

Fig 6 ISOTHERMAL REACTION CALORIMETER PROCESS POWER OUTPUT WITH TIME AT 77°C Nitro reduction by Hydrazine - Ni alloy added after 5% N₂H₄ added

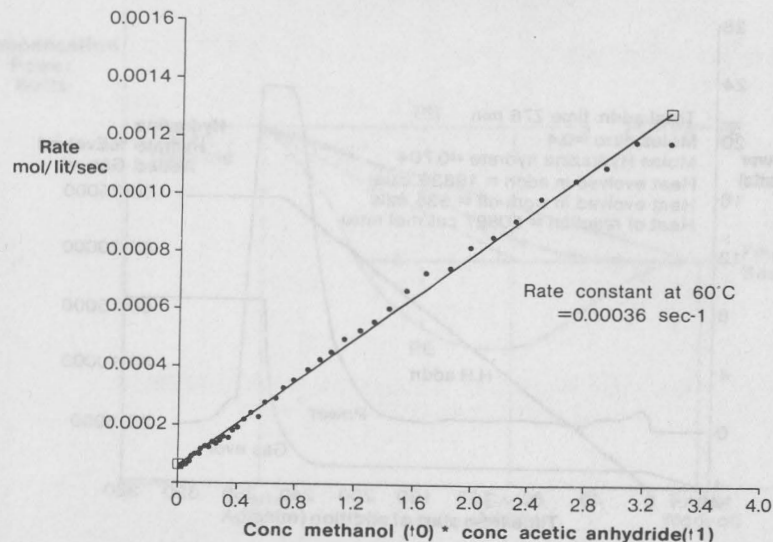


Fig 7 ISOTHERMAL REACTION CALORIMETER PLOT OF RATE AGAINST PRODUCT OF CONCENTRATIONS IN WORK-OFF Addition of Acetic Anhydride (1.5 mol) to Methanol (3 mol)

A SIMPLE METHOD OF ESTIMATING EXOTHERMICITY BY AVERAGE BOND ENERGY SUMMATION

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A simple method is described whereby the approximate exothermicity of a chemical reaction or decomposition can be predicted from the atomization energies of the reactants and the assumed products. The atomization energies of many compounds can be determined by average bond energy summation using published data.

Keywords: Thermodynamics; Calculation; Exothermicity; Combustion; Explosion; Bond Energies

1. INTRODUCTION

When TNT degrades explosively about 1100 calories of chemical energy are released from every gram. This energy excursion is not the result of the decomposition into the elements carbon, hydrogen, oxygen and nitrogen. The 1100cal/g results from a complete rearrangement of the chemical bonds from those originally present in the trinitrotoluene molecule to those present in the solid and gaseous products arising from the decomposition and chemical recombination of the four elements into water, carbon dioxide, carbon monoxide, carbon and nitrogen. The number of calories per gram which are released will depend upon the final temperature and the physical state of these products. There is sufficient energy to raise the temperature to several thousand centigrade degrees and the total energy release may only be truly manifest if the products are cooled down in a calorimeter when even the latent heat of the water vapour is recovered by condensation to liquid (10.52kcal/mol H₂O).

The gross energy excursion is usually considered to be the result of breaking all the chemical bonds originally present in the TNT molecule (this requires the addition of energy) and then recovering this energy and more when the chemical bonds are reformed in the product molecules.

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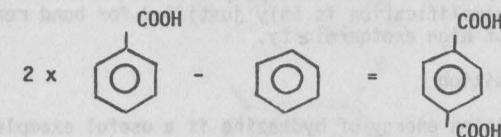
It so happens that both water, carbon dioxide and carbon monoxide are produced in a TNT explosion and it is well known that these compounds have relatively high heats of formation. An approximate estimate of the heat of explosion of TNT can be obtained by simply estimating the energy arising from the heat of formation of these reaction products.

At first sight it would appear that parts of the TNT molecule are "burning" in the oxygen available within the molecule and the same may be deduced from the explosive properties of organic peroxides. This oversimplification gives rise to references to molecules containing "their own internal oxygen for combustion" although this is a phrase which is completely devoid of any technical significance. In reality the major proportion of the combined oxygen present in many organic molecules such as alcohols, acids, esters, ketones and even ethers makes no significant contribution to any energy excursion which may result from a complete rearrangement of the chemical bonds into the decomposition product molecules.

In order to assess the danger inherent in producing and handling unstable materials, a simple method of estimating the approximate exothermic potential of any chemical compound, or mixture of chemical compounds is essential. High order accuracy is not necessarily justified since we only want to know whether the material has an exothermic potential of the order of say 1000, 600, 300cal/g to act as a warning indicator in any hazard analysis.

A method widely used is to subtract the heats of formation of the reactants from the heats of formation of the products to give the heat of the reaction which is often expressed in kcal/mol. Two problems arise immediately here. Since the ability to explode is related to the reaction energy per unit mass and not to the energy on a molar basis, the molar heat of reaction should really be divided by the total molecular weight of the reactants. This is often overlooked with mixtures. The second problem is rather more serious in cases where the heat of formation of one or more of the reactants is not known.

More complex methods are available whereby computer programs are devised to estimate heats of formation by additive assessment of the chemical groups present in the molecule. The CHETAH ASTM project (Chemical Thermodynamic and Energy Release Evaluation Program) is one such approach (reference 1). A typical example given in reference 1 relates to the heat of formation of terephthalic acid which is derived from the sum of the heats of formation of two benzoic acids molecules minus one benzene molecule.



Hf° (Calculated = -158.5 kcal/mol
 (Experimental) = -161.4 kcal/mol

Reference 1

In my view however a very much simpler method is available which is perfectly adequate "to be used as a screening tool to help set priorities for physical testing" (reference 1). The method which I have used is probably not suitable for full computerization since it assumes that the user has a basic working knowledge of organic chemistry. On the other hand it is suitable for use with the aid of a programmable pocket calculator since it involves a relatively small data base.

2. AVERAGE BOND ENERGY SUMMATION (ABES)

The average bond energy summation method does not use heats of formation at all. It is a simplification of the method described by R.T. Sanderson (reference 2) based on bond energies. The energy excursion per mol of reactant (pure compound or mixture) is calculated by subtracting the total bond energies present before the reaction from the total bond energies of the products.

An alternative way of looking at it is to calculate the total atomization energy of the reactants which can be based on either bond energy summation of novel molecules or well established data from e.g., reference 2. This value is then subtracted from the atomization energy of the assumed products to give the exothermicity or so called excess enthalpy either on a molar (kcal/mol) or preferably on a mass basis (cal/g).

All that is required is the structural formula of the molecule involved, a table of average bond energies, or ready summations in the form of atomization energies and a knowledge of the products. Difficulties may arise in this latter part of the input data but in most cases assumptions regarding the products can be tested and those relating to the maximum theoretical energy can be used for the purpose of hazard analysis.

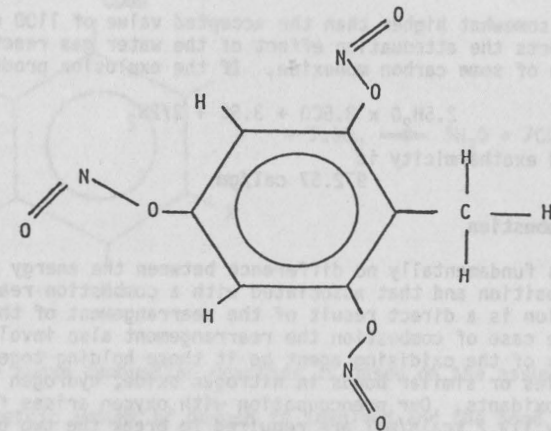
As with most exothermicity determination methods, no account is taken of the effect of distributing the resulting excess enthalpy into the reaction products. At 1100 cal/g the temperature could be several thousand centigrade degrees which would lead to dissociation. Thus the reaction products would change. All estimates are therefore based on the assumption that the heat is removed and that the products remain undissociated. It is assumed however for the purposes of most hazard analyses that the water vapour will not be condensed to liquid. As I have already indicated average bond energies are used since this is

usually sufficiently accurate for this purpose. it must be stressed however that this simplification is only justified for bond rearrangement energy excursions of high exothermicity.

2.1 Decomposition

The decomposition energy of hydrazine is a useful example. The hydrazine molecule comprises one N-N bond and four N-H bonds. The total atomization energy of one mol of hydrazine is therefore 40.0kcal/mol (bond energy N-N) plus 4 x 92.7 (bond energy N-H) equals 410.8 kcal/mol. The recombination into nitrogen 226 kcal/mol (N₂) and hydrogen 208.4 (2 x H₂) releases 434.4 kcal/mol. The net heat release per mol is therefore 23.6 kcal/mol or 737.5 cal/g. This would clearly represent a very dangerous chemical to handle which is common knowledge. However it would probably not qualify hydrazine for the reputation of "super fuel" which could propel rockets without any oxidant. In actual fact, hydrazine was the super-fuel which did propel rockets without any oxidant since the main decomposition product was essentially ammonia. The recombination to one mol of ammonia (280.3 kcals) and half a mol each of hydrogen (52.1 kcals) and nitrogen (113 kcals) releases 445.4 kcals which promotes hydrazine immediately to the super-fuel class with 1081.25 cal/g (TNT 1100 cal/g). This can be extended to 1202.2 cal/g by further product manipulation (all ammonia and nitrogen).

The precise nature of the decomposition products seldom causes such a large difference in the estimated exothermicity. TNT is a good example. The atomization of TNT can be estimated as follows:



	Kcal/mol
Benzene ring bonds	6 x 122.6
Phenyl alkyl bond	1 x 84.9
Phenyl hydrogen bonds	2 x 97.3
Alkyl hydrogen bonds	3 x 98.7
To nitro group C - O	3 x 79.0
In nitro group O - N	3 x 64.4
In nitro group N = O	3 x 143.6
TNT atomisation energy	2172.2

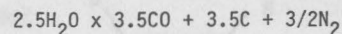
If it is assumed that the decomposition products are:

$$\begin{aligned}
 &5.25C + 1.5N_2 + 2.5H_2O + 1.75CO_2 \\
 &(5.25 \times 171.3) + (1.5 \times 226) + (2.5 \times 221.6) \\
 &\quad + (1.75 \times 384.2) \\
 &= 2464.68 \text{ kcals Atomization energy products} \\
 &\text{Excess enthalpy} = 292.48\text{kcal/mol}
 \end{aligned}$$

(MW TNT = 227.13)

$$\begin{aligned}
 \text{Exothermicity} &= 292.48 \times 1000/227.13 \\
 &= 1287.7 \text{ cal/g}
 \end{aligned}$$

This is somewhat higher than the accepted value of 1100 cal/g which probably reflects the attenuation effect of the water gas reaction and the production of some carbon monoxide. If the explosion products are assumed to be



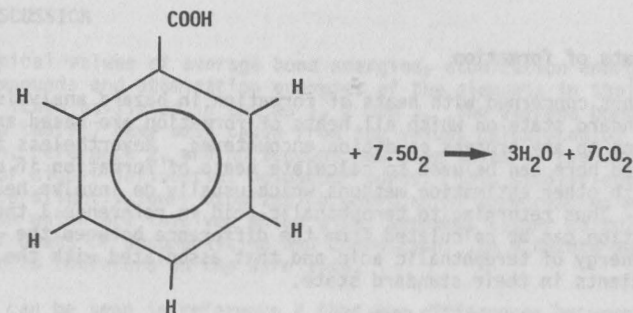
the calculated exothermicity is
972.57 cal/gm

2.2 Combustion

There is fundamentally no difference between the energy resulting from a decomposition and that associated with a combustion reaction. The energy excursion is a direct result of the rearrangement of the chemical bonds. In the case of combustion the rearrangement also involves the chemical bonds of the oxidising agent be it those holding together the oxygen molecules or similar bonds in nitrogen oxide, hydrogen peroxide or more complex oxidants. Our preoccupation with oxygen arises from the fact that only 119.2 kcal/mol are required to break the two oxygen atoms apart whereas the recombination of those two atoms with either hydrogen or carbon involves the formation of chemical bonds with the resulting release of ca 200 kcal for each gram atom of oxygen.

The same method of calculating the energy excursion resulting from the bond rearrangement associated with combustion can be used as that described in the previous section. Thus when hydrogen burns in oxygen the atomization of two hydrogen molecules and one oxygen molecule requires only 327.6 kcal/mol whereas the recombination of the resulting atoms to form four O-H bonds is accompanied by the release of 443.2 kcal/mol. This net escape of 115.6 kcal/mol is equivalent to 3211 cal/g of reactants: products. Since the two reactants are in their conventional basic state the above 57.8 kcal/mol of H₂O represents the heat of formation of water vapour. In this respect we are only concerned with the production of water vapour in any hazard analysis relating to exothermicity and not the 10.52 kcal/mol of latent heat of evaporation which might be recovered in the classical calorimetric measurement. This applies to any heat of combustion which in most tables is usually based on gross calorific value (H₂O to liquid). In this respect all heats of combustion quoted in this text relate to net calorific value (H₂O as vapour) and this usually involves the reduction of the normally quoted gross heat of combustion values by 5.26 kcal/g atom of hydrogen present in the fuel molecule. Thus, as with the CHETAH approach no account is taken of any phase change in the hazard analysis.

This point is illustrated with regard to the heat of combustion of benzoic acid which is used as a calorimetric standard with a gross calorific value of 6319 cal/g. With a molecular weight of 122 this is equivalent to 770.92 kcal/mol of benzoic acid (gross). If however the water vapour is not condensed to liquid the net value would be 739.36 kcal/mol of benzoic acid (i.e. -6 x 5.26 : 6 hydrogen atoms per mol).



The above combustion reaction is based on the assumption that a stoichiometric amount of oxygen is involved and the bond atomization summation involves

	Kcal/mol
Acid O - H bond	1 x 114
Acid C - O bond	1 x 110
Acid C = O bond	1 x 173.1
Phenyl alkyl bond	1 x 84.9
Benzene ring bonds	6 x 122.6
Alkyl hydrogen bonds	5 x 97.3
7½ Oxygen mols	7.5 x 119.2
Benzoic acid atomization energy	2598.1

The combustion products are:-

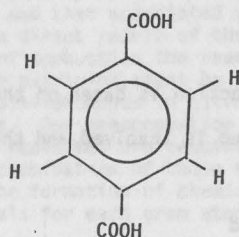


$$(3 \times 221.6) + (7 \times 384.6) = 3354.2 \text{ kcal/mol Recombination}$$

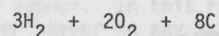
ie 756.1 kcal/mol (6197 cal/g) benzoic acid which is ca. 2% of the recognised standard value.

2.3 Heats of formation

We are not concerned with heats of formation in hazard analysis since the standard state on which all heats of formation are based are seldom relevant to any process condition encountered. Nevertheless the method outlined here can be used to calculate heats of formation if only to compare with other estimation methods which usually do involve heats of formation. Thus returning to terephthalic acid in reference 1 the heat of formation can be calculated from the difference between the atomization energy of terephthalic acid and that associated with the atomic ingredients in their standard state.



		Kcal/mol
Phenyl hydrogen bonds	H6	4 x 97.3
Acid O-H bonds	H2	2 x 114
Acid C-O bonds	O4	2 x 110
Acid C=O bond	O5	2 x 173.1
Phenyl alkyl bonds	C4	2 x 84.9
Benzene ring bonds	C6	6 x 122.6
Terephthalic acid atomization Energy	=	<u>2088.8kcal/mol</u>
Base state		



$$312.6 + 238.4 + 1370.4 = 1921.4 \text{ kcal}$$

(atomization energy of constituent elements in standard state)
Thus calculated heat of formation = -167.4 kcal/mol

3. DISCUSSION

Typical values of average bond energies, atomization energies of known compounds and atomization energies of the elements in their standard state as listed in tables 1, 2 and 3. The average bond energies listed in table 1 have been taken from the values calculated by Sanderson, reference 2, and no account has been taken of the abnormal effects of highly influential neighbour bonds. This simplification tends to produce slightly lower atomization energies of more complex molecules than those which are involved which gives somewhat higher calculated values of heats of decomposition and combustion. In a hazard analysis the error is therefore on the safe side.

It can be seen in reference 2 that the differences between the estimated values and experimental values of bond energies are small. The experimental values therefore have been used in table 2 which is usually the source data for the reaction products. The atomization energies of the elemental species have been taken directly from reference 2 and are given in terms of energy per gram atom. For most elements encountered this is equal to half that associated with the standard state i.e. H₂, O₂, N₂ etc. By adopting this convention problems associated with carbon C₂ and other materials with complex values do not arise. I have also found that the data is more easily programmed in this form.

A number of other authors have referred to this method but using both "bond energies" and "resonant energies" in their assessment of atomization energies. Thus the carbon to carbon bond energy in hexane could be considered to be 83.2 kcals and in acetylene 144.5 kcals. In benzene this could give a total carbon to carbon bond energy of (3 x 83.2) + (3 x 144.5) = 683.1. This is below the estimated value for the six carbon bonds in benzene which is 735.6 and the shortfall of about 50 kcals may be referred to as residual "resonant" energy. In the method described in this paper however it is accepted that the carbon to carbon bonds in benzene, TNT, benzoic acid etc. are not represented by alternate single and double bonds but are unique and requiring 122.6 kcals each to break them. Any resonant energy is thereby built into the individual bonds. Using the data from tables 1, 2 and 3 the reliability of the method has been checked against standard heats of combustion (see table 4) and heats of formation (see table 5). It can be seen that the agreement between the measured values and those predicted using the readily available data is sufficient for a preliminary survey relating to either a compound or a mixture of compounds.

The largest percentage errors occur with heats of formation (see table 5). With the large heats of formation of the water and carbon dioxide however, the heats of formation of the initial fuels are lost in the resulting heats of combustion. With small molecules however the errors arising from this method are greatest. It is recommended therefore that with such small molecules the bond energies should be either calculated from first principles by the method given in reference 2 or taken directly from tables.

This exploitation of Hess's Law enables the thermochemistry to be measured on an absolute zero basis. Thus if the energy available from the formation of any chemical bond is derived from the condition of the solitary atoms in space, any resulting release of chemical energy must be equal to the total bond energy in the molecule under consideration. In this respect it must be stressed that the single bond energies are not the classical dissociation energies which can be applied to kinetics. The bond energy summation method assumes that all the bonds are broken at the same instant in time to give the total atomization energy of the molecule. The same is assumed in the reverse process with the formation of the reaction products. From this simple and fundamental approach, the contribution of either molecular substitution or addition and dilation can be assessed for any process or product at the conceptual stage.

ACKNOWLEDGEMENT

I wish to express my thanks to my friends and colleagues Dr. J.H. Burgoyne and Dr. P.V. Rutledge for their advice during the preparation of this paper and to Dr. R.T. Sanderson who I have never met but whose interesting book (reference 2) is the source of both the data and the scientific principles which I have so briefly outlined in this paper.

REFERENCES

- Reference 1. Carole A. Davies et al. The Thermochemical and Hazard Data of Chemicals. (Estimation Using the ASTM CHETAH Program). Chapter 9 from Chemical Process Hazard Review Proceedings of Symposia No. 274 of the American Chemical Society 1985 SBN 08 41 2 09022
- Reference 2. R.T. Sanderson. Chemical Bond and Bond Energy. Academic Press. New York. London 1971.
- Reference 3. Handbook of Chemistry and Physics. 55th Edition 1974 - 75. CRC Press.

TABLE 1
SUGGESTED AVERAGE BOND ENERGIES

BOND DESCRIPTION	ENERGY PER MOL KCAL/MOL
Hydrogen to carbon ; alkyl	98.7
Hydrogen to oxygen ; acid, alcohol, phenol	114.0
Hydrogen to phenyl (benzene ring)	97.3
Oxygen to carbon ; alcohol	81.2
Oxygen to carbon ; phenol	85.4
Oxygen to carbon ; aldehyde	117.2
Oxygen to carbon ; C-O acid	110.0
Oxygen to carbon ; C=O acid	173.1
Oxygen to carbon ; ether	81.2
Oxygen to carbon ; amide	173.0
Nitrogen to carbon ; amine	72.2
Nitrogen to hydrogen ; amine	92.7
Nitrogen to carbon ; amide	100.1
Nitro group NO ₂	287
Carbon to carbon : single, alkyl	83.2
Carbon to carbon ; double, ethylenic	144.5
Carbon to carbon ; treble, acetylenic	187.5
Carbon to carbon ; alkyl - phenyl	84.9
Carbon to carbon ; phenyl (benzene ring)	122.6
Hydrogen to sulphur Mercaptan sulphide	88.4

Values from reference 2

TABLE 2

TYPICAL MOLAR ATOMIZATION ENERGIES

Values in kilocalories per mol.

COMPOUND	FORMULA	KCALS
Water vapour	H ₂ O	221.6
Carbon dioxide	CO ₂	384.2
Carbon monoxide	CO	257.3
Hydrogen sulphide	H ₂ S	175.7
Sulphur dioxide	SO ₂	256.7
Methane	CH ₄	397.6
Nitrogen dioxide	NO ₂	224.2
Nitric oxide	NO	151.0
Nitrous oxide	N ₂ O	226.1
Ammonia	NH ₃	280.3
Nitric acid	HNO ₃	376.2
Hydrogen fluoride	HF	135.8
Hydrogen chloride	HCl	103.3

Values from reference 2

TABLE 3

Examples of Experimental Atomization Energies

Values in kilocalories per gram atom

ELEMENT	DESCRIPTION	KCALS
Hydrogen	H ₂ /2	52.1
Nitrogen	N ₂ /2	113.0
Oxygen	O ₂ /2	59.6
Carbon	C _n /n	171.3
Sulphur	S _n /n	66.6
Fluorine	F ₂ /2	18.9
Chlorine	Cl ₂ /2	29.1
Bromine	Br ₂	26.7
Iodine	I ₂ /2	25.5

Values from reference 2

TABLE 4

COMPARISON OF HEATS OF COMBUSTION CALCULATED ON AVERAGE BOND ENERGY BASIS WITH MEASURED VALUES
(All values in kcal/mol)

	Atomization Energies		Exp.*
	Reactants	Products	
Acetylene	$C_2H_2 + 5(O) \rightarrow 2CO_2 + H_2O$	990.0	300.1
Dipropargyl	$(CH_3C_2CH_2)_2 + 15(O) \rightarrow 6CO_2 + 3H_2O$	2110.6	851.3
Ethyl chloride	$C_2H_5Cl + 6(O) \rightarrow 2CO_2 + 2H_2O + HCl$	1016.5	295.7#
Isobutyraldehyde	$(CH_3)_2CHCHO + 11(O) \rightarrow 4CO_2 + 4H_2O$	1872	554.7
Methyl ethyl ether	$CH_3OC_2H_5 + 9(O) \rightarrow 3CO_2 + 4H_2O$	1571.6	461.6
Propane	$C_3H_8 + 10(O) \rightarrow 3CO_2 + 4H_2O$	1552	488.5
Pentane	$C_5H_{12} + 16(O) \rightarrow 5CO_2 + 6H_2O$	2470.8	775.7
Formaldehyde	$CH_2O + 2(O) \rightarrow CO_2 + H_2O$	493.8	112
Tetraphenyl methane	$(C_6H_5)_4C + 60(O) \rightarrow 25CO_2 + 10H_2O$	8825.2	2997.2
Trimethyl ethylene	$(CH_3)_2C : CHCH_3 + 15(O) \rightarrow 5CO_2 + 5H_2O$	2275.1	751.0
Nitromethane	$CH_3NO_2 + 1.5(O) \rightarrow CO_2 + 1.5H_2O + (N)$	672.5	169.4

* Reference 3 pages D243-248 but with net value correction applied i.e. $-(N \times 5.26)$ where N = number of hydrogen atoms per mol.
(Conversion gross to net involves only 4H atoms per mol due to formation of HCl)

TABLE 5

Estimation of Heats of Formation by Average Bond Energy Summation
(All values in kcal/mol)

COMPOUND	FORMULA	COMPOUND	ELEMENTS	HEATS OF FORMATION	
				ADC	REF.3
Ammonia	NH ₃	280.3	269.3	-11	-11.04
Ethyl alcohol	C ₂ H ₅ OH	771.9	714.8	-57.1	-56.2
Ethylene	C ₂ H ₄	539.3	551.0	+11.7	+12.5
Methanol	CH ₃ OH	491.3	439.3	-52	-48.1
Dichloromethane	CH ₂ Cl ₂	361.4	333.7	-27.7	-21
Methyl amine	CH ₃ NH ₂	553.7	544.8	-8.9	-6.7
Carbonyl chloride	COCl ₂	337.1	289.1	-48	-53.3
Hydrazine	H ₂ NNH ₂	410.8	434.4	+23.6 (gas)	+12.05 (liquid)
Dimethyl sulphide	(CH ₃) ₂ S	735.8	721.8	-14	-6.9
Ethane diol (glycol)	C ₂ H ₄ (OH) ₂	868.4	774.4	-94	-108.6 (liquid)
Nitromethane	CH ₃ NO ₂	583.1	559.8	-23.3	-21.3

Reference 3 D73