CHAPTER 4
EXPLOSION CHEMISTRY

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4 EXPLOSION CHEMISTRY

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4.1 AWARENESS SUMMARY

All explosives when they function produce heat by chemical reaction, which in simple terms is the same chemistry used since mankind discovered fire, that is the chemistry of combustion. Fuels such as coal, wood and oil are burned for domestic and industrial heating and cooking and these fuels consist of carbon and hydrogen often called hydrocarbons. When hydrocarbons burn they require oxygen, which for the above uses comes from the air and the products of this chemistry are the gases carbon dioxide and water (a gas above 100 °C). If there is insufficient oxygen then carbon monoxide may be formed as well as or instead of carbon dioxide.

Carbon + Oxygen → Carbon Dioxide or Carbon Monoxide

Hydrogen + Oxygen → Water

Although it is not usually observed this burning chemistry produces both heat and gas as the gas products are invisible and are vented to atmosphere. Also, the rate of burning is relatively slow and so the gases do not cause any build-up of pressure. This is because the rate at which the oxygen in the air can react with the fuel is controlled, either by the low surface area of solid fuels such as lumps of coal or the controlled release of liquid fuels such as for oil fired boilers.

Chapter 1 (link to 1.3.1) explains that an explosion is a rapid expansion of gas and this can be produced by chemical reaction if both heat and gas are produced at the required speed. Therefore the chemistry of combustion provides heat and gas but it must be at a much faster speed than conventional burning of fuels. This is achieved by providing an intimate mixture of the fuel (carbon and hydrogen) with a source of oxygen before the combustion starts. An example of this is the cause of a common accident when a gaseous fuel such as methane is released in to a closed space such as a building and mixes with air. When ignited the combustion chemistry can travel through the mixture at such a speed it causes an explosion usually destroying the building (link to 9.4.1).

This concept can be applied to solids but now the fuel and source of oxygen must be solid materials and the more intimately mixed the quicker will be the chemical reaction. The first recorded explosive material, black powder or gunpowder, is a good example of a solid explosive, where in this case the fuel, carbon, is mixed with a chemical that can release oxygen, a solid called potassium nitrate known historically as saltpetre. Sulphur is also used in the mixture. Over 50% of the reaction products are solids and so do not contribute to gas production, although they do assist in the production of heat from the reaction.

Carbon + Sulphur + Potassium Nitrate → Carbon Dioxide + Nitrogen + Solids

As the components of this explosive are individual materials the manufacturer can alter the ratio of fuel to source of oxygen and so optimise the combustion to best effect. The manufacturing process developed to make the mixture as intimate as possible through milling, a hazardous activity when working with explosives.

A method by which the fuel elements carbon and hydrogen can be more intimately associated with a source of oxygen is to put all of these elements in the same molecule as shown in Figure 4-1.

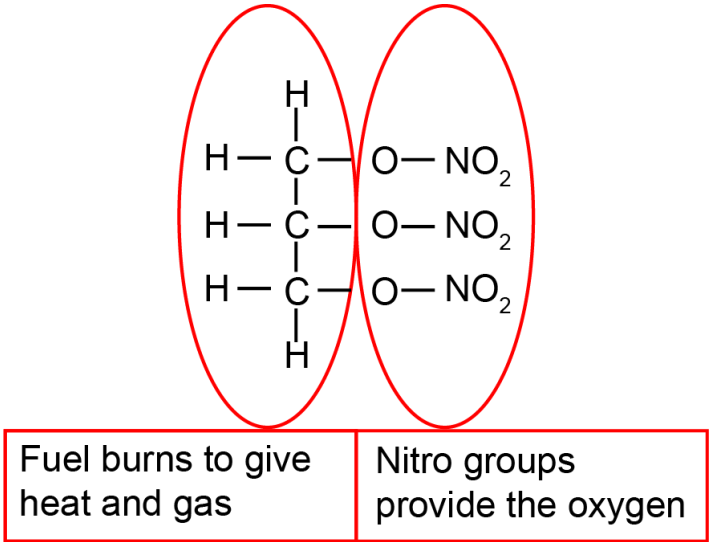


Figure 4-1 Nitroglycerine a molecular explosive

To understand just how much closer the fuel and oxygen atoms are in a molecule, if the carbon particles in a modern black powder were considered to be the size of England a molecule would be the size of a house.

Further examples of explosive mixtures and molecules can be found in the next section of the chapter including more detailed chemistry.

4.2 EXPLOSIVE MIXTURES AND MOLECULES

Chemical explosives can be divided into two groups, depending on their chemical nature; those that are classed as molecular explosives, and those that are explosive mixtures such as black powder.

4.2.1 Explosive Mixtures

Explosive mixtures can be gaseous, liquid or solid where the fuel and the oxidiser are mixed together. An example is when hydrogen gas is mixed with oxygen gas and initiated resulting in a fuel air explosion (FAE).

$$\tfrac{1}{2}O_2(g) + H_2(g) \rightarrow H_2O(g) \qquad \textbf{(4-1)}$$

Liquid fuel can also be mixed with a liquid oxidiser for example; the fuel unsymmetrical dimethylhydrazine is mixed with the oxidiser inhibited red fuming nitric acid and initiated to give gaseous products, as shown below.

$$5(CH_3)_2NNH_2(l) + 16HNO_3(l) \rightarrow 10CO_2(g) + 28H_2O(g) + 13N_2(g) \quad \textbf{(4-2)}$$

An example of a solid explosive mixture is black powder where the fuels carbon and sulphur are mixed with the oxidiser potassium nitrate. On initiation gaseous and solid products are formed. An example is given below.

$$10KNO_3(s) + 3S(s) + 8C(s) \rightarrow 2KCO_3(s) + 3K_2SO_4(s) + 6CO_2(g) + 5N_2(g) \quad \textbf{(4-3)}$$

Pyrotechnics are generally solid explosives mixtures. The reaction below is known as a thermite reaction.

$$Fe_2O_3(s) + 2Al(s) \rightarrow Al_2O_3(s) + 2Fe(s) \quad \textbf{(4-4)}$$

Another pyrotechnic mix is flash powder where aluminium powder is mixed with potassium perchlorate. The reaction is given below.

$$3KClO_4(s) + 8Al(s) \rightarrow 4Al_2O_3(s) + 3KCl(s) \quad \textbf{(4-5)}$$

All of these compositions require the fuel and the oxidiser being mixed together, where a poorly mixed composition results in a slow rate of burn compared to a mixture where the ingredients are in intimate contact.

4.2.2 Molecular Explosives

In order to improve the burn rate and hence the performance of explosives, molecular explosives have the fuel and oxidiser atoms on the same molecule as shown in Figure 4-2.

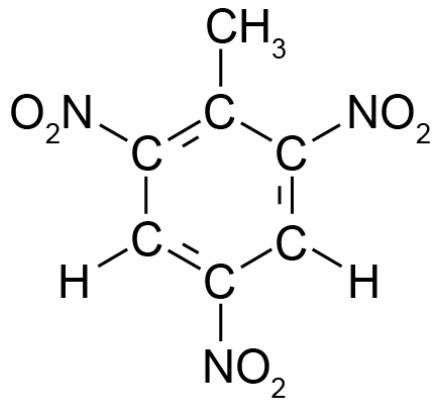


Figure 4-2 The molecular explosive trinitrotoluene (TNT)

Molecular explosives can be classified according to where the NO_2 groups are located in the molecule. There are three categories as shown in Figure 4-3.

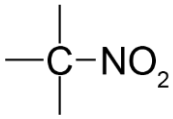
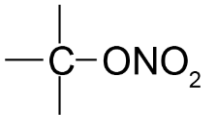
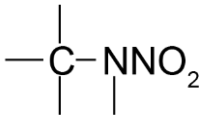
C-nitration	***O-nitration***	***N-nitration***
nitro compound	nitrate ester	nitramine
		
nitro group attached to carbon atom	nitro group attached to oxygen atom	nitro group attached to nitrogen atom

Figure 4-3 Classification of molecular explosives

Figure 4-4 gives an example of molecular explosives for the 3 categories.

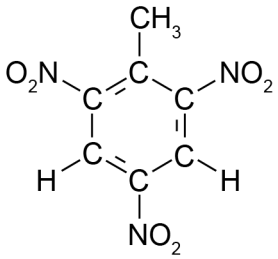
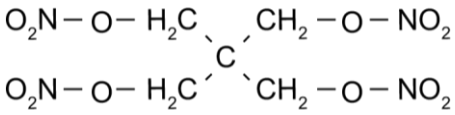
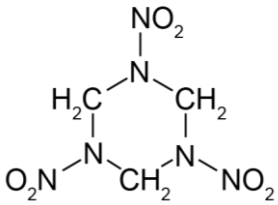
Nitro compound Trinitrotoluene (TNT)	
Nitrate ester Pentaerythrytoltetranitrate (PETN)	
Nitramine Cyclotrimethylene trinitramine (RDX)	

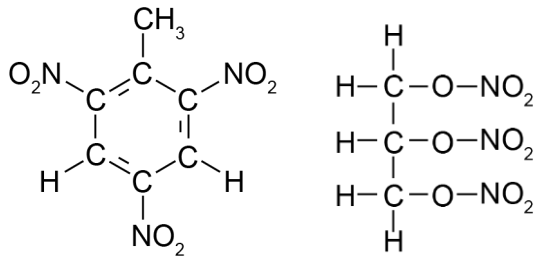
Figure 4-4 Examples of molecular explosives

4.3 CHEMICAL REACTIONS FOR THE EXPLOSIVE PROCESS

All molecular explosives when suitably initiated will undergo a chemical reaction. The products will depend upon the amount of oxygen available during the reaction. This supply of oxygen will depend in turn upon the quantity of oxidizing atoms which are present in the explosive molecule which can be quantified as the oxygen balance.

4.3.1 Oxygen Balance

This oxygen balance can be defined as the amount of oxygen, expressed in weight percent, liberated as a result of the complete conversion of the explosive material to CO_2, H_2O, SO_2, Al_2O_3 etc. If the amount of oxygen present in the explosive molecule is insufficient for the complete oxidation a negative oxygen balance will result. This can be seen in the molecule TNT Figure 4-5(a). Nitroglycerine, Figure 4-5(b), however has a high proportion of oxygen, more than required for complete oxidation of its fuel elements and therefore has a positive oxygen balance.



(a) (b)

Figure 4-5 (a) TNT and (b) Nitroglycerine

The oxygen balance Ω is calculated from an explosive containing the general formula $C_aH_bN_cO_d$ with molecular mass M as shown in Equation (4-6).

$$\Omega = \frac{[d - (2a) - (b/2)] \text{ x } 1600}{M} \qquad \textbf{(4-6)}$$

Using Equation (4-6) the oxygen balance for RDX ($C_3H_6N_6O_6$) is found to be-21.6 % as shown in the calculation below.

For RDX a=3, b=6, c=6 and d=6

Molecular mass is a sum of the atomic masses in the molecule, carbon = 12, hydrogen = 1, nitrogen = 14 and oxygen = 16:

$$\text{therefore } M = (3x12) + (6x1) + (6x14) + (6x16) = 222$$

$$\Omega = \left[\frac{6 - (2x3) - (6/2)}{222}\right] x\ 1600 = -21.6\ \%$$

The calculated oxygen balances for some explosive substances are presented in Table 4-1. It can be seen from Table 4-1 that explosive substances may have a positive or negative oxygen balance. If the oxygen balance is large and negative then there is not enough oxygen for carbon dioxide to be formed. Consequently carbon monoxide will be liberated or even elemental carbon.

The oxygen balance does not provide information on the energy changes which take place during an explosion. This information can be obtained by calculating the heat liberated during decomposition of explosive substances, known as the 'heat of explosion'. In order to calculate the heat of explosion, the decomposition products of the explosive must be determined, since the magnitude of the heat of explosion is dependent upon the thermodynamic state of its products. The decomposition process will be by detonation in the case of primary and secondary explosives and burning in the case of gun powders and propellants.

4.3.2 Product of Detonation

The detonation of RDX ($C_3H_6N_6O_6$) will result in the formation of its decomposition products. These may be carbon monoxide, carbon dioxide, carbon, water etc., as shown below.

$$C_3H_6N_6O_6(s) \rightarrow 3CO(g) + 3H_2O(g) + 3N_2(g), \text{ or} \quad \textbf{(4-7)}$$

$$C_3H_6N_6O_6(s) \rightarrow 3CO_2(g) + 3H_2(g) + 3N_2(g), \text{ or} \quad \textbf{(4-8)}$$

$$C_3H_6N_6O_6(s) \rightarrow CO(g) + 2CO_2(g) + 3H_2O(g) + 3N_2(g), \text{ or} \quad \textbf{(4-9)}$$

$$C_3H_6N_6O_6(s) \rightarrow 2CO_2(g) + C(s) + 2H_2O(g) + H_2(g) + 3N_2(g), \text{ etc} \quad \textbf{(4-10)}$$

In order to clarify this problem a set of rules were developed by Kistiakowsky and Wilson, known as the 'Kistiakowsky-Wilson' rules (K-W) rules. These rules should only be used for moderately oxygen deficient explosives with an oxygen balance greater than -40.0 % i.e. for oxygen rich explosives.

Table 4-1 Oxygen Balance of Some Explosives[1]

Explosive substance	Empirical formula	Oxygen balance % (w/w)
Ammonium nitrate	NH_4NO_3	+19.99
Nitroglycerine	$C_3H_5N_3O_9$	+3.52
Silver Azide	AgN_3	0.00
EGDN	$C_2H_4N_2O_6$	0.00
Lead Azide	PbN_6	0.00
PETN	$C_5H_8N_4O_{12}$	-10.12
CL-20	$C_6H_6N_{12}O_{12}$	-10.95
TNAZ	$C_3H_4N_4O_6$	-16.66
Mercury Fulminate	$HgC_2N_2O_2$	-16.86
Lead Styphnate	$PbC_6H_3N_3O_9$	-18.79
FOX-12	$C_2H_7N_7O_5$	-19.13
FOX-7	$C_2H_4N_4O_4$	-21.61
RDX	$C_3H_6N_6O_6$	-21.61
HMX	$C_4H_8N_8O_8$	-21.61
Nitrocellulose (14.14 % N)	$C_6H_7O_{11}N_3$	-24.24
Nitroguanidine	$CH_4N_4O_2$	-30.75
Picric acid	$C_6H_3N_3O_7$	-45.39
Tetryl	$C_7H_5N_5O_8$	-47.36
NTO	$C_2H_2N_4O_3$	-49.18
TATB	$C_6H_6N_6O_6$	-55.78
Tetrazene	$C_2H_8N_{10}O$	-59.52
HNS	$C_{14}H_6N_6O_{12}$	-67.52
TNT	$C_7H_5N_3O_6$	-73.96

4.3.3 Kistiakowsky-Wilson Rules

The Kistiakowsky-Wilson rules (K-W) rules are presented below in order of priority.

1. Carbon atoms are converted to carbon monoxide
2. If any oxygen remains then hydrogen is then oxidized to water
3. If any oxygen still remains then carbon monoxide is oxidized to carbon dioxide
4. All the nitrogen is converted to nitrogen gas N_2

Using these rules the decomposition products of RDX ($C_3H_6N_6O_6$) can be determined.

1. Carbon atoms are converted to carbon monoxide
   $3C \rightarrow 3CO$
2. If any oxygen remains then hydrogen is then oxidized to water
   $6H \rightarrow 3H_2O$
3. If any oxygen still remains then carbon monoxide is oxidized to carbon dioxide
   No more oxygen
4. All the nitrogen is converted to nitrogen gas N_2
   $6N \rightarrow 3N_2$

Therefore the overall reaction for the decomposition of RDX is:

$$C_3H_6N_6O_6(s) \rightarrow 3CO(g) + 3H_2O(g) + 3N_2(g) \qquad \textbf{(4-11)}$$

For explosive materials which have a lower oxygen balance than -40 the modified Kistiakowsky-Wilson rules must be employed.

4.3.4 Modified Kistiakowsky-Wilson Rules

The modified Kistiakowsky-Wilson rules (mod. K-W) rules are presented below in order of priority.

1. Hydrogen atoms are converted to water
2. If any oxygen remains then carbon is converted to carbon monoxide
3. If any oxygen still remains then carbon monoxide is oxidized to carbon dioxide
4. All the nitrogen is converted to nitrogen gas N_2

Using the modified Kistiakowsky-Wilson rules the decomposition products for TNT ($C_7H_5N_3O_6$) can be determined.

1. Hydrogen atoms are converted to water
   $5H \rightarrow 2\frac{1}{2}H_2O$
2. If any oxygen remains then carbon is converted to carbon monoxide
   $3\frac{1}{2}C \rightarrow 3\frac{1}{2}CO$
3. If any oxygen still remains then carbon monoxide is oxidized to carbon dioxide

No more oxygen

4. All the nitrogen is converted to nitrogen gas N_2
   $3N \rightarrow 1\frac{1}{2}N_2$
5. The remaining carbon remains as elemental carbon
   $3\frac{1}{2}C \rightarrow 3\frac{1}{2}C$

Therefore the overall reaction for the decomposition of TNT is:

$$C_7H_5N_3O_6(s) \rightarrow 3\frac{1}{2}CO(g) + 3\frac{1}{2}C(s) + 2\frac{1}{2}H_2O(g) + 1\frac{1}{2}N_2(g) \quad \textbf{(4-12)}$$

The reaction for the decomposition of explosive substances can therefore be determined using either the Kistiakowsky-Wilson (K-W) rules or the modified Kistiakowsky-Wilson (mod. K-W) rules.

Table 4-2 and

Table 4-3 present equations for the decomposition for some explosive materials using the K-W rules and the modified K-W rules respectively.

The K-W and modified K-W rules will only provide an insight to the decomposition products, they do not give any information as to the energy released on decomposition but are essential when calculating the heat of explosion. They are simple to apply and do give fairly good approximations.

Table 4-2 Reactions for Decomposition Products Using the K-W Rules[1]

Explosive substance	Reaction for decomposition products
Nitroglycerine	$C_3H_5N_3O_9(l) \rightarrow 3CO_2(g) + 2½H_2O(g) + ½O(g) + 1½N_2(g)$
EGDN	$C_2H_4N_2O_6(s) \rightarrow 2CO_2(g) + 2H_2O(g) + N_2(g)$
PETN	$C_5H_8N_4O_{12}(s) \rightarrow 2CO(g) + 3CO_2(g) + 4H_2O(g) + 2N_2(g)$
CL-20	$C_6H_6N_{12}O_{12}(s) \rightarrow 3CO(g) + 3CO_2(g) + 3H_2O(g) + 6N_2(g)$
TNAZ	$C_3H_4N_4O_6(s) \rightarrow 2CO(g) + CO_2(g) + 2H_2O(g) + 2N_2(g)$
FOX-12	$C_2H_7N_7O_5(s) \rightarrow 2CO(g) + 3H_2O(g) + ½H_2(g) + 3½N_2(g)$
FOX-7	$C_2H_4N_4O_4(s) \rightarrow 2CO(g) + 2H_2O(g) + 2N_2(g)$
RDX	$C_3H_6N_6O_6(s) \rightarrow 3CO(g) + 3H_2O(g) + 3N_2(g)$
HMX	$C_4H_8N_8O_8(s) \rightarrow 4CO(g) + 4H_2O(g) + 4N_2(g)$
Nitrocellulose (14.14 % N)	$C_6H_7O_{11}N_3(s) \rightarrow$ $4½CO(g) + 1½CO_2(g) + 3½H_2O(g) + 1½N_2(g)$
Nitroguanidine	$CH_4N_4O_2(s) \rightarrow CO(g) + H_2O(g) + H_2(g) + 2N_2(g)$

Table 4-3 Reactions for Decomposition Products Using Modified K-W Rules[1]

Explosive substance	Reaction for decomposition products
Picric acid	$C_6H_3N_3O_7(s) \rightarrow 5½CO(g) + ½C(s) + 1½H_2O(g) + 1½N_2(g)$
Tetryl	$C_7H_5N_5O_8(s) \rightarrow 5½CO(g) + 1½C(s) + 2½H_2O(g) + 2½N_2(g)$
NTO	$C_2H_2N_4O_3(s) \rightarrow 2CO(g) + H_2O(g) + 2N_2(g)$
TATB	$C_6H_6N_6O_6(s) \rightarrow 3CO(g) + 3C(s) + 3H_2O(g) + 3N_2(g)$
Tetrazene	$C_2H_8N_{10}O(s) \rightarrow ½H_2O(g) + 2C(s) + 3½H_2(g) + 5N_2(g)$
HNS	$C_{14}H_6N_6O_{12}(s) \rightarrow 9CO(g) + 5C(s) + 3H_2O(g) + 3N_2(g)$
TNT	$C_7H_5N_3O_6(s) \rightarrow 3½CO(g) + 3½C(s) + 2½H_2O(g) + 1½N_2(g)$

4.4 HEAT OF EXPLOSION AND GAS PRODUCTION

4.4.1 Heat of Formation

The heats of formation of a reaction can be described as the heat released or absorbed during the formation of a pure substance from its elements, at constant pressure and usually denoted by ΔH_f. For explosive substances which do not contain sufficient oxygen in its molecule for complete oxidation ie TNT, products such as CO, carbon and H_2 are formed. The energy liberated during the formation of these products is known as the 'heat of explosion'. If these products are then isolated and allowed to burn in excess oxygen to form substances like CO_2, H_2O etc., the heat evolved added to the heat of explosion would be equal to the 'heat of combustion'. Consequently the value for the heat of combustion is higher than the value for the heat of explosion for explosive substances which have insufficient oxygen for complete oxidation. For explosive substances with positive oxygen balances i.e. nitroglycerine, there is generally no difference between the values for the heat of explosion and the heat of combustion.

The value for the heats of formation can be negative or positive. If the value is negative, heat is liberated during the reaction and the reaction is exothermic, whereas if the value is positive heat is absorbed during the reaction and the reaction is endothermic. For reactions involving explosive components the reaction is always exothermic. In an exothermic reaction the energy evolved may appear in many forms, but for practical purposes it is usually obtained in the form of heat. The energy liberated when explosives deflagrate is called the 'heat of deflagration', whereas the energy liberated by detonating explosives is called the 'heat of detonation' in kJ mol^{-1} or the 'heat of explosion' in kJ kg^{-1}.

In a chemical reaction involving explosives, molecules of an explosive are first raised to a higher energy level through input of the 'heats of atomization' to break their interatomic bonds. Then the atoms rearrange themselves into new

molecules, releasing a larger quantity of heat and dropping to an energy level lower than the original as shown in Figure 4.6.

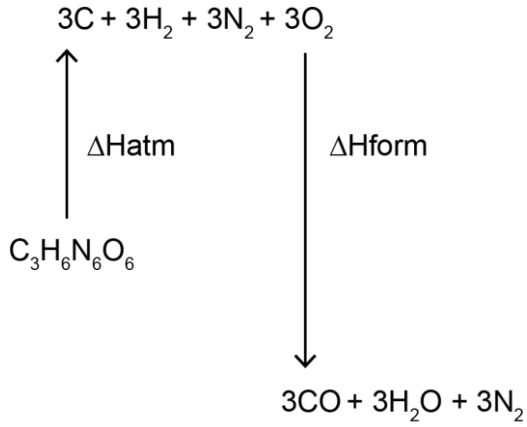


Figure 4-6 Energy diagram for RDX and its reaction products

The thermodynamic path presented in Figure 4.1 will most likely not be the same as the 'kinetic path'. For instance, the reaction may take place in several stages involving complex systems of reaction chains etc. Nevertheless, the energy evolved depends only on the initial and final states and not on the intermediate ones. Once the reaction is completed, the net heat evolved is exactly the same as if the reactant molecules were first dissociated into their atoms, and then reacted directly to form the final products (Hess's Law).

4.4.2 Heat of Explosion

When an explosive is initiated either to burning or detonation, its energy is released in the form of heat. The liberation of heat under adiabatic conditions is called the 'heat of explosion' notated by the letter Q. The heat of explosion provides information about the work capacity of the explosive, where the propellants and secondary explosives generally have high values of Q. For propellants burning in the chamber of a gun, and secondary explosives in detonating devices, the heat of explosion is conventionally expressed in terms of constant volume conditions Q_v. For rocket propellants burning in the combustion chamber of a rocket motor under conditions of free expansion to the atmosphere, it is conventional to employ constant pressure conditions. In this case, the heat of explosion is expressed as Q_p.

Under constant volume conditions Q_v can be calculated from the standard internal energies of formation for the products $\Delta U_f^{\ominus}$(products) and the standard internal energies of formation for the explosive components $\Delta U_f^{\ominus}$(explosive components) as shown in Equation (4-13).

$$Q_v = \Sigma\Delta U_f^{\ominus}(\text{products}) - \Sigma\Delta U_f^{\ominus}(\text{explosive components}) \quad \textbf{(4-13)}$$

A similar equation is given for the heat of explosion under constant pressure conditions as shown in Equation (4-14), where $\Delta H_f^{\ominus}$ represents the corresponding standard enthalpies of formation.

$$Q_p = \Sigma\Delta H_f^{\ominus}{}_{(\text{products})} - \Sigma\Delta H_f^{\ominus}{}_{(\text{explosive components})} \quad \textbf{(4-14)}$$

In considering the thermochemistry of solid and liquid explosives, it is usually adequate, for practical purposes, to treat the state functions ΔH and ΔU as approximately the same. Consequently heats, or enthalpy terms tend to be used for both constant pressure and constant volume conditions.

Therefore the heat of explosion Q can be calculated from the difference between the sum of the energies for the formation of the explosive components and the sum of the energies for the formation of the explosion products, as shown in Equation (4-15).

$$Q = \Delta H_{(\text{reaction})} = \Sigma\Delta H_{f(\text{products})} - \Sigma\Delta H_{f(\text{explosive components})} \quad \textbf{(4-15)}$$

The calculated values do not exactly agree with those obtained experimentally since the conditions of loading density, temperature, pressure etc, are not taken into consideration.

The value for Q in kJ kg^{-1} is generally derived from the heat of detonation ΔH_d kJ mol^{-1}. The heat of detonation ΔH_d for RDX can be illustrated using Hess's law as shown in Figure 4-7.

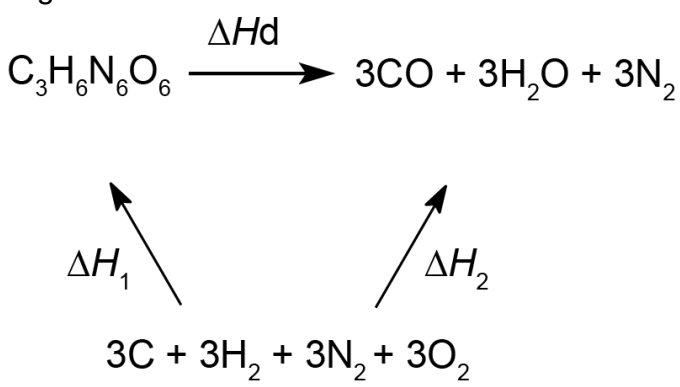


Figure 4-7 Enthalpy of detonation for RDX using Hess's law

Using the diagram in Figure 4-7 the heat of detonation for RDX can be calculated as shown below.

Heat of formation of RDX = ΔH_f(RDX) =+70.29 kJ mol^{-1}
Heat of formation of carbon monoxide = ΔH_f(CO) = -110.525 kJ mol^{-1}
Heat of formation of water in the vapour phase = $\Delta H_f(H_2O_{(g)})$= -241.830 kJ mol^{-1}
Therefore $\Delta H_1 = \Delta H_f$(RDX) = +70.29 kJ mol^{-1}

ΔH_2 = [3 x ΔH_f(CO)] + [3 x $\Delta H_f(H_2O_{(g)})$]
= [3 x (-110.525)] + [3 x (-241.830)]
= -1057.065 kJ mol^{-1}

$\Delta H_d = \Delta H_2 - \Delta H_1$
$= - 1057.065 - (+70.29)$
$= -1127.355$ kJ mol^{-1}

The heat of detonation for RDX is -1127.355 kJ mol^{-1}. This value can be converted to the heat of explosion Q as shown in Equation (4-16), where M is the molecule mass of RDX (222.117):

$$\boldsymbol{Q = \frac{\triangle H_d \, x \, 1000}{M} = \frac{-1127.355 \, x1000}{222.117} = -5075.5 \, kJ \, kg^{-1}} \qquad \textbf{(4-16)}$$

Table 4-4 presents calculated heat of explosions together with their calculated heat of detonation for some primary and secondary explosive substances. The negative sign for the heat of explosion is generally omitted since it only denotes an exothermic reaction. From this table it can be seen that secondary explosives generate far more heat during an explosion than primary explosives.

4.4.3 Gas Production

The volume of gas produced during an explosion will provide information on the amount of work done by the explosive. In order to measure the volume of gas generated standard conditions must be established, because the volume of gas will vary according to the temperature at which the measurement is taken. These standard conditions also enable comparisons to be made between one explosive and another. The standard International Union of Pure and Applied Chemistry (IUPAC) conditions set the temperature at 0 °C or 273 K, and the pressure at 1 atm. These conditions are known as 'Standard, Temperature and Pressure', (STP). Under these standard conditions one mole of gas will occupy 22.4 dm^3, which is known as the molar gas volume. The volume of gas V produced from an explosive during detonation can be calculated from its equation of decomposition, an example of which is shown below for RDX.

$$C_3H_6N_6O_6(s) \rightarrow 3CO(g) + 3H_2O(g) + 3N_2(g) \qquad \textbf{(4-17)}$$

The production of water will be turned into steam as the temperature of explosion will be very high, therefore water will be regarded as a gaseous product. From the equation above it can be seen that 9 moles of gas are produced from one mole of RDX. Therefore 9 moles of gas will occupy 201.6 dm^3 and one kilogram of RDX will produce 907.6 dm^3 kg^{-1} of gas at STP as shown in the calculation below:

1 mole of gas at STP will occupy 22.4 dm^3
9 moles of gas will occupy 22.4 x 9 = 201.6 dm^3
Therefore 1 mole of RDX produces 201.6 dm^3 of gas
1 kilogram of RDX produces

$$V = \frac{201.6}{222.117} \, x1000 = 907.6 \, dm^3 \, kg^{-1}$$

where the molecular mass of RDX is 222.117.

Table 4-5 presents the calculated volumes of gases produced by some explosive substances at STP.

Table 4-4 Heat of Explosion and Heat of Detonation for Some Primary and Secondary Explosives[1]

Explosive substance	Empirical formula	ΔH_d/kJ mol^{-1}	Q_v/kJ kg^{-1}
Primary explosives			
Mercury fulminate	$HgC_2N_2O_2$	-500.00	1756.70
Lead styphnate	$PbC_6H_3N_3O_9$	-868.00	1853.49
Lead azide	PbN_6	-469.00	1610.36
Tetrazene	$C_2H_8N_{10}O$	-310.04	1647.79
Secondary explosives			
Nitroglycerine	$C_3H_5N_3O_9$	-1414.40	6228.46
Nitrocellulose (14.14%N)	$C_6H_7O_{11}N_3$	-1281.37	4312.84
EGDN	$C_2H_4N_2O_6$	-1021.31	6716.30
PETN	$C_5H_8N_4O_{12}$	-1838.37	5815.08
RDX	$C_3H_6N_6O_6$	-1127.36	5075.50
HMX	$C_4H_8N_8O_8$	-1484.44	5012.30
Nitroguanidine	$CH_4N_4O_2$	-260.31	2501.36
Picric acid	$C_6H_3N_3O_7$	-756.28	3301.02
Tetryl	$C_7H_5N_5O_8$	-1246.35	4340.50
TATB	$C_6H_6N_6O_6$	-902.89	3497.52
NTO	$C_2H_2N_4O_3$	-362.08	2783.90
TNAZ	$C_3H_4N_4O_6$	-1131.86	5891.01
CL-20	$C_6H_6N_{12}O_{12}$	-2609.59	5955.43
FOX-12	$C_2H_7N_7O_5$	-591.54	2828.70
FOX-7	$C_2H_4N_4O_4$	-574.71	3881.13
HNS	$C_{14}H_6N_6O_{12}$	-1798.46	3994.48
TNT	$C_7H_5N_3O_6$	-929.34	4091.63

Table 4-5 Calculated Volume of Gas Produced by Some Explosives at STP(1)

Explosive substance	Decomposition products	V/dm^3 kg^{-1}
Nitroglycerine	$3CO_2(g) + 2½H_2O(g) + ½O(g) + 1½N_2(g)$	739.80
Nitrocellulose (14.14%N)	$4½CO(g) + 1½CO_2(g) + 3½H_2O(g) + 1½N_2(g)$	821.79
EGDN	$2CO_2(g) + 2H_2O(g) + N_2(g)$	736.53
PETN	$2CO(g) + 3CO_2(g) + 4H_2O(g) + 2N_2(g)$	779.41
RDX	$3CO(g) + 3H_2O(g) + 3N_2(g)$	907.63
HMX	$4CO(g) + 4H_2O(g) + 4N_2(g)$	908.12
Nitroguanidine	$CO(g) + H_2O(g) + H_2(g) + 2N_2(g)$	1076.22
Picric acid	$5½CO(g) + ½C(s) + 1½H_2O(g) + 1½N_2(g)$	831.06
Tetryl	$5½CO(g) + 1½C(s) + 2½H_2O(g) + 2½N_2(g)$	819.90
TATB	$3CO(g) + 3C(s) + 3H_2O(g) + 3N_2(g)$	780.94
NTO	$2CO(g) + H_2O(g) + 2N_2(g)$	861.13
TNAZ	$2CO(g) + CO_2(g) + 2H_2O(g) + 2N_2(g)$	816.29
CL-20	$3CO(g) + 3CO_2(g) + 3H_2O(g) + 6N_2(g)$	766.80
FOX-12	$2CO(g) + 3H_2O(g) + ½H_2(g) + 3½N_2(g)$	964.04
FOX-7	$2CO(g) + 2H_2O(g) + 2N_2(g)$	907.63
HNS	$9CO(g) + 5C(s) + 3H_2O(g) + 3N_2(g)$	746.28
TNT	$3½CO(g) + 3½C(s) + 2½H_2O(g) + 1½N_2(g)$	739.65

4.5 EXPLOSIVE POWER AND TNT EQUIVALANCE

4.5.1 Explosive Power

In an explosive reaction heat and gases are liberated. The volume of gas *V* and the heat of explosion *Q* can both be calculated independently but these values can be combined to give the value for the explosive power as shown in Equation (4-18).

$$Explosive\ Power = Q\ x\ V \tag{4-18}$$

4.5.2 Power Index

The value for the explosive power can be compared to the explosive power of a standard explosive (picric acid) resulting in the power index, as shown in Equation (4-19), where $Q_{picric\ acid}$ and $V_{picric\ acid}$ are 3301.02 kJ kg^{-1} and 831.06 dm^3 kg^{-1} respectively.

$$Power\ Index = \frac{Q\ x\ V}{Q_{picric\ acid}\ x\ V_{picric\ acid}}\ x\ 100 \tag{4-19}$$

4.5.3 TNT Equivalence

The value for explosive power can also be compared to the explosive power of TNT resulting in the TNT equivalence value as shown in Equation (4-20). The term "TNT equivalence" is a normalisation technique for equating properties of an explosive to TNT, the standard. There are many ways to calculate "TNT equivalence" and the term is often misused because the property in question and basis for the equivalence are not defined.

$$TNT\ equivalence = \frac{Q\ x\ V}{Q_{\ TNT}\ x\ V_{TNT}} \tag{4-20}$$

The explosive power, power index and TNT equivalence of some primary and secondary explosives are presented in

Table 4-6. As expected the values for the power, power index and TNT equivalence of secondary explosives are much higher than the values for primary explosives.

4.6 TEMPERATURE OF DETONATION

When an explosive detonates the reaction is extremely fast and, initially, the gases do not have time to expand to any great extent. The heat liberated by the explosion will raise the temperature of the gases which will in turn cause them to expand and work on the surroundings to give a 'lift and heave effect'. The effect of this heat energy on the gas can be used to calculate the temperature of explosion.

The temperature of explosion T_e is the maximum temperature which the explosion products can attain under adiabatic conditions. It is assumed that the explosive at an initial temperature T_i is converted to gaseous products which are also at the initial temperature T_i. The temperature of these gaseous products is then raised to T_e by the heat of explosion Q. Therefore the value of T_e will depend on the value of $\underline{Q}$ and on the separate molar heat capacities of the gaseous products as shown in Equation (4-21), where C_v is the molar heat capacities of the products at constant volume and Σ represents the summation of the heat capacity integrals corresponding to the separate components of the gas mixture.

$$Q = \Sigma \int_{T_i}^{T_e} C_v . dT \qquad \textbf{(4-21)}$$

The rise in temperature of the gases is calculated by dividing the heat generated $\underline{Q}$ by the mean molar heat capacity of the gases at constant volume ΣC_v as shown in Equation (4-22), where T_i is the initial temperature.

$$T_e = \frac{Q}{\Sigma C_v} + T_i \qquad \textbf{(4-22)}$$

Table 4-6 The Calculated Explosive Power, Power Index and TNT Equivalence of Some Explosives[1]

Explosive substance	Qv/ kJ kg^{-1}	V/ dm^3 kg^{-1}	Explosive Power*	Power index/%	TNT Equiv.
Primary explosives					
Mercury fulminate	1756.70	215	37.77	13.77	0.12
Lead styphnate	1853.49	301	55.79	20.34	0.19
Lead azide	1610.36	218	35.11	12.80	0.16
Secondary explosives					
Nitroglycerine	6228.46	739.80	460.78	167.97	1.52
Nitrocellulose (14.14%N)	4312.84	821.79	354.42	129.19	1.17
EGDN	6716.30	736.53	494.68	180.32	1.63
PETN	5815.08	779.41	453.23	165.21	1.50
RDX	5075.50	907.63	460.67	167.92	1.52
HMX	5012.30	907.63	454.99	165.85	1.50
Nitroguanidine	2501.36	1076.22	269.20	98.13	0.89
Picric acid	3301.02	831.06	274.33	100.00	0.91
Tetryl	4340.50	819.90	355.88	129.73	1.18
TATB	3497.52	780.94	273.13	99.56	0.90
NTO	2783.90	861.13	239.73	87.39	0.79
TNAZ	5891.01	816.29	480.88	175.29	1.59
CL-20	5955.43	766.80	456.66	166.46	1.51
FOX-12	2828.70	964.04	272.70	99.41	0.90
FOX-7	3881.13	907.63	352.26	128.41	1.16
HNS	3994.48	746.28	298.10	108.66	0.98
TNT	4091.63	739.65	302.64	110.32	1.00

*Q x V $x10^4$/kJ dm^3 kg^{-2}

Table 4-7 Mean Molar Heat Capacities at Constant Volume (C_v) J mol^{-1} K^{-1}[1]

Temp (K)	CO_2	CO	H_2O	H_2	N_2
2000	45.371	25.037	34.459	22.782	24.698
2100	45.744	25.204	34.945	22.966	24.866
2200	46.087	25.359	35.413	23.146	25.025
2300	46.409	25.506	35.865	23.322	25.175
2400	46.710	25.640	36.292	23.493	25.317
2500	46.991	25.769	36.706	23.665	25.451
2600	47.258	25.895	37.104	23.832	25.581
2700	47.509	26.012	37.485	23.995	25.703
2800	47.744	26.121	37.849	24.154	25.820
2900	47.965	26.221	38.200	24.309	25.928
3000	48.175	26.317	38.535	24.260	26.029
3100	48.375	26.409	38.861	24.606	26.129
3200	48.568	26.502	39.171	24.748	26.225
3300	48.748	26.589	39.472	24.886	26.317
3400	48.924	26.669	39.761	25.025	26.401
3500	49.091	26.744	40.037	25.158	26.481
3600	49.250	26.819	40.305	25.248	26.560
3700	49.401	26.891	40.560	25.405	26.635
3800	49.546	26.962	40.974	25.527	26.707
3900	49.690	27.029	41.045	25.644	26.778
4000	49.823	27.091	41.271	25.757	26.845
4500	50.430	27.372	42.300	26.296	27.154
5000	50.949	27.623	43.137	26.769	27.397

The mean molar heat capacities of the gaseous products vary with temperature in a non-linear manner. Some gaseous products at various temperatures are presented in

Table 4-7.

Using this information the heat liberated by an explosion at various temperatures can be calculated. T_e can then be determined from a graphical representation of T_e versus Q, as shown in the example below.

The heat (energy) liberated Q during an explosion of RDX was calculated earlier to be 1127.36 kJ mol^{-1}. This heat is then used to raise the temperature of 1 mole of the gaseous products from their initial temperature T_i to their final temperature T_e. Let us assume that the temperature of explosion T_e equals 3500 K and the initial temperature equals 300 K. The heat liberated by the explosion of RDX at a temperature of 3500 K is calculated from the mean molar heat capacities (C_v) of the gaseous products at 3500K as shown below.
Mean molar heat capacities (C_v) at 3500 K, using

Table 4-7 are:

CO = 26.744 J mol^{-1} K^{-1}
H_2O = 40.037 J mol^{-1} K^{-1}
N_2 = 26.481 J mol^{-1} K^{-1}

Heat liberated by the explosion RDX at 3500K = Q_{3500K} = (ΣC_v) x (T_e -T_i)

Q_{3500K} = [(3x26.744) + (3x40.037) + (3x26.481)] x (3500-300)
Q_{3500K} = 895315 J mol^{-1}
Q_{3500K} = 895.3 kJ mol^{-1}

The calculated value of Q_{3500K} is 895.3 kJ mol^{-1} which is too low since the heat liberated during an explosion of RDX is 1127.36 kJ mol^{-1}. Therefore the temperature of explosion must be higher. Let us now assume that T_e equals 4500K, the heat liberated by the explosion of RDX at this higher temperature is calculated to be 1220.0 kJ mol^{-1} as shown below.

Mean molar heat capacities (C_v) at 4500 K are:

CO = 27.372 J mol^{-1} K^{-1}
H_2O = 42.300 J mol^{-1} K^{-1}
N_2 = 27.154 J mol^{-1} K^{-1}

Q_{4500K} = [(3x27.372) + (3x42.300) + (3x27.154)] x (4500-300)
Q_{4500K} = 1220007.6 J mol^{-1}
Q_{4500K} = 1220.0 kJ mol^{-1}

This value of Q_{4500K} is too high since the heat liberated during an explosion of RDX is 1127.36 kJ mol^{-1}. By calculating the values of Q at various temperatures of T_e a graph can be drawn and the correct value for T_e can be obtained as shown in Figure 4-8. From this the value for the temperature of explosion for RDX is found to be ~4215 K.

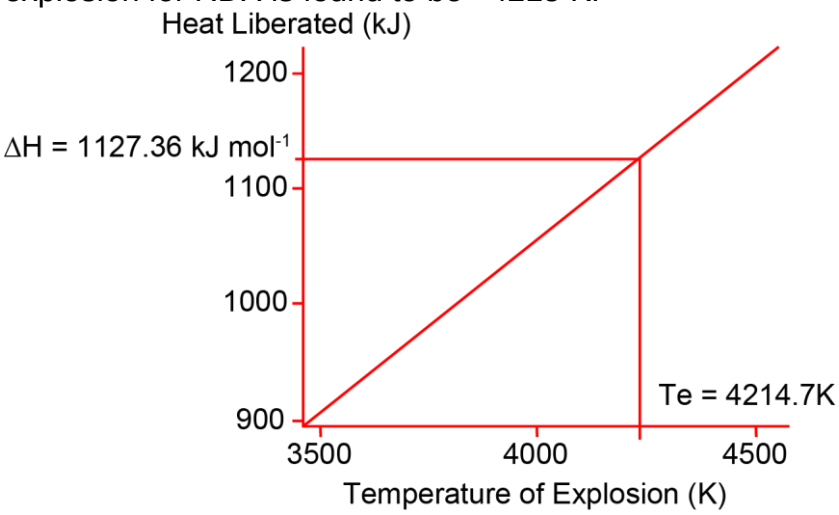


Figure 4-8 Calculated values of heat liberated at various temperatures of explosion using C_v for RDX[1]

These calculations were based on mean molar heat capacities at a constant volume (C_v). However the enthalpies of formation and therefore heats of explosion were based on values at constant pressure. It is possible to convert the mean molar heat capacities at a constant volume (C_v) to the mean molar heat capacities at a constant pressure (C_p) using Equation (4-23)[2] where R is the gas constant (8.3145 J mol^{-1} K^{-1}).

$$C_p = C_v + R \qquad \textbf{(4-23)}$$

The calculated C_p values are presented in Table 4-8 and the recalculated values for T_e using this Table are shown below.

Mean molar heat capacities (C_p) at 3500 K:

CO = 35.058 J mol^{-1} K^{-1}
H_2O = 48.351 J mol^{-1} K^{-1}
N_2 = 34.795 J mol^{-1} K^{-1}

Heat liberated by the explosion RDX at 3500K = Q_{3500K} = (ΣC_p) x (T_e -T_i)

Q_{3500K} = [(3x35.058) + (3x48.351) + (3x34.795)] x (3500-300)
Q_{3500K} = 1134758 J mol^{-1}
Q_{3500K} = 1134.8 kJ mol^{-1}

The calculated value of Q_{3500K} is 1134.8 kJ mol^{-1} which is too high since the heat liberated during an explosion of RDX is 1127.36 kJ mol^{-1}. Therefore the temperature of explosion must be lower when using C_p values. Now assume that T_e equals 3000K, then the heat liberated by the explosion of RDX at this lower temperature is calculated to be 938.2 kJ mol^{-1} as shown below.

Mean molar heat capacities (C_p) at 3000 K

CO = 34.631 J mol^{-1} K^{-1}
H_2O = 46.849 J mol^{-1} K^{-1}
N_2 = 34.343 J mol^{-1} K^{-1}

Q_{3000K} = [(3x34.631) + (3x46.849) + (3x34.343)] x (3000-300)
Q_{3000K} = 938166.3 J mol^{-1}
Q_{3000K} = 938.2 kJ mol^{-1}

This value of Q_{3000K} is too low since the heat liberated during an explosion of RDX is 1127.36 kJ mol^{-1}. The value for T_e can now be measured from the graph in Figure 4-9, which gives a value of 3481 K.

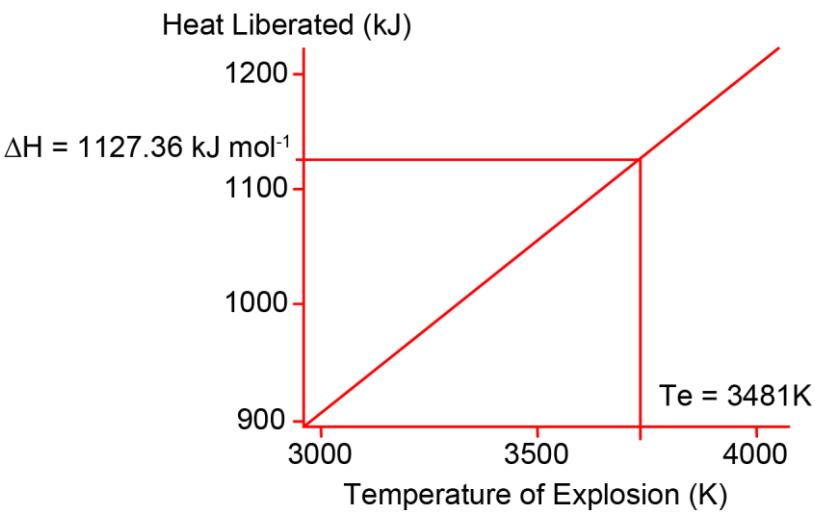


Figure 4-9 Calculated values of heat liberated at various temperatures of explosion for RDX using C_p

Therefore, when using C_p instead of C_v to calculate the temperature of explosion, a lower T_e value is obtained because the values for the mean molar heat capacities C_p is higher compared to C_v.

Table 4-8 Mean Molar Heat Capacities at Constant Pressure (C_p) J mol^{-1} K^{-1}

Temp (K)	CO_2	CO	H_2O	H_2	N_2
2000	53.685	33.351	42.773	31.096	33.012
2100	54.058	33.518	43.259	31.28	33.18
2200	54.401	33.673	43.727	31.46	33.339
2300	54.723	33.82	44.179	31.636	33.489
2400	55.024	33.954	44.606	31.807	33.631
2500	55.305	34.083	45.02	31.979	33.765
2600	55.572	34.209	45.418	32.146	33.895
2700	55.823	34.326	45.799	32.309	34.017
2800	56.058	34.435	46.163	32.468	34.134
2900	56.279	34.535	46.514	32.623	34.242
3000	56.489	34.631	46.849	32.574	34.343
3100	56.689	34.723	47.175	32.92	34.443
3200	56.882	34.816	47.485	33.062	34.539
3300	57.062	34.903	47.786	33.2	34.631
3400	57.238	34.983	48.075	33.339	34.715
3500	57.405	35.058	48.351	33.472	34.795
3600	57.564	35.133	48.619	33.562	34.874
3700	57.715	35.205	48.874	33.719	34.949
3800	57.86	35.276	49.288	33.841	35.021
3900	58.004	35.343	49.359	33.958	35.092
4000	58.137	35.405	49.585	34.071	35.159
4500	58.744	35.686	50.614	34.61	35.468
5000	59.263	35.937	51.451	35.083	35.711

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