Thermodynamic analysis of atmospheric deterioration of portland cement

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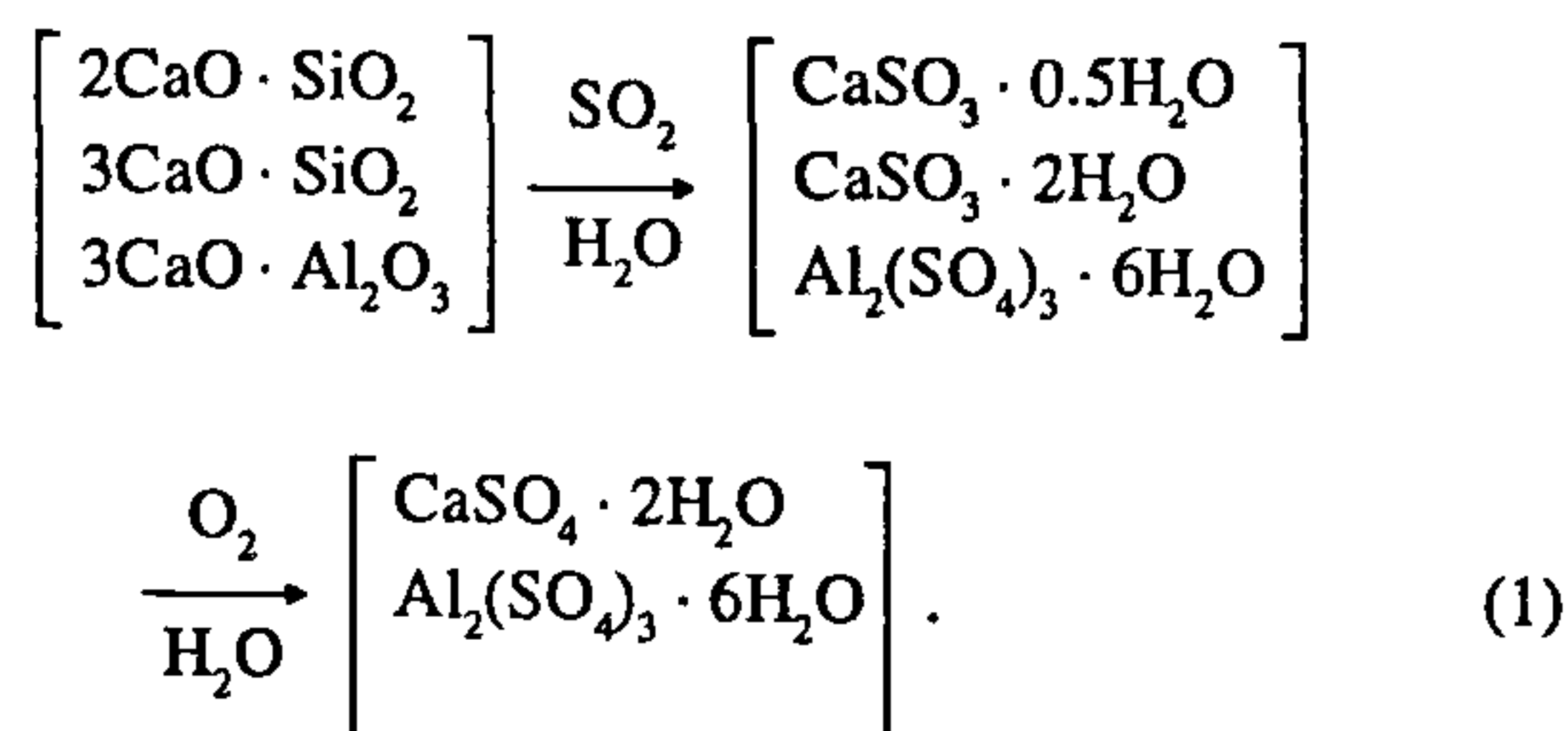Department of Chemistry, Dayalbagh Educational Institute, Dayalbagh, Agra 282 005, India

Using thermodynamic data, the effect of atmospheric SO_2 and acid deposition on the deterioration of portland cement has been estimated. Though increases with acid depositions, deterioration is possible under normal atmospheric conditions and even by natural rain. Cement deteriorates faster by reacting with SO_2 than with H^+.

THERE has been a growing interest in studying the deterioration of buildings. Largely, research reports are on deterioration processes, mechanisms and weathering rates of marble buildings[1,2]. Instead of marble, the buildings of present time are generally made up of concrete, of which cement is an important constituent. Studies concerning the deterioration of cemented buildings are quite scanty and no thermodynamic analysis is reported for such a decay. Dicalcium silicate (DCS, $2CaO \cdot SiO_2$), tricalcium silicate (TCS, $3CaO \cdot SiO_2$), and tricalcium aluminate (TCA, $3CaO \cdot Al_2O_3$) are three main constituents of portland cement, which form a hydrated colloid gel of unknown composition on setting of cement. The purpose of this paper is to estimate the thermodynamic equilibrium between DCS, TCS and TCA on the one hand, and gaseous SO_2 and H^+ of rain on the other, and to present a thermodynamic analysis of the effect of acid deposition on cement.

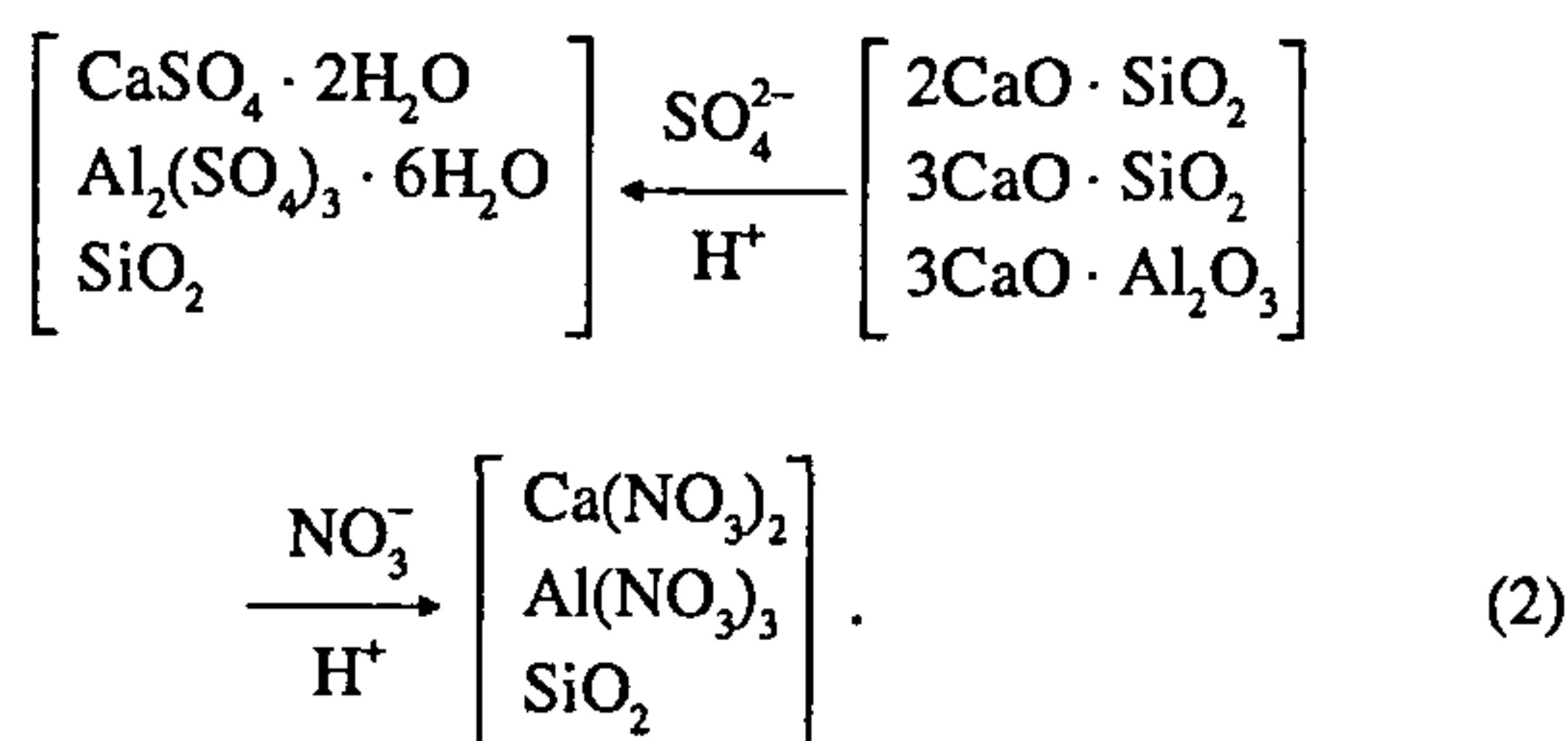## The deterioration of cement in atmosphere

The reaction of SO₂ with cement

The main damage to buildings is caused by the reaction between SO_2 gas deposited on or in the building surface and the building constituents, specially cement, which occurs in the presence of catalysts and under high relative humidity. Initially, the constituents of cement, i.e. DCS, TCS and TCA, are converted to calcium sulphite ($CaSO_3$), silica (SiO_2) and aluminium sulphate ($Al_2(SO_4)_3 \cdot 6H_2O$) by SO_2. In the presence of water vapour and other atmospheric catalysts, the process may get accelerated. $CaSO_3$ is then rapidly converted to calcium sulphate ($CaSO_4$), which may get hydrated to gypsum ($CaSO_4 \cdot 2H_2O$) by water and oxygen:

$$\begin{bmatrix} 2CaO \cdot SiO_2 \\ 3CaO \cdot SiO_2 \\ 3CaO \cdot Al_2O_3 \end{bmatrix} \xrightarrow[H_2O]{SO_2} \begin{bmatrix} CaSO_3 \cdot 0.5H_2O \\ CaSO_3 \cdot 2H_2O \\ Al_2(SO_4)_3 \cdot 6H_2O \end{bmatrix}$$

$$\xrightarrow[H_2O]{O_2} \begin{bmatrix} CaSO_4 \cdot 2H_2O \\ Al_2(SO_4)_3 \cdot 6H_2O \end{bmatrix} . \tag{1}$$

The reaction of H⁺ with cement

The pH of natural rain (when it is in equilibrium with atmospheric CO_2) is 5.6. However, the acidity of rain increases in the presence of industrial emissions of SO_2 and NO_x. Rain water may dissolve and absorb SO_2 and NO_x. On reaction with cement, SO_2 and NO_x may form gypsum ($CaSO_4 \cdot 2H_2O$), calcium nitrate ($Ca(NO_3)_2$), aluminium sulphate ($Al_2(SO_4)_3 \cdot 6H_2O$) and aluminium nitrate ($Al(NO_3)_3$). In addition, acid rain may also act as a solvent for these products[4,5]:

$$\begin{bmatrix} CaSO_4 \cdot 2H_2O \\ Al_2(SO_4)_3 \cdot 6H_2O \\ SiO_2 \end{bmatrix} \xleftarrow[H^+]{SO_4^{2-}} \begin{bmatrix} 2CaO \cdot SiO_2 \\ 3CaO \cdot SiO_2 \\ 3CaO \cdot Al_2O_3 \end{bmatrix}$$

$$\xrightarrow[H^+]{NO_3^-} \begin{bmatrix} Ca(NO_3)_2 \\ Al(NO_3)_3 \\ SiO_2 \end{bmatrix} . \tag{2}$$

Thermodynamic calculations

Under thermodynamic equilibrium, the standard Gibbs free energy depends on the equilibrium constant (K):
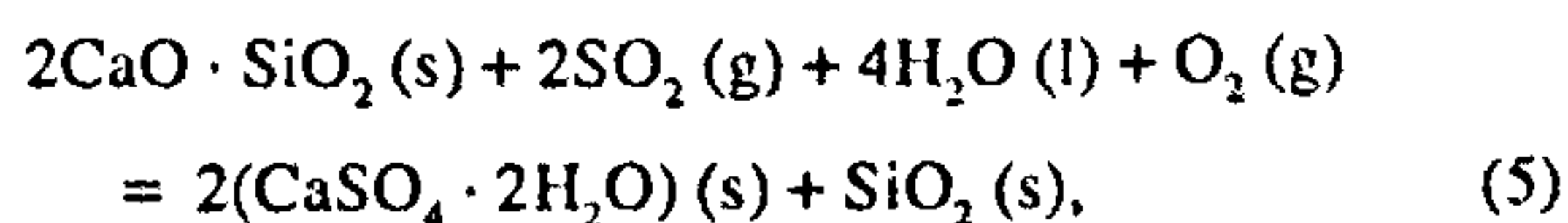
$$\Delta G^0 = -RT \ln K , \tag{3}$$

where T is the temperature and R the gas constant (1.98 cal mol^{-1} K^{-1}). At 298 K, equation (3) becomes

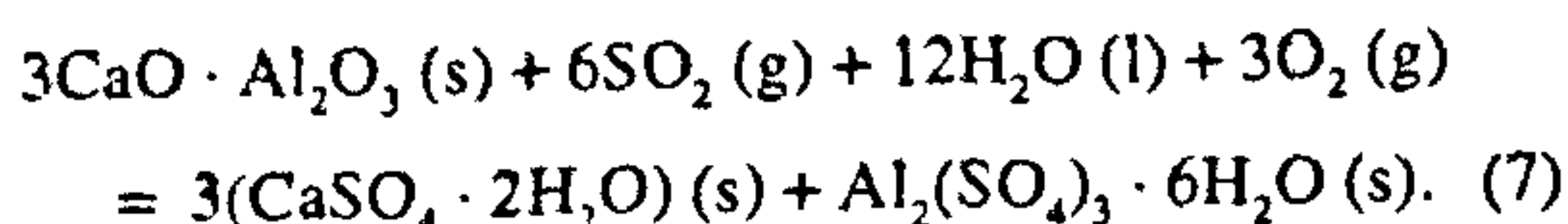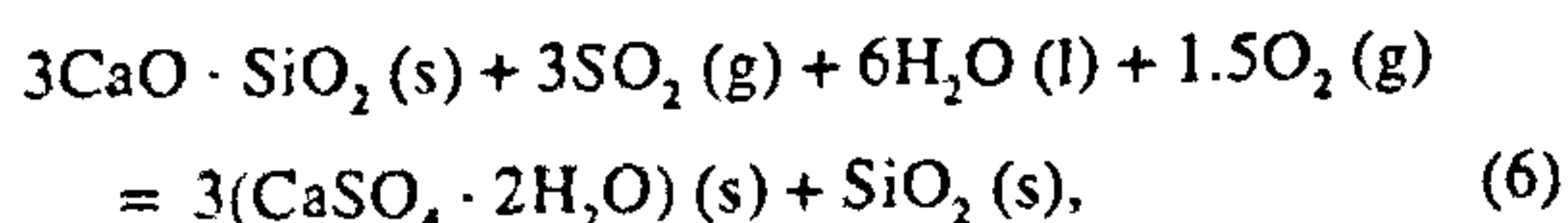$$\Delta G^0 = -1.36 \lg K . \tag{4}$$

The SO₂–cement system

Determination of ΔG⁰

The mass balance equations for the reaction between SO_2 and cement constituents (DCS, TCS and TCA) can be written from Equation (1):

$$2CaO \cdot SiO_2 \text{ (s)} + 2SO_2 \text{ (g)} + 4H_2O \text{ (l)} + O_2 \text{ (g)}$$
$$= 2(CaSO_4 \cdot 2H_2O) \text{ (s)} + SiO_2 \text{ (s)}, \tag{5}$$

$$3CaO \cdot SiO_2 \text{ (s)} + 3SO_2 \text{ (g)} + 6H_2O \text{ (l)} + 1.5O_2 \text{ (g)}$$

$$= 3(CaSO_4 \cdot 2H_2O) \text{ (s)} + SiO_2 \text{ (s)}, \qquad (6)$$

$$3CaO \cdot Al_2O_3 \text{ (s)} + 6SO_2 \text{ (g)} + 12H_2O \text{ (l)} + 3O_2 \text{ (g)}$$

$$= 3(CaSO_4 \cdot 2H_2O) \text{ (s)} + Al_2(SO_4)_3 \cdot 6H_2O \text{ (s)}. \quad (7)$$

Using thermodynamic data[6], the standard Gibbs free energy for reactions (5)–(7) can be calculated from equation (8); the values are -169.59, -272.76 and -467.44 kcal mol^{-1}, respectively,

$$\Delta G^0 = \Delta G^0_{products} - \Delta G^0_{reactant} . \qquad (8)$$

Determination of P(SO$_2$)

For the reaction between SO$_2$ and DCS, the equilibrium constant is

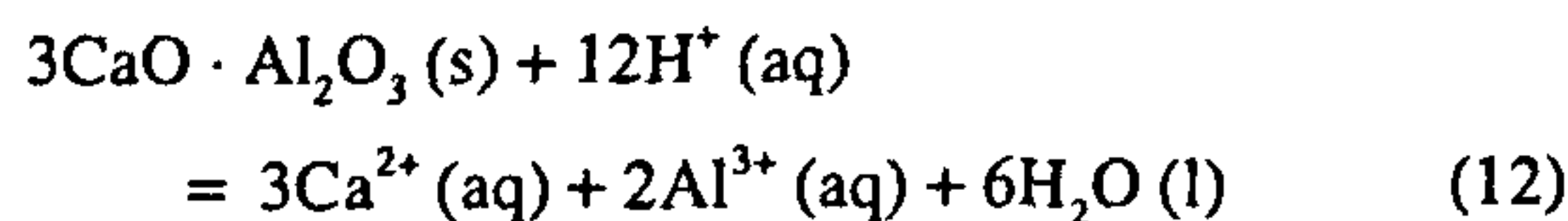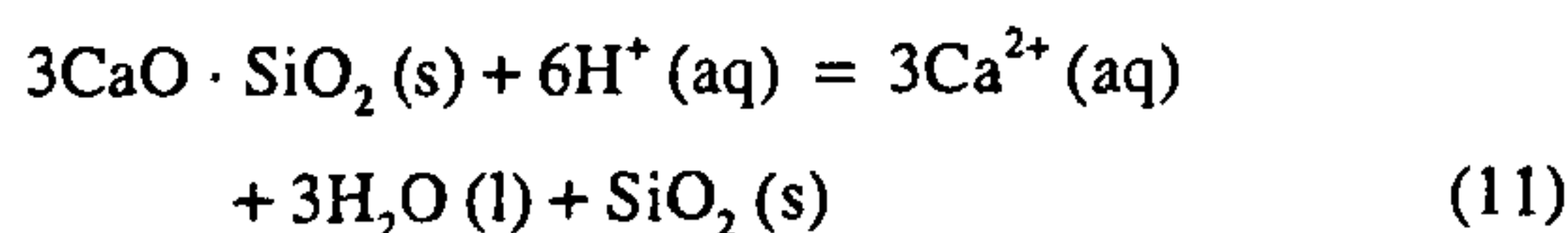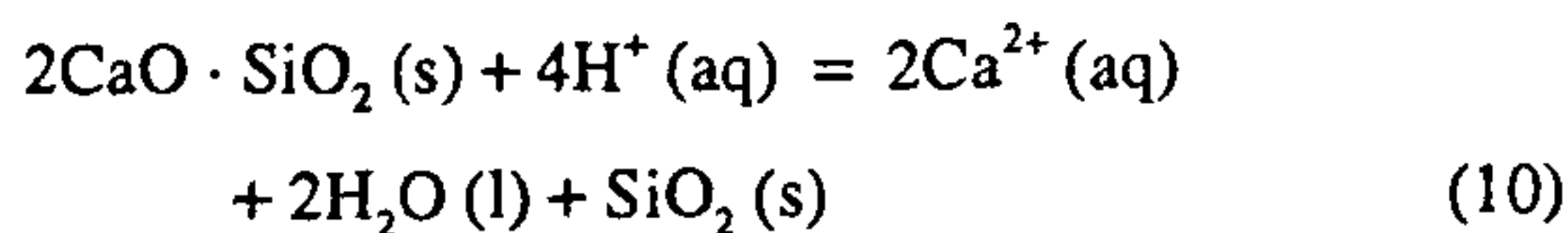$$K = 1/P^2 (SO_2) \cdot P(O_2), \qquad (9)$$

where $P(SO_2)$ and $P(O_2)$ are partial pressures of SO$_2$ and O$_2$, respectively, in the atmosphere. Under thermodynamic equilibrium, using equations (4) and (9), ΔG^0 value (already calculated) and $P(O_2) = 0.20946$ atm (ref. 7), we get $P(SO_2) = 9.78 \times 10^{-63}$ atm. Similar calculations can be made for the reaction of atmospheric SO$_2$ with TCS and TCA and the obtained values of $P(SO_2)$ are 3.07×10^{-67} and 1.13×10^{-57} atm, respectively.

The H$^+$–cement system

Determination of ΔG^0

From equation (2), mass balance equations for the reaction of H$^+$ with DCS, TCS and TCA can be written as

$$2CaO \cdot SiO_2 \text{ (s)} + 4H^+ \text{ (aq)} = 2Ca^{2+} \text{ (aq)}$$
$$+ 2H_2O \text{ (l)} + SiO_2 \text{ (s)} \qquad (10)$$

$$3CaO \cdot SiO_2 \text{ (s)} + 6H^+ \text{ (aq)} = 3Ca^{2+} \text{ (aq)}$$
$$+ 3H_2O \text{ (l)} + SiO_2 \text{ (s)} \qquad (11)$$

$$3CaO \cdot Al_2O_3 \text{ (s)} + 12H^+ \text{ (aq)}$$
$$= 3Ca^{2+} \text{ (aq)} + 2Al^{3+} \text{ (aq)} + 6H_2O \text{ (l)} \qquad (12)$$

Using thermodynamic data, the standard Gibbs free energy for reactions (10)–(12) can be calculated; the values are -58.43, -106.02 and -153.34 kcal mol^{-1}, respectively.

Determination of pH

The equilibrium constant for the H$^+$–DCS reaction is

$$K = a^2 (Ca^{2+}) / a^4(H^+), \qquad (13)$$

where $a(Ca^{2+})$ and $a(H^+)$ refer to the activities of Ca^{2+} and H$^+$. Under equilibrium conditions, using Equation (4), (13) and ΔG^0 value, we get

$$pH = 10.74 - 0.5 \lg a(Ca^{2+}). \qquad (14)$$

Similar equations for pH developed in case of TCS and TCA are

$$pH = 12.99 - 0.5 \lg a(Ca^{2+}), \qquad (15)$$

$$pH = 9.4 - 0.25 \lg a(Ca^{2+}) - 0.17 \lg a(Al^{3+}). \qquad (16)$$

For the interaction of H$^+$ with DCS, TCS and TCA, equations (14), (15) and (16), respectively, give the relationship between pH, $a(Ca^{2+})$ and $a(Al^{3+})$. Some results are shown in Table 1.

The negative values of Gibbs free energies for the reaction of DCS, TCS and TCA with SO$_2$ and H$^+$ indicate that these reactions are thermodynamically feasible. For the reaction of SO$_2$ with DCS, TCS and TCA, the equilibrium partial pressure of SO$_2$ required is of the order of 10^{-57}–10^{-67} atm. However, background partial pressure of SO$_2$ in the natural atmosphere is of the order of 10^{-10} atm (ref. 7). Thus, the above-mentioned reactions occur spontaneously in the atmosphere. In a polluted atmosphere the SO$_2$ concentration is increased, thus $\Delta G_{polluted} < \Delta G_{normal} < 0$, so the deterioration of buildings is accelerated.

With the decrease in pH, $a(Ca^{2+})$ and $a(Al^{3+})$ increase (Table 1), showing that acid rain leads to faster deteriora-

Table 1. Relationship between pH, $a(Ca^{2+})$ and $a(Al^{3+})$ for DCS, TCS and TCA

	pH	$a(Ca^{2+})$	$a(Al^{3+})$
DCS	11.24	10^{-1}	—
	10.24	10	—
	9.74	10^2	—
	9.24	10^3	—
TCS	13.49	10^{-1}	—
	12.49	10	—
	11.99	10^2	—
	11.49	10^3	—
TCA	9.82	10^{-1}	10^{-1}
	9.48	10^{-1}	10
	9.31	10^{-1}	10^2
	9.14	10^{-1}	10^3
	9.32	10	10^{-1}
	9.07	10^2	10^{-1}
	8.82	10^3	10^{-1}

tion of buildings. A pH of 5.6 is often regarded as the acidity of natural rainwater and calculations show that even alkaline rain may also damage cemented surface considerably. Since Gibbs free energies for SO_2 interaction are more negative than for H^+ interaction, the deterioration is likely to be faster due to SO_2 reaction with buildings.

Thermodynamic calculations show that (1) interactions between major constituents of cement and SO_2 and H^+ are possible in the atmosphere, (2) cement deteriorates faster by reacting with SO_2 than with H^+ and the deterioration is possible under normal atmospheric conditions and even by natural rain and (3) acid deposition increases the rate of deterioration.

Finally, it should be stated that correct predictions regarding the deterioration of cemented surface by atmosphere require both thermodynamic analysis and kinetic study of the systems. From this angle the present report is only a half exercise.

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5. Knofel, D., *Corrosion of Building Materials*, Van Nostrand Reinhold, New York, 1978, pp. 34–37.

6. Weast, R. C., *C. R. C. Handbook of Chemistry and Physics*, CRC Press, Boca Raton, Florida, 1988, pp. D35–37.

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Spatial gradients of calcium in the slug of *Dictyostelium discoideum*

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Starved amoebae of *D. discoideum* aggregate and give rise to a long and thin multicellular structure called the slug. The cells within the slug eventually differentiate according to a simple anterior/posterior dichotomy. This motivates a search for gradients of putative morphogens along its axis. Calcium may be one such morphogen. On the basis of observations made by using the calcium-sensitive fluorescent dyes fura-2 and chlortetracycline, we report that there are spatial gradients in cytoplasmic and sequestered calcium in the slug. Anteriorly located and genetically defined prestalk cells (ecmA/pstA, ecmB/pstAB) contain significantly higher levels of calcium than the prespore cells in the posterior. However, the proportion of 'calcium-rich' cells in the slug is greater than that of the subset of prestalk cells defined by the expression of the ecmA or ecmB genes.

THE cellular slime mould *Dictyostelium discoideum* is an excellent system for the study of spatial patterning in multicellular development[1]. One of the main reasons for saying this is that the fate map at the 'embryonic' slug stage in the life cycle of *D. discoideum* is extremely simple, being based on the relative position of a cell along the slug axis (anterior prestalk versus posterior prespore).

Traditionally, there have been two broad approaches to the problem of pattern formation in multicellular development, and these are typified by the words 'regulative' and 'mosaic'[2]; the two approaches are not mutually exclusive[3]. Analogously, there are two conceptually distinct ways of looking at patterning in *D. discoideum*. One possibility is that starting from a homogenous aggregate, relative positions along the long axis of the slug cause the cells to adopt different fates. This could be the consequence either of local cell-to-cell interactions leading to a prepattern[4] or of relative position *per se* – as sensed via morphogenetic gradients, say ('positional information'[5]). A second possibility is that cell fates are predetermined before aggregation and the cells sort out within the slug according to these fates. It is becoming increasingly clear that *D. discoideum* does not follow any one of these strategies to the exclusion of the other. Instead, it adopts what may be called a policy of multiple insurance and, depending on circumstances, makes use of both[6]. There are feedback interactions regulating the relative proportions of presumptive cell types[7]; but there are also gradients of putative morphogens along the slug axis (though their interpretation is not straightforward[8]). On the other hand, it is known that differences in preaggregation phenotype can bias cell fate in heterogenous populations[9,10]. We have shown that naturally occurring variations in cellular calcium between preaggregation amoebae anticipate future prestalk–prespore differences[11]. Based on the findings reported here as well as other results, it appears that the calcium ion is a candidate morphogen at the slug stage.

It has long been hypothesized that calcium could be important for cell differentiation and morphogenesis in *D. discoideum*. A high concentration of externally added calcium has been claimed to induce differentiation of stalk-like cells[12], and we have substantiated this recently (R. Baskar and V. Nanjundiah, in preparation). Calcium