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Effect of endothermic reactions associated with lightning on atmospheric chemistry

Shivkumar Chopkar
Artificial Rainfall Research Foundation, Sant Chokhaba Ward, Hinghanghat, Wardha (Maharashtra) 442 301

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Lightning creates high temperature which breaks N_2 and O_2 and form NO and O_3 through an endothermic process. These endothermic reactions absorb large amount of heat energy from the surroundings, as a result of which cooling may take place. An estimation of cooling produced has been made in this paper. The cooling thus produced may lead to several effects in the atmosphere; one among them could be an increase in rainfall rates.

1 Introduction

Nitrogen (78%) and oxygen (21%) are two major gases which exist in the atmosphere. Thunderstorm electric discharge or lightning creates high temperature up to 3000 K. At high temperature, N_2 and O_2 bonds break out into active [N] and [O]:

$$N \equiv N \rightarrow 2[N] \quad \ldots (1)$$

$$O = O \rightarrow 2[O] \quad \ldots (2)$$

Under normal conditions these [N] and [O] form NO and O_3 as follows :

$$O + O_2 + M \rightarrow O_3 + M \quad \ldots (3)$$

$$N + O_2 \rightarrow NO + O \quad \ldots (4)$$

Reactions (3) and (4) are exothermic. However, at the high temperature of lightning (~ 3000 K), formation of NO and O_3 from N and O are also endothermic[1]. In the present paper, a model estimation is made about how much heat energy is available in the lightning channel and how much heat energy is required for the reactions (3) and (4). Calculations also show that energy in the latter is larger than the former. An implication of this finding is also reported in this paper.

2 Model calculations

In thunderclouds, on an average, 70 flashes occur per minute and they are well distributed. For the sake of simplicity, let us consider the process occurring inside one lightning flash which is equivalent to one channel. In this paper, a lightning channel is considered in the atmosphere with 5 km length in between clouds and a diameter of 0.15 m, at a height of 5.5 km from the ground level. Within thunderclouds, the relative humidity exceeds 90%, pressure is 550 mbar and temperature is −2°C.

Therefore, the total volume of fluid in the channel is 88.31 m³. The density of clouds is found to be 0.6 kg/m³ at temperature −2°C and at pressure 550 mbar. Thus, the weight of fluid in the said cloud channel is 52.98 kg.

Saturation mixing ratio of water vapour over dry air at temepratute −2°C and at pressure 550 mbar is 6.09 g/kg (Smithsonian Tables for Meteorology). Therefore, weight of water vapour in the said channel is 322.68 g. Mixing ratio of solid particles over dry air in the clouds is 5.10 g/kg at temperature −2°C and pressure 550 mbar. Therefore, weight of the solid particles contained in the said cloud channel is 270.19 g. The total weight of water vapour and solid particles in the said cloud channel is 592.87 g at temperature −2°C and pressure 550 mbar, which is the general conditions of clouds in the atmosphere. Water vapour concentration in excess of 7 g of water per kg of dry air (7 g/kg to 17 g/kg) is required generally for warm season thunderstorm formation, although lightning has been reported in winter clouds[2].

So, the water vapour/solid particles mixing ratio, on an average, is 12 g/kg of dry air in thunderstom formation. Therefore, 592.87 g of water vapour/solid particles mix with 49.4 kg of dry air for thunderclouds formation in the atmosphere. Density of air is found to be 0.70 kg/m³ at temperature −2°C and pressure 550 mbar in the atmosphere. Therefore, volume of dry air in the said channel is 70.57 m³ in thunderclouds formation. Thus the weight of water vapour/solid particles contained in the said channel in thunderstorm formation is 3.58 kg.

2.1 Heat released from thunderstorm electric discharge or lightning in the atmospheric channel

Thunderstorm electric discharge or lightning creates high temperature up to 3000 K and releases large amount of heat energy. Some amount of heat energy is dissipated by radiation and some is used up for warming the surrounding atmosphere that exists in the air and breaks the nitrogen and oxygen bonds into active nitrogen and oxygen in the atmosphere.

The heat energy generated due to lightning in the channel can be estimated from the following expression.

$$Q_1 = (M_1 S_1 T_1)_{\text{water vapour}} + (M_2 S_2 T_2)_{\text{air}} \quad \ldots (5)$$

where,

- M_1 Mass of water vapour in the said channel (3.58 kg)
- S_1 Specific heat of water vapour (0.661)
- T_1 Rise in temperature of water vapour (3000 K)
- M_2 Mass of air in the said channel (49.4 kg)
- S_2 Specific heat of air (0.237)
- T_2 Rise in temperature of air (3000 K).

Therefore, with the values given in the parentheses for different parameters, we get

$$Q_1 = 4.22 \times 10^4 \text{ kcal}$$

Out of generated heat, a portion Q_2 is lost due to radiation and is given by

$$Q_2 = e.\sigma.T^4 \quad \ldots (6)$$

where, e is the emissivity of the radiative body (0.8), σ the Stefan's constant (5.669×10^{-5} erg s^{-1} cm^{2}K^4), and T the absolute temperature of the body (3000 K).

Therefore, with the above values in the parenthesis we have

$$Q_2 = 87.74 \text{ cal}$$

Heat loss due to radiation is negligible, because lightning appeared in a fraction of a second. Hence, the net heat energy retained by lightning in the channel is $Q = 4.2 \times 10^4$ kcal which is utilized for breaking nitrogen and oxygen bonds and produces atomic nitrogen and atomic oxygen in active state. These active nitrogen and oxygen react and form NO and O_3 as follows :

$$N_2 + O_2 \rightleftharpoons 2\,NO - \triangle H \quad \ldots (7)$$
$$(\triangle H = 43.2 \text{ kcal/mol})$$

and

$$3\,O_2 \rightleftharpoons 2\,O_3 - \triangle H \quad \ldots (8)$$
$$(\triangle H = 67.6 \text{ kcal/mol})$$

Reactions (7) and (8) are endothermic and heat energy is required for these endothermic reactions to occur.

2.2 Heat absorption in endothermic reactions

We have considered that the volume of dry air is 70.57 m^3 in the said channel. Therefore, the volumes of nitrogen and oxygen present in the channel are 70.57×0.78 m^3 and 70.57×0.21 m^3, respectively.

2.2.1 *Calculation of number of molecules of N_2 and O_2 in the atmospheric channel* — We know that Avagadro's number of molecules (6.024×10^{23}) is contained in 22.4 litres of any gas at N.T.P. Therefore, 10.98×10^{23} molecules of gas are contained in 40.83 litres of any gas at temepratute −2°C and pressure 550 mbar.

Hence, 70.57×780 litres of nitrogen will contain 14.8×10^{26} molecules of nitrogen in the said channel. Therefore, number of nitrogen moles contained in the said channel is

$$n_1 = 2.35 \times 10^3 \quad \ldots (9)$$

Similarly, 70.57×210 litres of oxygen will contain 3.98×10^{26} molecules of oxygen and the number of oxygen moles contained in the said channel will be

$$n_2 = 6.6 \times 10^2 \quad \ldots (10)$$

In the reaction

$$N_2 + O_2 \rightarrow 2NO - \triangle H$$
(n moles of $N_2 + n$ moles of $O_2 \rightarrow 2n$ moles of NO − $n\triangle H$)

4.4% of nitric oxide is formed at 3000 K in an electric arc[1]. Therefore, approximately 100 moles of nitrogen take part in NO formation, i.e.

100 moles of N_2 + 100 moles of $O_2 \rightarrow$
2×100 moles of NO − 100 $\triangle H$

Hence, heat absorbed during NO formation in the said channel is $H_1 = 4.32 \times 10^3$ kcal. Further, 557 moles of oxygen remaining in the said channel are consumed for ozone formation according to the following reaction :

$$3\,O_2 \rightarrow 2\,O_3 - \triangle H$$
($3n$ moles of $O_2 \rightarrow 2n$ moles of O_3 − $n\,\triangle H$)

About 10% of O_3 is formed at 3000 K in an electric arc[3]. Therefore, approximately 60 moles of oxygen take part in ozone formation, i.e.

$$3 \times 60 \text{ moles of } O_2 \rightarrow 2 \times 60 \text{ moles of } O_3 - 60\,\triangle H$$

Hence, heat energy absorbed during ozone formation in the said channel is $H_2 = 4.05 \times 10^3$ kcal. Thus, the total heat energy absorbed from surrounding by endothermic reactions is $H = 8.37 \times 10^3$ kcal. It is found that, out of 2.35×10^3 moles of nitrogen and 6.60×10^2 moles of oxygen in the said atmospheric channel, a total of 100 moles of nitrogen and 160 moles of oxygen have taken part in both the reations.

2.3 Calculation for bonds breaking energy

Bonds strength in diatomic molecules of nitrogen[4] is

$$N - N \rightarrow 226.8 \text{ kcal/mol.}$$

Therefore, 2.26×10^4 kcal of heat energy is utilized for breaking 100 moles of nitrogen.

Bond strength in diatomic molecules of oxygen[4] is

$$O - O \rightarrow 118.86 \text{ kcal/mol.}$$

Therefore, 1.90×10^4 kcal of heat energy is utilized for breaking 160 moles of oxygen.

Hence, a total of $\sim 4.16 \times 10^4$ kcal of heat energy is utilized for breaking oxygen and nitrogen bonds in the said lightning channel and is taken from $\sim 4.22 \times 10^4$ kcal of lightning energy generated in the lightning channel.

In this way $\sim 6.0 \times 10^2$ kcal of heat energy remain in the lightning channel.

3 Results and discussion

The typical thunderclouds are shown in Fig.1. It is shown that the endothermic reactions absorb large amount of heat energy ($\sim 8.37 \times 10^3$ kcal) which is more than the heat energy ($\sim 6.0 \times 10^2$ kcal) remained in the lightning channel. Thus, it is likely that the temperaturte of the region would fall.

3.1 Heat energy compared to dew point

The cooling thus produced may increase the water vapour pressure of the region. In that process dew point may be reached, which would lead to more precipitation. When temperature of 3.58 kg of water vapour contained in that said channel comes down from 100°C to 0°C and then to dew point at −8°C, the amount of heat released would be

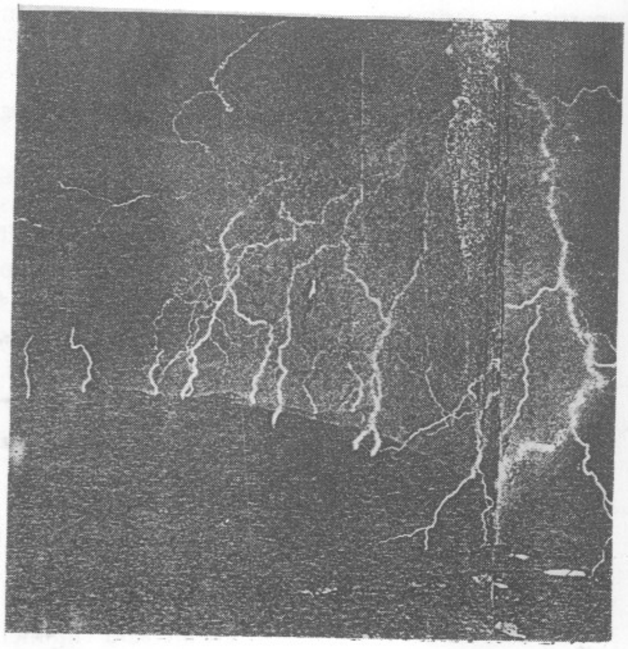

Fig. 1—Typical thunderclouds

$$Q_3 = M(t_2 - t_1) + M(t_3 - t_2) + ML \quad \ldots (11)$$

where,

$M = 3.58 \times 10^3$ gm; $t_1 = 100$°C; $t_2 = 0$°C; $t_3 = -8$°C; $L = 540$ cal/gm/0°C

i.e.,

$$Q_3 = 1.58 \times 10^3 \text{ kcal}$$

This amount ($\sim 1.58 \times 10^3$ kcal) is much less than the heat energy ($\sim 8.37 \times 10^3$ kcal) required for endothermic reactions in the said channel. Therefore, it is expected that the endothermic reactions will affect not only the inside of the said channel, but also the surrounding atmosphere. Thus, one may conclude that the endothermic reactions absorb large amount of heat from the surroundings, produce super cooling and achieve the dew point of the water vapour in the atmosphere.

The present approach does not, however, violate the second law of thermodynamics. The high temperature produced due to lightning breaks N_2 and O_2 into 2[N] and 2[O] in active states. The lightning energy is, thus, used up in this process. After this reaction, the temperature of this region will start falling down, when NO and O_3 will start forming. For the latter processes, heat energy will be absorbed from the surrounding. As the temperature of the region starts falling down, the water vapour pressure of the region increases. Then the dew point is reached which leads to more precipitation.

3.2 Indirect evidences

The rainforming mechanism suggested above has several indirect evidences.

A number of radar observations have already been reported as to where intense precipitation was not even present in the clouds before the first discharge, but it developed abruptly in the same regions after discharge from which the lightning flashes originated (Ref.1 and Refs there in). Blevins and Marwitz (within Ref.1, 1968), investigating the incidence of lightning flashes during hail storms, found that storms having high flashing rates were the most likely ones to produce hails. They noted a limiting rate of 70 lightning flashes per minute. Louis Battan[5] showed that the very rapid growth of precipitation particles/ice crystals is caused by electrical forces following a lightning discharge. In many cases, the onset of strong electrification follows the appearance of heavy precipitation within the cloud in the form of hailstones[6].

The correlation between lightning and precipitation is given as follows: Heavy gushes of rain or hail often reach the ground 2-3 min after the lightning flash and it is evidenced that the lightning is the cause rather than the result of the rapid intensificatioin of the precipitation[7]. It is further speculated that the rapid intensification of the precipitation from about 1 mm/h to 50 mm/h in this 2-3 min period is brought about by a greatly accelerated rate of coalescence of water drops under the influence of electrical forces by a mechanism that is obscure and has no convincing experimental or theoretical bases[8]. Is it possible that this phenomenon is related to endothermic reactions associated with lightning ?

4 Conclusions

When precipitation in the atmosphere occurs due to lightning, the water droplets become the nuclei and form yet another set of rain drops which act as seeding and give rise to an appreciable increase in rainfall rates in the atmosphere.

If this finding is confirmed experimentally, then this knowledge may be used in developing technology for making artificial rain in the atmosphere.

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