetate	11.93	12.70	-6.04
1,2-Propylene glycol	12.50	12.50	0.00

actions by using a line skeleton formula of a molecule. Domalski and Hearing describe a different method for taking gauche interactions into account [9]. In their work, they compute the number of gauche interactions as the number of methyl groups which are attached to either a tertiary or quaternary carbon atom. In the work of this project, it has been found that the method of Domalski and Hearing not only yields better results but it also is much easier to apply. It is noted that the gauche interaction, when present, makes an important contribution to the estimated flammable limit.

The data in Tables 3 and 4 are arranged to facilitate an examination of the errors within groups of similar compounds, within homologous series of compounds, and with increasing polarity of the compounds. It can be observed that certain groups of compounds seem to have excessively large errors but the errors do not seem to vary in any systematic manner with either molecular weight or polarity. In Table 3, the esters of acrylic acid seem to have excessively large errors. In Table 4, ethers seem to have excessively large errors. It can also be observed in Table 4 that the experimentally measured upper flammable limit for diethyl ether appears to be much too high when compared to the values reported for the other members of this series. An anomaly of this type does not necessarily indicate experimental carelessness because, as reported by Van Dolah et al. [10], differing experimental conditions can make large differences in the value of an observed flammable limit. Other groups and homologous series have at least one or two members which have excessive errors while most of the members are accurately correlated. The author believes that this pattern of errors provides strong evidence for the need for all future data to be measured by standardized and reliable methods.

Much of the difficulty with the development of the parameters in Tables 1 and 2 was imposed by the scatter in published data. There was initially no criterion by which the more accurate data could be selected. This greatly in-

TABLE 5

Lower and upper flammable limit data from different sources

Compound [source]	Flammable limit	
	Lower (vol.%)	Upper (vol.%)
Methanol [15]	6.00	36.00
Methanol [8]	6.40	37.00
Methanol [17]	6.70	50.00
Methanol [19]	6.72	36.50
Methanol [14]	7.30	36.00
Vinyl chloride [14]	3.60	33.00
Vinyl chloride [13]	4.00	22.00
Vinyl chloride [19]	4.00	21.70
Ethylene [14]	2.70	36.00
Ethylene [19]	2.75	28.60
Ethylene [13]	3.10	32.00
Ethylene [17]	4.00	28.60
Acetaldehyde [14]	1.60	10.40
Acetaldehyde [19]	3.97	57.00
Acetaldehyde [18]	4.00	6.00
Acetaldehyde [15]	4.00	60.00
Acetaldehyde [13]	4.10	55.00
Trichloroethylene [14]	8.00	10.50
Trichloroethylene [18]	12.50	90.00
Ethanol [19]	3.28	17.95
Ethanol [15]	3.30	19.00
Ethanol [14]	4.30	19.00
Methyl formate [15]	4.50	23.00
Methyl formate [18]	5.00	23.00
Methyl formate [19]	5.05	22.70
Methyl formate [14]	5.90	20.00
Acetic acid [15]	4.00	19.90
Acetic acid [18]	5.40	16.00
Acrylonitrile [14]	2.42	17.34
Acrylonitrile [4]	3.05	
Acrylonitrile [13]	3.00	17.00
Propylene [14]	2.00	11.00
Propylene [17]	2.20	12.10
Propylene [13]	2.40	10.30
Dimethyl ether [14]	3.40	27.00
Dimethyl ether [13]	3.40	18.00
Acetone [17]	2.50	13.00
Acetone [19]	2.55	12.80
Acetone [14]	2.60	12.80
Acetone [13]	3.00	11.00
Ethyl formate [14]	2.70	13.50
Ethyl formate [19]	2.75	16.40
Ethyl formate [15]	2.80	16.00

Compound [source]	Flammable limit	
	Lower (vol.%)	Upper (vol.%)
Methyl acetate [14]	3.10	16.00
Methyl acetate [19]	3.15	15.60
Propane [14]	2.00	9.50
Propane [19]	2.12	9.35
Propane [13]	2.20	9.50
Propane [17]	2.40	9.50
2-Methoxyethanol [15]	1.80	14.00
2-Methoxyethanol [14]	2.30	24.50
2-Methoxyethanol [13]	2.50	19.80
n-Butyric acid [15]	2.00	10.00
n-Butyric acid [14]	2.19	13.40
Ethyl acetate [15]	2.00	11.50
Ethyl acetate [18]	2.20	11.00
Ethyl acetate [14]	2.20	11.40
Ethyl acetate [13]	2.50	9.00
n-Butane [14]	1.50	9.00
n-Butane [19]	1.86	8.41
n-Butane [18]	1.90	8.50
Diethyl ether [19]	1.85	36.50
Diethyl ether [13]	1.90	48.00
Diethyl ether [20]	1.90	36.00
n-Propyl acetate [16]	1.70	8.00
n-Propyl acetate [19]	1.77	8.00
n-Propyl acetate [14]	2.00	8.00
Monochlorobenzene [15]	1.30	9.60
Monochlorobenzene [14]	1.30	7.10
Propionic anhydride [14]	1.48	11.90
Propionic anhydride [15]	1.30	9.50
n-Butyl acetate [14]	1.70	7.60
n-Butyl acetate [19]	1.39	7.55
n-Hexane [14]	1.10	7.70
n-Hexane [19]	1.18	7.40
n-Hexane [13]	1.20	7.50
n-Hexane [17]	1.30	8.60
Triethylamine [14]	1.20	8.00
Triethylamine [19]	1.25	7.90
Butyric anhydride [14]	1.09	7.60
Butyric anhydride [15]	0.90	5.80
2-Butoxyethanol [13]	1.10	10.60
2-Butoxyethanol [14]	1.10	12.70

creased the difficulty of defining good values for the parameters. As the project progressed, it became possible to select published values on the basis of consistency with the correlation. The values presented in Tables 3 and 4 have been

selected from the available values by this process. Data for selected compounds are presented in Table 5 to indicate the amount of scatter in published values. The inconsistency of the reported values suggests that reliable and standardized methods of measurement were needed when most of the measurements were made. Others apparently agree with this conclusion [11]. ASTM responded to this need by providing standard method E-681 which is titled "Standard Test Method for Concentration Limits of Flammability of Chemicals" [12].

Conclusion

A new method has been developed for the estimation of the lower and the upper flammable limits of vapors in air. The new method is based on the second order groups of Benson and Buss and, in principle, its range of applicability can be extended to include any compound whose structure can be decomposed into these second order groups [1].

The scatter in the data of Table 5 indicates the need to make future experimental measurements by accurate and reliable standardized methods. ASTM has responded to this need by providing standard method E-681 [12]. It is believed that the accuracy and the reliability of eq. (3) will be improved as more consistent data become available from accurate and standardized methods of measurement.

Acknowledgments

The author is grateful to David J. Frurip, Dow Chemical Company, and to Dennis K. Jones, Eastman Chemical Company, for providing most of the data which have been used in this project. The author is also grateful to Jack K. Lavender, Eastman Chemical Company, for assistance with the literature search for recent articles and data related to the flammability of vapors. Helpful advice from M. W. Chase, National Institute of Standards and Technology, is also appreciated.

References

- 1 S.W. Benson and J.H. Buss, *J. Chem. Phys.*, 29 (1958) 546.
- 2 Robert W. Van Dolah and David S. Burgess, *Explosion Problems in the Chemical Industry*, ACS Short Courses, American Chemical Society, Washington, DC, 1970, p. 69.
- 3 C.A. Davies, E. Freedman, D.J. Frurip, G.R. Hertel, W.H. Seaton and D.N. Treweek, CHETAH Version 4.4, The ASTM Chemical Thermodynamic and Energy Release Evaluation Program (2nd edn.), Data Series Publication 51A, ASTM, Philadelphia, PA, 1990.
- 4 M. Ducros and H. Sannier, *J. Hazardous Mater.*, 19 (1988) 33-49.

- 5 R.P. Danner and T.E. Daubert, *Manual for Predicting Chemical Process Data, Data Prediction Manual, Design Institute for Physical Property Data, American Institute of Chemical Engineers, 345 East 47th Street, New York, NY, 10017, 1983, pp. 11B1-11C3.*
- 6 S.W. Benson, *Thermochemical Kinetics, 2nd edn., Wiley-Interscience, New York, NY, 1976.*
- 7 H. Le Chatelier, *Ann. Mines, 19, ser. 8, (1891) 388-395; H. Le Chatelier and O. Boudouard, Bull. Soc. Chim. (Paris), 19 (1898) 483-488.*
- 8 W. Bartknecht, *Explosions, Springer-Verlag, Berlin, 1980, p. 7.*
- 9 E.S. Domalski and E.D. Hearing, *J. Phys. Chem. Ref. Data, 17 (1988) 1637.*
- 10 R.W. Van Dolah, M.G. Zabetakis, D.S. Burgess and G.S. Scott, *Review of Fire and Explosion Hazards of Flight Vehicle Combustibles, Bureau of Mines Information Circular 8137, United States Department of the Interior, Washington, DC, 1963.*
- 11 W. Berthold, D. Conrad, T. Grewer, H. Grosse-Wortmann, T. Redeker and H. Schacke, *Development of Standard Apparatus for Measurement of Explosion Limits, Chem. Ing.-Tech., 56 (1984) 126-127.*
- 12 *ASTM Standard Method E-681-85, ASTM, Philadelphia, PA, 1985.*
- 13 H.F. Coward and G.W. Jones, *Limits of Flammability of Gases and Vapors, Bureau of Mines Bulletin 503, United States Government Printing Office, Washington, DC, 1952.*
- 14 T.E. Daubert and R.P. Danner, *Computer tape source file sent from Penn State University to Eastman Chemicals Division by DIPPR Project 801 Data Compilation, Design Institute for Physical Property Data, AIChE, 345 East 47th Street, New York, NY 10017, January, 1989.*
- 15 *Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids, NFPA 325M, National Fire Protection Association, Batterymarch Park, Quincy, MA, 1984.*
- 16 Michael G. Zabetakis, *Flammability Characteristics of Combustible Gases and Vapors, Bureau of Mines Bulletin 627, United States Department of the Interior, Washington, DC, 1965.*
- 17 J.F. Dean (Ed.), *Lange's Handbook of Chemistry, 12th edn., McGraw-Hill, New York, NY, 1979, pp. 11-16.*
- 18 J.A. Dean (Ed.), *Lange's Handbook of Chemistry, 13th edn., McGraw-Hill, New York, NY, 1985, pp. 11-16.*
- 19 B. Lewis and G. von Elbe, *Combustion Flames and Explosions of Gases, Academic Press, New York, NY, 1951 as reported by R.C. Weast (Ed.), Handbook of Chemistry and Physics, 57th edn., CRC Press, Cleveland, OH, 1976, p. D-106.*
- 20 M. Cumo and A. Naviglio, *Safety Design Criteria for Industrial Plants, Vol. II, CRC Press, Boca Raton, FL, 1989.*