

APPENDICES

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Calculation of the saturated vapour pressure of organic liquids

Based on the article of Hass and Newton in CRC Handbook of Chemistry and Physics (annexed) the following formula has been derived:

$$p_{20} = (1013/760) \times 10^c$$

p_{20} = saturated vapour pressure at 20°C in mbar.

$$c = 2.8808 - \frac{(a_n \times t_b + b_n) (t_b - 20)}{296.1 - 0.15 t_b}$$

t_b = boiling point at 1013 mbar in °C.

n = substance or compound group number

The group number can be found in the list in the article of Hass and Newton or by using the group number classification (see below).

After the group number has been determined, a_n and b_n can be read from the table:

n	a_n	b_n	n	a_n	b_n
1	0.0021	4.31	5	0.0023	5.22
2	0.0021	4.54	6	0.0023	5.44
3	0.0021	4.77	7	0.0023	5.67
4	0.0022	5.00	8	0.0023	5.90

Group number classification:

Substance group - hydrocarbons and substances with relatively few elements other than C and H	n
- ethers - silicones - sulphides	2
- aldehydes - epoxy-compounds - esters (higher) - ketones - compounds containing N	3
- esters (lower; relatively high O ₂ content) - phenols (also higher and polyvalent phenols)	4
- carboxylic acids - acid anhydrides	5
- alcohols - glycols - water	7

Halogen derivatives: same group as though halogen were H.

Select $n = 4$ for substances difficult to classify.

N.B.: Calculated p_{20} values < 0.1 mbar can deviate considerably from the real value.

Divide by 10 to convert p_{20} from mbar (=hPa) into kPa.

Calculation of the density of vapours as a means of estimating their pattern of dispersion

When vapours that are dangerous for reasons of health or flammability can be liberated from a liquid, it is necessary to know their density ratio to air in order to be able to estimate their pattern of dispersion.

Vapours which are approximately as heavy as, or slightly heavier than, air will mix easily with the surrounding air, while heavy vapours will travel along the ground without diluting themselves, causing accumulation in lower spaces.

The vapour density ratio to air is therefore mentioned in most of the important handbooks on dangerous substances. In these handbooks the density (d) is calculated with the formula $d \text{ (to air)} = M/29$, where M = the molecular mass of the vapour and 29 = the molecular mass of air. This formula follows from the fact that all gases and vapours have equal molar volumes at the same temperature and pressure. Using this formula for acetic acid ($M = 60.0$) leads to the conclusion that the vapour of the acid is 2.1 x heavier than air.

However, this formula is only valid for a pure vapour unmixed with air. With evaporating liquids, however, a vapour/air mixture is formed in which the percentage of vapour increases with the temperature. When the boiling point of the liquid is reached and the vapour pressure becomes 1 atmosphere, the vapour will not contain air. The formula $d \text{ (to air)} = M/29$ will only then be valid.

Thus, the vapour of acetic acid is 2.1 times as heavy as air only when the temperature of both the acid and the air is above 118°C (the boiling point of acetic acid). At all temperatures below the boiling point, a vapour/air mixture is formed which has a much lower density ratio to the surrounding air. In order to calculate the real density to air ratio of the vapour/air mixture of a liquid at for instance 20°C, the following formula has to be used:

$$d_m \text{ (to air)} = 1 + \frac{(M - 29) p_{20}}{29 \times 1013}$$

$$= 1 + 34 \times p_{20} \times 10^{-6} (M - 29)$$

where p_{20} = the saturated vapour pressure in mbar at 20°C.

Comparing the results of both formulae for a number of liquids results in the following values:

	d	d_m
- acetic acid	2.1	1.02
- acetone	2.0	1.2
- hexachlorobutadiene	9.0	1.004
- n-pentane	2.5	1.8
- perchloroethylene	5.8	1.08
- trichloroethylene	4.5	1.3

It is clear from this table that an estimation of the dispersion pattern of a vapour at room temperature based on a d value given in one of the handbooks can be grossly incorrect.

Moreover, it is probable that the vapour concentration will rarely, if ever, reach the saturation point, so that in practice the density of the vapour will be under the calculated d_m value.

Finally, a rule of thumb for the application of d_m to air values at 20°C:

At values under 1.1, one may expect a reasonably fast mixing of the vapour with the surrounding air in most situations; at values above 1.1, one should be prepared to find the forming of vapours which travel along the ground and mix poorly with the surrounding air.

Derivation of the formula:

d_m = density of the vapour/air mixture which is formed at 20°C in relation to air.

$$= \frac{\text{vapour mass} + \text{air mass (in 1 litre mixture) at 20°C and 1013 mbar}}{\text{air mass (in 1 litre air)}}$$

$$= \frac{(M/22.4 \times 273/293 \times p_{20}/1013) + (29/22.4 \times 273/293 \times (1013 - p_{20})/1013)}{29/22.4 \times 273/293 \times 1013/1013}$$

(The molar vapour volume at 0°C and 1013 mbar is 22.4 liter)

$$= 1 + \frac{(M - 29) p_{20}}{29 \times 1013}$$

$$= 1 + 34 \times p_{20} \times 10^{-6} (M - 29)$$

Reference:

Mutgeert, B.J. (1983) The calculation of the density of vapours, Proceedings 10th World Congress of Occupational Accidents and Diseases, Ottawa.

Appendix 3

Minimum ignition energy in mJ

acetaldehyde	0.37		heptane	0.24
acetone	1.15		hexane	0.24
acetylene	0.017		hydrogen	0.011
acrolein	0.16		hydrogen sulphide	0.068
acrylonitrile	10.16		isooctane	1.35
ammonia (NH ₃)	680		isopentane	0.21
aziridine	0.48		isopropyl alcohol	0.65
benzene	0.20		isopropyl amine	2.0
1,3-butadiene	0.13		isopropyl chloride	1.55
butane	0.25		isopropyl ether	1.14
carbon monoxide	<0.3		isopropyl mercaptan	0.53
carbon disulphide		0.009	methane	0.28
cyclohexane	0.22		methanol	0.14
cyclopentane	0.54		methyl acetylene	0.11
1,3-cyclopentadiene	0.67		methylal	0.5
cyclopropane	0.17		methyl cyclohexane	0.27
di-(tert)-butylperoxide	0.5		methyl ethyl ketone	0.27
diethyl ether	0.19		methylformate	0.5
2,3-dihydropyran	0.36		pentane	0.22
diisobutylene	0.96		2-pentene	0.18
diisopropyl ether	1.14		propane	0.25
dimethyl amine	<0.3		propene	0.28
2,2-dimethyl butane	0.25		propionaldehyde	0.4
dimethyl ether	0.29		propylchloride	1.08
dimethyl propane	1.57		propylene	0.28
dimethyl sulfide	0.5		propylene oxide	0.13
dioxane	<0.3		tetrahydrofuran	0.54
ethane	0.24		tetrahydropyran	0.22
ethene	0.07		thiophene	0.39
ether	0.19		triethyl amine	0.75
ethyl acetate	0.46		2,3-trimethyl butane	1.0
ethyl amine	2.4		vinyl acetate	0.7
ethyl chloride	<0.3		vinyl acetylene	0.082
ethylene oxide	0.065		vinyl chloride	<0.3
furan	0.22			

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Calculation of the pH of medium strong or weak acids and bases

1. The pH is defined as the pH of the saturated solution of an acid or base in water at 20°C, with a maximum concentration of 10 molar.
For liquid acids or bases that will mix with water in any proportion to form one phase, the molarity of the acid or base itself can be considered to be not much more than 10.

- 1.1 Calculation of the molarity of the saturated solution (C_s):

$$C_s = \frac{1000 dS}{M(100d+S)} \quad \text{in which:}$$

C_s = concentration in mol/litre saturated solution in water at 20°C

S = solubility in g per 100 ml water at 20°C

d = density of the acid or base, relative to water

M = relative molecular mass

For liquid acids or bases, mixable with water in all proportions, this formula transforms into:

$$C_s = 1000 d/M$$

- 1.2 The molarity exponent of the saturated solution is defined as:

$$pC_s = -\log C_s$$

If $C_s > 10$, set $pC_s = -1$

- 1.3 The pH can now be calculated for acids:

$$pH = \frac{pK_a + pC_s}{2}$$

for bases:

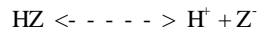
$$pH = 14 - \frac{pK_b + pC_s}{2}$$

in which:

pK_a and pK_b are the dissociation exponents of the acid and the base respectively. Values for pK_a and pK_b are given in CRC Handbook of Chemistry and Physics or other handbooks.

N.B. : Sometimes the dissociation exponent of a base is given as a pK_a value; to get pK_b apply $pK_b = 14.0 - pK_a$.

2. Derivation of the formula.



$$K_a = \frac{[\text{H}^+] \times [\text{Z}^-]}{[\text{HZ}]}$$

$$[\text{Z}^-] = [\text{H}^+] \quad [\text{HZ}] = [\text{C}_s] \text{ (by approximation)}$$

$$[\text{H}^+] = [K_a \times [\text{C}_s]]^{1/2}$$

$$-\log[\text{H}^+] = \text{pH} = -\log [K_a \times [\text{C}_s]]^{1/2}$$

$$-\log K_a = \text{p}K_a - \log[\text{C}_s] = \text{p}C_s$$

$$\text{pH} = \frac{\text{p}K_a + \text{p}C_s}{2}$$

3. Criteria for "strong", "medium strong" and "weak".

Strong acids and bases are chemically defined as having a dissociation exponent of nearly zero: they dissociate in water to a very high degree. Strong acids and bases such as hydrochloric acid and caustic soda etc., are generally known. The borderline for "strong" is set at $\text{pH} \leq 0.2$ for acids and at $\text{pH} \geq 13.0$ for bases. For bases a rather wide definition of "strong" has been chosen because of the very strong action on skin and eyes, even when chemically the base should not be regarded as strong.

A second area has been defined as "medium strong" for those acids and bases which cannot be regarded as chemically "strong" but are nevertheless harmful for the human skin and eyes. Because of the higher sensitivity of skin and eyes for bases the range for 'medium strong' has once more been chosen somewhat wider than for acids. The borderlines of $\text{pH} 2.5$ for acids and $\text{pH} 11.0$ for bases have been chosen from literature references and experience.

Because exposure of the skin to concentrated solutions should be taken into account (solid acids or bases form a saturated solution on a damp skin!) the borderlines are set for the pH values of saturated solutions up to 10 molar. Acids and bases weaker than medium strong should be called "weak" on the Card, in this way giving positive information to the reader of the Card on the strength of an acid or base that he/she is handling.

Relative Inhalation Risk index (RIR index)

The RIR index indicates how fast the OEL/ST value of a liquid (or solid) is reached on evaporation at 20°C under standard conditions. When the OEL/ST is used as toxicity parameter, the RIR index gives only a rough idea of acute inhalation hazards. OEL/ST values (and their definition) can be found in the appropriate national OEL list or in the List of Threshold Limit Values, issued by the ACGIH, Cincinnati, USA.

In this Appendix OEL/ST is also indicated as STEL (in ppm).

Calculation of the RIR index:

- a. if $p_{20} < 200$ mbar: $RIR = C_s/STEL$
- b. if $p_{20} \geq 200$ mbar: $RIR = (10^6/STEL) \ln(10^6/(10^6 - C_s))$

in which:

p_{20} = saturated vapour pressure of the substance in mbar at 20°C.

\ln = natural logarithm

C_s = saturated vapour concentration in ppm at 20°C. Calculation:

$$C_s = (10^6 / 1013)p_{20}$$

If the list does not mention a STEL value then use instead:

- OEL/C (if applicable), or
 - OEL/TWA value, multiplied by 3 (if TLV/TWA > 500, then multiply by 2), or
 - an estimated STEL value, based on other toxicological data, provided that these data are sufficient.
- Even then great care should be taken!

(If a national system of occupational exposure limits deviates widely from the ACGIH concept, the latter should be used; see also ind. 13420. In the Card explanation the text should be adapted accordingly).

The classification of a substance by the value of its RIR index (phrases 13605/13) should always be done in association with other data for the substance.

Using the following standard conditions as an example, the RIR index can be used to calculate the time to reach the STEL value:

- liquid surface: 1 m²
- air velocity over the liquid surface: 0.1 m/s
- space volume: 100 m³
- temperature: 20°C
- no air change (closed space)
- homogeneous air vapour mixing

In that case the following applies:

$$t_{STEL} = 3714/RIR$$

t_{STEL} = time in minutes to reach the STEL value in the air of the closed space.

The following values for t_{STEL} can now be calculated:

<u>RIR index value</u>	<u>t_{STEL} in minutes</u>
12	310 (ab. 5 hours)
120	31 (1/2 hour)
4000	0.9 (ab. 1 minute)

(For gases RIR = 4 so t_{STEL} = 0)

The t_{STEL} values calculated in this way have a very limited practical value and should not be applied to real situations since there is always some ventilation.

The RIR class limits 12-120-4000 which are used for the selection of some of the standard phrases, are based on professional experience of the editorial staff of Handling Chemicals Safely, published by the Dutch Association of Safety Experts, the Dutch Chemical Industry Association and the Dutch Safety Institute.

Reference:

Mutgeert, B.J. (1979) Een index voor het relatieve inhalatie risico van organische oplosmiddelen. De veiligheid 55: 355-361 (a summary in English is available).

Odour Safety Factor (O.S.F.)

The Odour Safety Factor as introduced by Amoore and Hautala is defined as:

$$\text{O.S.F.} = \frac{\text{OEL/TWA (8h/d), ppm}}{\text{Odour Threshold Value, ppm}}$$

where

- OEL/TWA is the applicable occupational exposure limit value, time weighted average for 8h/d.
- Odour Threshold Value, as contained in the annexed list from the article of Amoore and Hautala.

If an appropriate applying value is not available, the most recent TLV from the ACGIH list can be used.

An O.S.F. value = 26 means that 50% of the distracted (not concentrated on perception of the odour) persons perceive a warning of the OEL concentration by the odour. Of the attentive persons 99% can detect the OEL at an O.S.F. value of 26.

Odour Threshold Values can deviate very strongly, depending on various factors. Amoore and Hautala made a critical selection from the available literature and averaged them in a justified manner. Therefore do not use Odour Threshold Values from other sources in calculating the Odour Safety Factor.

For further details refer to:

Amoore, J.E. and Hautala, E. (1983) *Journal of Applied Toxicology*, 3(6): 272.

Substance	Air odour threshold (ppm; v/v)	Substance	Air odour threshold (ppm; v/v)
Acetaldehyde	0.050	n-Butyl alcohol	0.83
Acetic acid	0.48	sec-Butyl alcohol	2.6
Acetic anhydride	0.13	tert-Butyl alcohol	47
Acetone	13	n-Butylamine	1.8
Acetonitrile	170	n-Butyl lactate	7.0
Acetylene	620	n-Butyl mercaptan	0.00097
Acrolein	0.16	p-tert-Butyltoluene	6.0
Acrylic acid	0.094	Camphor	0.27
Acrylonitrile	17	Carbon dioxide	74000
Allyl alcohol	1.1	Carbon disulphide	0.11
Allyl chloride	1.2	Carbon monoxide	100000
Ammonia	5.2	Carbon tetrachloride	96
n-Amyl acetate	0.054	Chlorine	0.31
sec-Amyl acetate	0.0020	Chlorine dioxide	9.4
Aniline	1.1	a-Chloroacetophenone	0.035
Arsine	0.50	Chlorobenzene	0.68
Benzene	12	Chlorobromomethane	400
Benzyl chloride	0.044	Chloroform	85
Biphenyl	0.00083	Chloropicrin	0.78
Bromine	0.051	β-Chloroprene	15
Bromoform	1.3	o-Chlorotoluene	0.32
1,3-Butadiene	1.6	m-Cresol	0.00028
Butane	2700	trans-Crotonaldehyde	0.12
2-Butoxyethano	10.10	Cumene	0.088
n-Butyl acetate	0.39	Cyclohexane	25
n-Butyl acrylate	0.035	Cyclohexano	10.15

Cyclohexanone	0.88	Hexylene glycol	50
Cyclohexene	0.18	Hydrazine	3.7
Cyclohexylamine	2.6	Hydrogen bromide	2.0
Cyclopentadiene	1.9	Hydrogen chloride	0.77
Decaborane	0.060	Hydrogen cyanide	0.58
Diacetone alcohol	0.28	Hydrogen fluoride	0.042
Diborane	2.5	Hydrogen selenide	0.30
o-Dichlorobenzene	0.30	Hydrogen sulphide	0.0081
p-Dichlorobenzene	0.18	Indene	0.015
trans-1,2-Dichloroethylene	17	Iodoform	0.0050
β,β -Dichloroethyl ether	0.049	Isoamyl acetate	0.025
Dicyclopentadiene	0.0057	Isoamyl alcohol	0.042
Diethanolamine	0.27	Isobutyl acetate	0.64
Diethylamine	0.13	Isobutyl alcohol	1.6
Diethylaminoethanol	0.011	Isophorone	0.20
Diethyl ketone	2.0	Isopropyl acetate	2.7
Diisobutyl ketone	0.11	Isopropyl alcohol	22
Diisopropylamine	1.8	Isopropylamine	1.2
N-Dimethylacetamide	47	Isopropyl ether	0.017
Dimethylamine	0.34	Maleic anhydride	0.32
N-Dimethylaniline	0.013	Mesityl oxide	0.45
N-Dimethylformamide	2.2	2-Methoxyethanol	2.3
1,1-Dimethylhydrazine	1.7	Methyl acetate	4.6
1,4-Dioxane	24	Methyl acrylate	0.0048
Epichlorhydrin	0.93	Methyl acrylonitrile	7.0
Ethane	120000	Methyl alcohol	100
Ethanolamine	2.6	Methylamine	3.2
2-Ethoxyethanol	2.7	Methyl n-amyl ketone	0.35
2-Ethoxyethyl acetate	0.0056	N-Methylaniline	1.7
Ethyl acetate	3.9	Methyl n-butyl ketone	0.076
Ethyl acrylate	0.0012	Methyl chloroform	120
Ethyl alcohol	84	Methyl 2-cyanoacrylate	2.2
Ethylamine	0.95	Methylcyclohexane	630
Ethyl n-amyl ketone	6.0	cis-3-Methylcyclohexanol	500
Ethyl benzene	2.3	Methylene chloride	250
Ethyl bromide	3.1	Methyl ethyl ketone	5.4
Ethyl chloride	4.2	Methyl formate	600
Ethylene	290	Methyl hydrazine	1.7
Ethylenediamine	1.0	Methyl isoamyl ketone	0.012
Ethylene dichloride	88	Methyl isobutyl carbinol	0.070
Ethylene oxide	430	Methyl isobutyl ketone	0.68
Ethylenimine	1.5	Methyl isocyanate	2.1
Ethyl ether	8.9	Methyl isopropyl ketone	1.9
Ethyl formate	31	Methyl mercaptan	0.0016
Ethylidene norbornene	0.014	Methyl methacrylate	0.083
Ethyl mercaptan	0.00076	Methyl n-propyl ketone	11
N-Ethylmorpholine	1.4	a-Methyl styrene	0.29
Ethyl silicate	17	Morpholine	0.01
Fluorine	0.14	Naphthalene	0.084
Formaldehyde	0.83	Nickel carbonyl	0.30
Formic acid	49	Nitrobenzene	0.018
Furfural	0.078	Nitroethane	2.1
Furfuryl alcohol	8.0	Nitrogen dioxide	0.39
Halothane	33	Nitromethane	3.5
Heptane	150	1-Nitro propane	11
Hexachlorocyclopentadiene	0.030	2-Nitropropane	70
Hexachloroethane	0.15	m-Nitrotoluene	0.045
Hexane	130	Nonane	47

Octane	48	Quinone	0.084
Osmium tetroxide	0.0019	Styrene	0.32
Oxygen difluoride	0.10	Sulphur dioxide	1.1
Ozone	0.045	1,1,2,2-Tetrachloroethane	1.5
Pentaborane	0.96	Tetrahydrofuran	2.0
Pentane	400	Toluene	2.9
Perchloroethylene	27	Toluene-2,4-diisocyanate	0.17
Phenol	0.040	o-Toluidine	0.25
Phenyl ether	0.0012	1,2,4-Trichlorobenzene	1.4
Phenyl mercaptan	0.00094	Trichloroethylene	28
Phosgene	0.90	Trichlorofluormethane	5.0
Phosphine	0.51	1,1,2-Trichloro-1,2,2-trifluorethane	45
Phthalic anhydride	0.053	Triethylamine	0.48
Propane	16000	Trimethylamine	0.00044
Propionic acid	0.16	1,3,5-Trimethylbenzene	0.55
n-Propyl acetate	0.67	Trimethyl phosphite	0.00010
n-Propyl alcohol	2.6	n-Valeraldehyde	0.028
Propylene	76	Vinyl acetate	0.50
Propylene dichloride	0.25	Vinyl chloride	3000
Propylene glycol 1-methyl ether	10	Vinylidene chloride	190
Propylene oxide	44	Vinyl toluene	10
n-Propyl nitrate	50	m-Xylene	1.1
Pyridine	0.17	2,4-Xylidine	0.056

ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
AFFF	Aqueous Film Forming Foam
AFFF/ACT	AFFF + Alcohol Type Concentrate
BCF	Bioconcentration Factor
BOD	Biological Oxygen Demand
C	Ceiling Value (of OEL or TLV)
CAS	Chemical Abstract Service
CEFIC	Conseil Européen des Fédérations de l'Industrie Chimique
CEU	Commission of the European Union
COD	Chemical Oxygen Demand
CSI	Chemical Substances Inventory
CSST	Commission de la Santé et de la Sécurité du Travail
EC	European Community
EINECS	European Inventory of Existing Commercial Chemical Substances
EPA	Environmental Protection Agency (USA)
EU	European Union
IARC	International Agency for Research on Cancer
ICSC	International Chemical Safety Card
ILO	International Labour Office
IRPTC	International Register of Potentially Toxic Chemicals
IUPAC	International Union of Pure and Applied Chemistry
LC ₅₀	Lethal Concentration 50
LD ₅₀	Lethal Dose 50
LEL	Lower Explosive Limit
Log Pow	Logarithm of the octanol/water partition coefficient
MAK	Maximale Arbeitsplatz Konzentration
NFPA	National Fire Protection Association

NIOSH	National Institute for Occupational Safety and Health (USA)
OEL	Occupational Exposure Limits
OEL/???	OEL combined with ??? abbreviation
P	Percutaneous (with PDK-absorption through skin)
PDK	Predel'no Dopustimeye Kotsentratsi (USSR-Maximum Allowable Concentration)
R	Risk - European Union System
RIR	Relative Inhalation Risk
RTECS	Registry of Toxic Effects of Chemical Substances
S	Safety - European Union System
SADT	Self-Accelerating Decomposition Temperature
STEL	Short-Term Exposure Limit
TEC	Transport Emergency Card
TLV	Threshold Limit Value
TSCA	Toxic Substances Control Act
TWA	Time Weighted Average
UN	United Nations
UN CEITDG	United Nations Committee of Experts on Transport of Dangerous Goods
UNEP	United Nations Environment Programme
WHO	World Health Organization

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