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A kinetic theory model for rain out and wash out of soluble gaseous air pollutants

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सार – गैसों के अणुगति सिद्धान्त का प्रयोग करते हुए गैसीय वायु प्रदूषकों के विलयन के लिए एक नया सिद्धान्त प्रस्तुत किया गया है जो प्रक्षालन और वर्षण दोनों के लिए उपयुक्त है। यह दर्शाया गया है कि हेलस (1972) द्वारा दी गई गैसों की प्रक्षालन का वर्तमान सिद्धान्त यहां प्रस्तुत किए गए सामान्य सिद्धान्त का एक विशेष विषय है।

ABSTRACT. A new theory, using kinetic theory of gases, for dissolution of gaseous air pollutants and applicable both for wash out and rain out processes has been proposed. It has been shown that the current theory of wash out of gases given by Hales (1972) is a special case of the general theory proposed here.

Key words — Rain chemistry, air pollution, scavenging model and kinetic theory.

1. Introduction

Air pollutants are removed by rain by two processes rain out and wash out. In the first it is dissolved in the cloud. In the second process, the pollutants are removed by a scavenging process. This is applicable for both particulate and gaseous pollutants. Engelemann (1968) summarised earlier attempts on wash out of pollutants. It is found that in those days, scavenging of particulate and gaseous pollutants were mathematically treated in the same way. Postma (1970) pointed out that dissolution of gas by rain should be treated differently. Thus a salt particle may get dissolved in rain and the process is one way and not reversible. But dissolution of gas is a two way process and reversible. Thus, if we keep some distilled water in a chamber containing ammonia, the water dissolves ammonia and a solution of ammonia is formed. If we want to remove this, we take the solution to a cleaner environment and warm for some time. Ammonia goes away. Thus ammonia could dissolve in first instance and could come out of the same solution in the second instance. In case of a solution of sodium chloride, it would not have given out the salt by heating. On boiling, the water would have evaporated and salt would have been left back. In case of ammonia solution, the dissolved gas went out leaving water behind. Thus dissolution of gas is a reversible process; in one condition it is absorbed by water in another condition it comes out of the solution. This is the basis of Henry's law of solution of gases as given in Physical Chemistry.

Taking this concept Hales (1972) postulated the current theory of gas scavenging by rain. As regards rain out of gaseous pollutants Chang (1984) comments that there has been practically no attempt on rain out of gaseous pollutants. Mukherjee (1960) implicitly approached the rain out of gaseous pollutants when he proposed a model of removal of gaseous pollutants by fog.

Hales' (1972) theory has been modified by Hill and Adamowicz (1977) and Chang (1984), but the basic concept remains. The process assumed is as follows :

A rain drop is falling through air containing gaseous air pollutant. Somehow some gas dissolves at the surface of the drop so that in the immediate vicinity of the surface of the drop a concentration gradient of the gas developes. As a result more gas diffuses towards the drop and the process continues.

This physical process presumes the following :

(*i*) Somehow the gas enters into the rain drop but the exact process is never defined;

(*ii*) Concentration of gas is sufficiently high so that diffusion concept of continuous gradient of concentration can be used.

Thus in this concept, the first dissolution process is never defined. It is also felt that in the concentration range of gaseous pollutants in air, it is doubtful whether continuous gradient of concentration of the gas can be assumed. A cloud particle has a linear dimension of the same order as the mean free path of polluting gas molecules. Thus, at least the rain out process can not be treated by the diffusion mechanism.

To overcome these two deficiencies, a new theory has been proposed here.

2. Assumptions

This theory has been termed kinetic theory model for rain out and wash out processes for gaseous pollutants The following are the assumptions:

(1) In a certain volume there are cloud droplets and/or rain drops, moist air and gaseous pollutants.

(2) The gas molecules are in perpetual motion by virtue of which they often hit the surface of the cloud droplets and/or rain drops. Since gases are soluble this leads to the dissolution of the gas.

(3) The dissolution process starts right from the time the droplets start forming.

(4) Following Postma (1970) and Hales (1972) the dissoluton of gaseous pollutants is a reversible process and hence Herny's law is applicable (Hill and Adamowicz 1977).

(5) Thus, at any instant some gaseous molecules striking the drop surface may be captured, while some molecules escape from the solution through the same surface to air outside. The net capture of molecules at any instant will be the algebraic sum of the two processes.

(6) There is no chemical reaction involved.

Probably there may be a special case for the last assumption. Let us take ammonia, when it dissolves in water it forms a weak base

$$NH_3 + H_2O \leftrightharpoons NH_4OH$$
$$NH_4OH \leftrightharpoons NH_4^+ + OH^-$$

Thus the gas after dissolution has undergone some chemical change. But we know that in case of weak acid or weak base Arrhenius' law of ionic equilibrium is applicable. This means that all the processes are reversible. Thus if more NH_3 is dissolved, more NH_4OH would be formed by the second reaction more ammonium and hydroxyl ions will be formed. Again when we take the solution to a clear environment, NH_3 will go out of solution. The chemical equations above will then follow the reverse process. The result will be similar to absorption and desorption of the gas in the same manner as if no chemical reaction has occurred.

3. Basic equation

With these assumptions we may now derive the basic equation assuming static droplets, *i.e.*: only Brownian motion exists.

The rate of growth of a droplet of mass m_r and radius r is given by the equation

$$\frac{dm_r}{dt} = 4\pi r K_1 \triangle p \tag{1}$$

where, $\triangle p$ is the difference of vapour pressure of the environment and that at the surface of the droplet and K_1 is a constant.

At the same time the pollutant gas is striking the droplet; the rate of dissolution is given by

$$\frac{dS_r}{dt} = A\mu \, 4\pi r^2 \tag{2}$$

where, S_r is the mass of the gas dissolved, μ the mass of gas striking unit area in unit time, and A is the fraction of the gas molecules captured. As per kinetic theory of gases, the mass of gas striking unit area of the wall of the container is given as $\frac{\rho}{6}\sqrt{RT/\pi M_g}$ where, M_g is the molecular weight of the gas, ρ the density of the gas, T the absolute temperature and R the universal gas constant.

If we assume the density of the droplet is unity, we get,

$$m_r = \frac{4}{3}\pi r^3 \tag{3}$$

The concentration of the dissolved substance in terms of mass of dissolved gas per unit mass of the solvent is given by

$$C_r = S_r / m_r \tag{4}$$

From these equations we get

$$\frac{dC_r}{dr} = \frac{d}{dr}\left(\frac{S_r}{m_r}\right) = \frac{1}{m_r}\left\{\frac{dS_r}{dt}\cdot\frac{dt}{dm_r} - \frac{S_r}{m_r}\right\}\frac{dm_r}{dr}$$

Substituting the values from Eqns. (1), (2) and (3) we get

$$\frac{dC_r}{dr} = \frac{3A\mu}{\triangle p K_1} - \frac{3C_r}{r} \tag{5}$$

Again, we may write,

$$\frac{dC_r}{dt} = \frac{d}{dt}\left(\frac{S_r}{m_r}\right) = \frac{1}{m_r}\frac{dS_r}{dt} - \frac{S_r}{m_r}\frac{dm_r}{dt}$$

From Eqns. (1), (2) and (3) we get

$$\frac{dC_r}{dt} = \frac{3A\mu}{r} - \frac{3K_1 \triangle p C_r}{r^2} \tag{6}$$

From assumption (5) we may assume that the fraction of the gas molecules captured will be proportional to the unsaturation of the solution. Thus

$$A = a\,(C_s - C_r) \tag{7}$$

where, C_s is the saturation concentration of the gas at the given temperature and partial pressure and a is a constant.

The Eqns. (5) and (6) then become

$$\frac{dC_r}{dr} = \frac{3a\mu\, C_s}{K_1 \triangle p} - \frac{3a\mu\, C_r}{K_1 \triangle p} - \frac{3C_r}{r} \tag{8}$$

and

$$\frac{dC_r}{dt} = \frac{3a\mu\, C_s}{r} - \frac{3a\mu C_r}{r} - \frac{3K_1 \triangle p\, C_r}{r^2} \tag{9}$$

It should be mentioned here that inspite of attaining the saturation, the solution is still dilute. The mole fraction of the dissolved gas is given by :

$$X = \frac{\text{Moles of dissolved gas}}{\text{Moles of dissolved gas and moles of water}}$$

$$\approx \frac{\text{Moles of dissolved gas}}{\text{Moles of water}}$$

$$= \frac{S_r / M_g}{m / 18}$$

If we write

C_g= Bulk gas phase concentration, and C_g^* = Concentration of the gas in equilibrium with aqueous solution of dissolved gas at the given instant, we get, as per Henry's law

$$X_s = HC_g \text{ and } X_r = HC_g^* \qquad (10)$$

where, X_s=Mole fraction of the gas in saturated solution, X_r=Mole fraction of the gas in solution at that instant, and H=Henry's constant.
Thus we may write

$$\frac{dX_r}{dr} = \frac{3a\mu X_s}{K_1 \triangle p} - \frac{3a\mu X_r}{K_1 \triangle p} - \frac{3X_r}{r} \qquad (11)$$

and

$$\frac{dX_r}{dt} = \frac{3a\mu X_s}{r} - \frac{3a\mu X_r}{r} - \frac{3K_1 \triangle p X_r}{r^2} \qquad (12)$$

From Eqn. (10) we get

$$\frac{dX_r}{dr} = \frac{3a\mu HC_g}{K_1 \triangle p} - \frac{3a\mu X_r}{\triangle p \cdot K_1} - \frac{3\,X_r}{r} \qquad (13)$$

and

$$\frac{dX_r}{dt} = \frac{3a\mu HC_g}{r} - \frac{3a\mu X_r}{r} - \frac{3K_1 \triangle p X_r}{r^2} \qquad (14)$$

Thus we get two equations giving us variations of concentration of dissolved gaseous pollutant in cloud or rain connecting with the concentration of the gas in air. Eqns. (11) and (13) may be ignored in case of raindrops since their growth are no longer due to condensation process.

4. Correspondence with diffusion theory

Our model considers the dissolution of gas as discontinuous process. In the classical theory, using diffusion concept, it is a continuous process. The deficiencies of the diffusion concept have been shown earlier. It is clear from the derivation given above that the present model should be applicable for any concentration of pollutant gas in air. Only Eqns. (5), (3) and (13) refer to growing cloud droplet due to condensation and hence cannot be used when the growth has stopped.

The difference between the present approach and the diffusion models should be reduced or even neglected when the concentration of the pollutant is high. We shall now try to find out the correspondence between these two theories.

According to Hales (1972) and Chang (1984) the the mass flux of any gas to the droplet is given by:

$$F = K_g\,(C_g - C_g^*) \qquad (15)$$

where, F is the mass flux and K_g is the convective diffusive mass transfer coefficient.

Thus

$$F = A\mu = a\mu\,(C_s - C_r)$$

We have seen

$$X_s = H\,C_g = H\,18\,C_s/M_g$$

and $\quad X_r = HC_g^* = H\;18\,C_r/M_g$

or $\quad C_s = H\,M_g\,C_g/18$

and $\quad C_r = H\,M_g\,C_g^*/18$

Thus $\quad F = A\mu = a\mu\,(C_s - C_r)$

$$= \frac{a\mu M_g H}{18}\left(C_g - C_g^*\right)$$

Thus we get

$$K_g = a\mu M_g H/18$$

According to Adamowicz (1979) this is determined from the semi-empirical Frossling (1938) equation

$$S_h = 2 + 0.6\;R_e^{1/2}\,S_c^{1/3} \qquad (17a)$$

$$S_h = 2K_g\,r/D_r \qquad (17b)$$

$$R_e = 2r\,V_r/\nu \qquad (18)$$

and

$$S_c = \nu/D_g \qquad (19)$$

where, r is the radius of the drop, V_r is the terminal velocity of fall of raindrop, D_g is the diffusivity of the gas and ν is the kinematic viscosity of air. Here S_h stands for Sherwood number, R_e for Reynold number and S_c for Schmidt number.

Thus K_g=D_r/r for a static drop as considered in the present treatment. For a moving drop, therefore, corrections used by the diffusion approach be used in the present model. From this we can find out the value of a

we have

$$K_g = \frac{D_g}{r}\left(1 + 0{\cdot}3\;R_e^{\frac{1}{2}}\,S_c^{\frac{1}{3}}\right)$$

$$= \frac{a\mu M_g H}{18}$$

$$\text{or}\quad a = \frac{18\,D_g}{\mu\,r\,M_g H}\left(1 + 0.3\;R_e^{\frac{1}{2}}\,S_c^{\frac{1}{3}}\right) \qquad (20)$$

5. Rain out process

Let us consider the case when $\triangle p$ is high, *i. e.*, at the initial stage of formation of the cloud droplet. The Eqn. (6) indicates that the rate of dissolution of gas will be low. Since at this stage r is also small, we have from Eqn. (8)

$$dC_r/dr = -\,3C_r/r$$

or

$$dC_r/C_r = -\,3dr/r \qquad (21)$$

This means that small droplets will be more concentrated than the bigger ones. This, in turn, will reduce the vapour pressure of the drop, with increase in $\triangle p$ the condensation process will be accelerated. Thus the rain out process is helpful to the growth of cloud droplets.

As the condensation proceeds the growth of the drop will lower the value of $\triangle p$ and r will increase. In that case we have to use the full equations.

In the limit $\triangle p \to 0$ there will be no growth, then as per Eqn. (9),

$$\frac{dC_r}{dt} = -\frac{d(C_s - C_r)}{dt} = \frac{3a\,\mu(C_s - C_r)}{r} \qquad (22)$$

As with no growth r is constant, the equation gives that the unsaturation, *i. e.*, $(C_s - C_r)$ will decrease exponentially with time. Or in other words in the rain out process the concentration will level off to C_s.

In case $\triangle p$ becomes negative, *i. e.*, unsaturated air enters into an area of fog or cloud (due to advection or entrainment), we get as per Eqn. (6) an increase in concentration should take place. Physically it means that the droplet will start to evaporate so that the concentration will increase.

6. Wash out process

In wash out process, the raindrop is falling through a polluted air. The value of a should then be adjusted as per Eqn. (20). The rate of dissolution will be as per Eqn. (14). If the drop is falling through saturated air, $\triangle p$ will approach zero. In that case, again, Eqn. (22) has to be used.

If, however, a raindrop first washes out from a place and falls through a clean air, the value of C_g will approach zero. As per Eqn. (9) we then get $\lim C_g \to 0$, $\lim \triangle p \to 0$

$$\frac{dC_r}{dt} = -\frac{3a\mu C_r}{r} \qquad (23)$$

Since $\triangle p \to 0$, r is a constant. Hence C_r will decrease exponentially. This means that the raindrop will give out polluting gas. Thus a falling raindrop may pollute an unpolluted air, a condition which does not happen in case of particulate scavenging.

8. Conclusion

A new model for rain out and wash out of gaseous pollutants have been presented using kinetic theory of gases. This has a correspondence with the classical approach assuming diffusion. But it has advantage over the latter in so far as rain out process is concerned.

References

Adamowicz, R.F., 1979, "A model for the reversible wash out of sulfur dioxide, ammonia and carbon dioxide from a polluted atmosphere and the production of sulfates in raindrops", *Atm. Environ.*, **13**, pp. 105-121.

Chang, T.Y., 1984, "Rain and snow scavenging by raindrops", *Atm. Environ.*, **18**, pp. 191-197.

Engelmann, R.I., 1968, "The calculation of precipitation scavenging" in *Meteorology and Atomic Energy*, Ed D.H. Slade (U.S.A.E.C.), pp. 208-221.

Frossling, N., 1938, "The evaporation of falling drops", *Ger. Beit. Geophys.*, **52**, pp. 170-216.

Hales, J.M., 1972, "Fundamentals of theory of gas scavenging", *Atm. Environ.*, **6**, pp. 635-659.

Hill, F.B. and Adamowicz, R.F., 1977, "A model for composition and wash out of sulfur dioxide", *Atm. Environ.*, **11**, pp. 917-927.

Mukherjee, A.K., 1960, "Removal of soluble gaseous air pollutants by fog", *Indian J. Met. Geophys.*, **11**, pp. 318-319.

Postma, A.K., 1970, "Effect of solubility of gases on their scavenging by raindrops", *Precipitation Scavenging*, pp. 247-259, AEC Symp., **Ser. 22**, CONF. 700601.