

PELLISTOR RELATIVE RESPONSES

SGX Sensortech are often asked for relative response figures when using the company’s range of pellistors for non-straight-chain hydrocarbons and more exotic gases. The well-known paper by Firth, Jones and Jones^[1] lists theoretical response figures for over ninety different materials and is a first reference point. This application note extends the published information and adds more information on calculating the relationship $\Delta H_{298}^0 D_{12}$ [LEL] in order to allow readers the opportunity to calculate values from fundamental data if required.

The values of ΔH_{298}^0 can simply be determined from standard heats of formation of the products and reactants^[2]. Should the heat of formation of the required molecule not be available, then it can be closely estimated using Benson’s group additivity theory^[3]. Complete combustion is to be assumed and therefore the correct combustion products should be considered in evaluating ΔH_{298}^0 . Such combustion products are assumed to be H₂O from hydrogen, CO₂ from carbon, N₂ from nitrogen, Cl₂ from chlorine, etc.

The value of the LEL for the target molecule can be obtained from numerous publications^[4]. Where the LEL is not available it may be estimated by considering the vapour pressure at the flash point as a first approximation.

It is the estimation of D₁₂ that can pose the greatest problems in arriving at relative response estimates. The fundamental equation for the binary diffusion coefficient is:

$$D_{12} = \frac{3f_D \sqrt{2kT(M_1 + M_2)/M_1M_2}}{16n\pi\sigma_{12}^2\Omega_D} \dots \dots \dots (1)$$

where M₁ and M₂ are the molecular weights of the reactants (one of which is oxygen from the air), f_D is a second order correction with a value close to 1.00, n is the number density of the molecular mixture, σ₁₂ is the Lennard-Jones force constant for the mixture and Ω_D is the collision integral. In the case of the Lennard-Jones potential function, the collision integral Ω_D depends only on the dimensionless ratio kT/ε₀₁₂, k being the Boltzmann constant. The value of Ω_D has been tabulated as a function of kT/ε₀ but can be expressed by the following empirical relationship:

$$\Omega_D = 1.41257(\epsilon_{0_{12}}/kT)^{1.66334} - 0.971012(\epsilon_{0_{12}}/kT)^{1.84982} + 0.994141(\epsilon_{0_{12}}/kT)^{0.141179} \dots \dots \dots (2)$$

The values of ε_{0₁₂}/kT and σ₁₂ for a gas pair can be estimated from the force constants for pure gases by using the combining rules:

$$\epsilon_{0_{12}} / k = \sqrt{(\epsilon_{0_1}/k)(\epsilon_{0_2}/k)} \dots \dots \dots (3)$$

$$\sigma_{12} = (\sigma_1 + \sigma_2) / 2 \dots \dots \dots (4)$$

Values for ϵ_{0_1}/k , ϵ_{0_2}/k , σ_1 and σ_2 can be obtained from viscosity measurements or the second virial coefficient and are tabulated for some gases^[5]. Where values are not tabulated they can be estimated using the Stiel and Thodos estimations^[6]:

$$\epsilon_{0_1}/k = 65.3 T_c (Z_c)^{3.6} \dots \dots \dots (5)$$

$$\sigma = 0.1866 (V_c)^{1/3} (Z_c)^{-1.2} \dots \dots \dots (6)$$

where T_c is the critical temperature, V_c is the critical volume and Z_c is the critical compressibility factor for the component molecule. The critical temperature may be defined as the maximum temperature at which liquid and vapour phases can coexist in equilibrium, the vapour pressure at this temperature is the critical pressure and the critical volume is the volume per mole or unit mass. The critical compressibility factor is given by $Z_c = P_c V_c / RT_c$.

Converting to usual technical units with n expressed by the ideal gas law, σ defined in Angstroms and dropping f_D converts equation 1 to:

$$D_{12} = \frac{0.001858 T^{3/2} \sqrt{(M_1 + M_2) / M_1 M_2}}{P \sigma_{12}^2 \Omega_D} \dots \dots \dots (7)$$

where D_{12} is in square centimetres per second, P is in atmospheres and T is in kelvin.

The procedure for estimating D_{12} is therefore:

- a) Obtain values for σ_1 , σ_2 , ϵ_{0_1}/k and ϵ_{0_2}/k from tabulated values or by calculation from the critical parameters for each component using equations 5 and 6 above. It is important to obtain values of the force constants from the same source wherever possible to minimise errors.
- b) Derive values for σ_{12} and $\epsilon_{0_{1,2}}/k$ for the gas pair using the combining rules given in equations 3 and 4 above.
- c) Calculate Ω_D from the derived value for $\epsilon_{0_{12}}/k$ at the required temperature (in kelvin) using equation 2 above.
- d) Substitute the values of σ_{12} and Ω_D derived above into equation 7 to obtain the theoretical value for D_{12} .

The values given by Firth, Jones and Jones for D_{12} are in arbitrary units and differ from those obtained using the above method by approximately a factor of 40. This factor is attributed to the presence of a conversion constant in the Firth, Jones and Jones paper to relate the value of D_{12} to the out of balance voltage^[7].

Once the values for ΔH_{298}^0 , LEL and D_{12} are determined, the value of $\Delta H_{298}^0 [\text{LEL}] D_{12}$ gives the response factor for the appropriate molecule in $\text{kJ mole}^{-1} \text{cm}^2 \text{sec}^{-1}$.

Alternatively, the response relative to a calibration molecule is obtained by evaluating:

$$\text{RR} = \frac{(\Delta H_{298}^0)^1 [\text{LEL}]^1 \sqrt{(M_1 + M_{\text{air}}) M_c (\sigma_{C2}^2 \Omega_{DC})}}{(\Delta H_{298}^0)^c [\text{LEL}]^c \sqrt{(M_c + M_{\text{air}}) M_1 (\sigma_{12}^2 \Omega_{D1})}} \dots \dots \dots (8)$$

The relative response calculation above is independent of both temperature and pressure and as such it is important to assume complete combustion on the pellistor of both target and reference gas. The significance of this becomes very important when a pellistor is being run at lower than optimum temperatures and also when a pellistor becomes poisoned.

The response to many hydrocarbons will peak at temperatures below that for methane and consequently a pellistor running cool will produce peak responses for the hydrocarbons but significantly reduced signal levels for methane. Under these cool running conditions the above equations become invalid since complete combustion of methane is unlikely to occur.

The effect of poisons and inhibitors will also affect the relative responses, particularly those compared to methane. The effect of a silicon containing poison, for instance, is more pronounced on the methane response than on, say, the butane response and since the methane response is reduced the relative response is also affected. This is particularly important when a pellistor is calibrated with a non-methane hydrocarbon for use in atmospheres containing methane since a non-methane calibration of a partially poisoned sensor would not show the reduced methane response.

The above equations have been used to derive response factors $\Delta H_{298}^0 [\text{LEL}] D_{12}$ for an extended range of molecules in the following table. These factors can then be used to estimate relative responses between various gases and vapours. It must be emphasised that these figures are purely theoretical and it is always more appropriate to calibrate with the gas of interest.

References

[1] Firth, J.G., Jones, A. and Jones, T.A., *Combustion and Flame* **21** (1973) 303 - 311.
 [2] See for example **JANAF Thermochemical Tables**, 2nd Edit., D.R. Stull and H. Prophet, Eds., NSRDS-NBS37, National Bureau of Standards, 1971.
 [3] Benson, S.W., *Thermochemical Kinetics*, 2nd Edit., New York, 1976, Chap. 2.
 [4] See for example **EN61779-1-2000**, *Electrical apparatus for the detection and measurement of flammable gases, General requirements and test methods*, Appendix A - Table A1.
 [5] Stiel, L.I. and Thodos, G., *Chem. Eng. Data Ser.*, **7** (1962) 234.
 [6] Reid, R.C., Sherwood, T.K. et al., *The Properties of Gases and Liquids*, 2nd Edit., McGraw-Hill (1966) 632 - 633.
 [7] Ballou, V., Sierra Monitor Corporation, Milpitas, CA., Private Communication.
 [8] Svehla, R.A., *NASA Tech. Rept. R-132*, Lewis Research Center, Cleveland, Ohio, 1962.

Molecule	LEL % vol	ΔH_{298}^0 kJmole ⁻¹	$D_{12}@ 300\text{ }^\circ\text{C}$ cm ² sec ⁻¹	$\Delta H_{298}^0 D_{12} LEL$	Response Rel to CH ₄	Gain Adjust
Nitrogen compounds:						
ammonia	15	317	0.7286	3465	1.43	0.70
hydrazine	4.7	579	0.4780	1301	0.54	1.86
methylhydrazine	2.5	1304	0.3578	1167	0.48	2.07
dimethylhydrazine	2.4	1978	0.3255	1545	0.64	1.57
cyanogen	6	1096	0.3953	2599	1.07	0.93
hydrogen cyanide	5.4	448	0.5159	1248	0.52	1.94
acetonitrile	3	1265	0.3266	1239	0.51	1.95
methylamine	4.2	977	0.4598	1887	0.78	1.28
ethylamine	2.68	1585	0.3558	1521	0.63	1.59
trimethylamine	2	2244	0.3151	1414	0.58	1.71
triethylamine	1.2	4075	0.2228	1090	0.45	2.22
n-propylamine	2	2199	0.3020	1328	0.55	1.82
aniline	1.2	3295	0.2346	928	0.38	2.61
nitromethane	7.3	664	0.2719	1318	0.54	1.84
Elementary:						
hydrogen	4	242	2.2898 ^v	2216	0.81	1.241
Paraffins:						
methane	4.4	803	0.6851 ^v	2421	1.00	1.00
ethane	2.5	1428	0.4613 ^v	1646	0.68	1.47
propane	1.7	2044	0.3574 ^v	1242	0.51	1.95
n-butane	1.4	2657	0.3383 ^v	1258	0.52	1.92
iso-butane	1.3	2649	0.3148 ^v	1084	0.45	2.23
pentane - mixed isomers	1.4	3272	0.2717 ^v	1245	0.51	1.94
iso-pentane	1.4	3262	0.2618	1110	0.46	2.18
neo-pentane	1.4	3250	0.2532 ^v	1152	0.48	2.10
hexane - mixed isomers	1.0	3887	0.2511 ^v	1171	0.40	2.48
methylpentane	1.1	3877	0.2385	1017	0.42	2.38
dimethylbutane	1.1	3865	0.2412	1025	0.42	2.36
heptane - mixed isomers	1.1	4502	0.2065	1023	0.42	2.37
methylhexane	1.2	4492	0.2147	1158	0.48	2.09
ethylpentane	1.2	4492	0.2168	1169	0.48	2.07
dimethylpentane	1.2	4480	0.2208	1187	0.49	2.04
trimethylbutane	1.2	4471	0.2233	1198	0.49	2.02
n-octane	0.8	5116	0.1884	771	0.32	3.14
n-nonane	0.7	5731	0.1713	687	0.28	3.52
decane - mixed isomers	0.7	6345	0.1588	705	0.29	3.43
Olefins:						
ethylene	2.3	1323	0.5010 ^v	1524	0.63	1.59
propene	2	1927	0.3886 ^v	1498	0.62	1.62
1-butene	1.6	2541	0.3153	1282	0.53	1.89
cis-but2ene	1.6	2534	0.3058	1240	0.51	1.95
trans-but2ene	1.8	2529	0.3211	1462	0.60	1.66
isobutylene	1.8	2528	0.3100	1411	0.58	1.72
1-pentene	1.4	3156	0.2652	1172	0.48	2.07

Molecule	LEL %vol	ΔH_{298}^0 kJmole ⁻¹	$D_{12}@ 300\text{ }^\circ\text{C}$ cm ² sec ⁻¹	$\Delta H_{298}^0 D_{12} LEL$	Response Rel to CH ₄	Gain Adjust
Diolefins:						
1,3-butadiene	1.4	2410	0.3203	1081	0.45	2.24
1,4-hexadiene	2	3644	0.2509	1828	0.76	1.32
Acetylenes:						
acetylene	2.3	1256	0.5262 ^v	1520	0.63	1.59
propyne	1.7	1850	0.3796	1194	0.49	2.03
Cycloparaffins:						
cyclopropane	2.4	1959	0.3854 ^v	1812	0.75	1.34
cyclohexane	1.2	3689	0.2494 ^v	1104	0.46	2.19
methylcyclohexane	1.15	4293	0.2178	1075	0.44	2.25
Aromatics:						
benzene	1.2	3169	0.2879 ^v	1095	0.45	2.21
toluene	1.1	3772	0.2460	1020	0.42	2.37
o-xylene	1	4376	0.2097	918	0.38	2.64
m-xylene	1.1	4374	0.2123	1021	0.42	2.37
p-xylene	1.1	4375	0.2062	992	0.41	2.44
ethylbenzene	1	4390	0.2252	989	0.41	2.45
styrene monomer	1.1	4267	0.2199	1032	0.43	2.35
Alcohols:						
methyl alcohol	5.5	676	0.5069 ^v	1885	0.78	1.28
ethyl alcohol	3.1	1277	0.3859 ^v	1527	0.63	1.58
n-propyl alcohol	2.2	1892	0.3437 ^v	1430	0.58	1.69
iso-propyl alcohol	2.0	1874	0.2814	1055	0.44	2.30
n-butyl alcohol	1.7	2508	0.2575	1098	0.45	2.20
iso-butyl alcohol	2.0	2499	0.2548	1273	0.53	1.90
tert-butyl alcohol	2.4	2471	0.2609	1547	0.64	1.56
Ethers:						
dimethyl ether	2.7	1327	0.4032 ^v	1445	0.60	1.68
ethyl methyl ether	2	1932	0.3089	1193	0.49	2.03
diethyl ether	1.7	2531	0.2797 ^v	1204	0.50	2.01
diiso-propyl ether	1.0	3735	0.2247	839	0.35	2.88
1,4 dioxane	1.9	2223	0.2591	1095	0.45	2.21
tetrahydrofuran	1.5	2636	0.2860	1131	0.47	2.14
Ketones:						
acetone	2.5	1690	0.3429 ^v	1449	0.60	1.67
methyl ethyl ketone (butanone)	1.8	2303	0.2523	1046	0.43	2.31
methyl propyl ketone (pentan-3-one)	1.6	2918	0.2333	1089	0.45	2.22
Aldehydes:						
acetaldehyde	4	1105	0.3483	1540	0.64	1.57

Molecule	LEL %vol	ΔH_{298}^0 kJmole ⁻¹	$D_{12}@ 300\text{ }^\circ\text{C}$ cm ² sec ⁻¹	$\Delta H_{298}^0 D_{12} \text{LEL}$	Response Rel to CH ₄	Gain Adjust
Organic Acids:						
acetic acid	4	836	0.2410	806	0.33	3.00
acetic anhydride	2.0	1723	0.2791	962	0.40	2.52
n-butyric acid	2	2062	0.2741	1130	0.47	2.14
Esters:						
methyl formate	5	921	0.3217	1481	0.61	1.63
methyl acetate	3.2	1492	0.2758	1317	0.54	1.84
methyl propionate	2.5	2135	0.2465	1316	0.54	1.84
ethyl formate	2.7	1540	0.2786	1159	0.48	2.09
ethyl acetate	2.2	2109	0.2423	1124	0.46	2.15
butyl acetate	1.3	3325	0.2254	974	0.40	2.48
Sulphur Compounds:						
carbonyl sulphide	6.5	552	0.4061 ^v	1457	0.60	1.66
carbon disulphide	0.6	1104	0.3473 ^v	230	0.10	10.5
hydrogen sulphide	4.0	518	0.5319 ^v	1102	0.46	2.20
dimethyl sulphide	2.2	1722	0.3125	1184	0.49	2.04
methyl mercaptan	3.9	1151	0.3824	1717	0.71	1.41
ethyl mercaptan	2.8	1764	0.3183	1572	0.65	1.54
Halides:						
methyl bromide	10	701	0.3718 ^v	2606	1.08	0.93
methyl chloride	7.6	672	0.4154 ^v	2122	0.88	1.14
methylene chloride	15.5	542	0.3192 ^v	2681	1.11	0.90
ethyl bromide	6.7	1308	0.3331	2919	1.21	0.83
ethyl chloride	3.6	1280	0.3416 ^v	1574	0.65	1.54
vinyl chloride	3.6	1171	0.3218	1357	0.56	1.78
ethylene dichloride	7.3	1046	0.2695	2058	0.85	1.18
n-propyl chloride	2.4	1897	0.3085	1405	0.58	1.72
chlorobenzene	1.3	3018	0.2356	924	0.38	2.62
Oxides:						
carbon monoxide	10.9	283	0.6235 ^v	1923	0.79	1.26
ethylene oxide	2.6	1220	0.3723	1181	0.49	2.05
1,2-propylene oxide	2.1	1814	0.2785	1061	0.44	2.28

Notes:

^v = D_{12} evaluated using values of σ and ϵ as derived from viscosity data^[8].

All other values of D_{12} are derived from estimated values of σ and ϵ via the Stiel and Thodos method^[5] using published critical data^[6].

LEL values taken from Firth, Jones and Jones^[1] and EN61779-1-2000^[4].