

## Kinetics of the Carbon Dioxide Hydration under Conditions of Enforced Stationarity

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The hydration of carbon dioxide has been investigated in a new way. A solution of sodium bicarbonate is kept saturated with carbon dioxide. When the pH of the solution has attained its equilibrium value,  $\text{pH}_0$ , a motor driven syringe is started, and strong acid or base is supplied at a constant rate,  $s$ . After a few minutes the pH is again stationary at  $\text{pH}_0 + \Delta\text{pH}$ .  $\Delta\text{pH}$  is plotted against  $s$ .

From the kinetic equations is derived the theoretical dependence of  $\Delta\text{pH}$  on  $s$  corresponding to the various possible routes of the reaction, and the experimental curves are analysed accordingly.

For the "spontaneous" reaction between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and for the base reaction,  $\text{CO}_2 + \text{OH}^-$ , our experiments gave results which are in agreement with those of Faurholt and others. Since we were able to measure under other conditions than previous workers we could also detect an acid catalysis and catalysis by  $\text{HCO}_3^-$  and by  $\text{H}_2\text{CO}_3$ , the latter to a high power of the  $\text{H}_2\text{CO}_3$ -concentration, indicating the existence of a polymeric carbonic acid intermediate.

In spite of the physiological and technical importance of the carbon dioxide hydration and in spite of the numerous studies which have been made on the kinetics of this reaction, our knowledge of its details is still not quite satisfactory. In particular no quantitative information is available in the literature regarding the catalytic influence of acid, presumably because the techniques of previous authors have not been well suited to investigate this question.

In our experiments we have enforced stationary conditions upon the system through the steady supply of base or acid to a solution which is kept saturated with carbon dioxide. By varying the concentration of sodium bicarbonate in the solution, we can thus measure at different pH, and get the velocity of the reaction directly under controlled circumstances and without addition of buffer substances other than bicarbonate-carbonic acid.

### EXPERIMENTAL

Three sets of experiments at  $0^\circ\text{C}$  are reported here with solutions, which were 1) 0.25 M  $\text{NaHCO}_3 + 0.50$  M  $\text{NaCl}$ , 2) 0.50 M  $\text{NaHCO}_3 + 0.25$  M  $\text{NaCl}$  and 3) 0.75 M  $\text{NaHCO}_3$ .

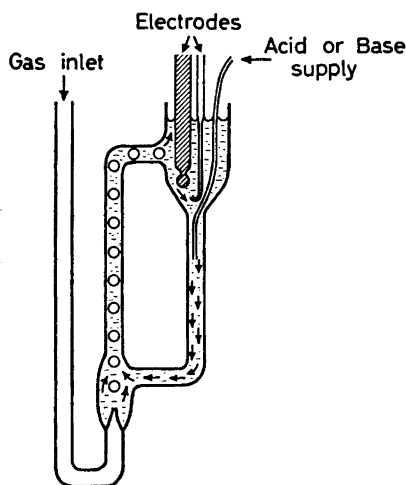


Fig. 1. The Pyrex glass apparatus. Contains 8 ml of solution.

8 ml of the solution is placed in the Pyrex apparatus drawn in Fig. 1. Carbon dioxide is washed in two bubble flasks in an ice bath and is blown through the solution to saturate it and to stir it vigorously by the Cottrell circulation pump arrangement. Circulation time is about one second.

pH is measured with a standardized glass electrode and a battery operated pH-meter (PHM4, Radiometer, Copenhagen) which reads to 0.002 in pH. Standard buffer was: 0.025 M  $\text{KH}_2\text{PO}_4$  + 0.025 M  $\text{Na}_2\text{HPO}_4$ ; pH = 6.98 at 0°C (NBS).

2 M NaOH or HCl is supplied from a calibrated polythene syringe which is driven by a worm gear operated through a torsion cable from an AC asynchronous motor with a variable friction gear. The motor is placed about one meter from the electrodes and is well screened to eliminate the influence of electrical noise on the pH-meter. A telephone-counter counts the number of rotations of the cable.

When the pH after some 10–15 min has attained its equilibrium value,  $\text{pH}_0$ , the syringe is started at some selected speed. pH and the telephone counter are read at regular intervals. After a few minutes the pH attains a stationary value,  $\text{pH}_0 + \Delta\text{pH}$ , because hydrogen ions are produced or used by the hydration reaction at exactly the same rate as they are consumed or supplied through the chemicals from the syringe.

After running for an interval of time sufficient to control steadiness of supply and of pH, the syringe is stopped. pH is followed until it has returned to  $\text{pH}_0$  or to a somewhat different value corresponding to a "secular" change caused by the change in bicarbonate concentration from the added chemicals.

In the high speed experiments this variation becomes appreciable and the true  $\Delta\text{pH}$  value must be found by extrapolation.

From the readings on the counter we calculate the reaction rate  $s$  in moles of hydrogen ions produced by the reaction per second and per liter. The values are in the range of 0 to  $5 \times 10^{-4} \text{ M l}^{-1} \text{ sec}^{-1}$ .

At low values of  $s$  a few runs can be made with the same filling, otherwise a new solution must be used for each run; that is, for each determination of a set of ( $s$ ,  $\Delta\text{pH}$ ) values.

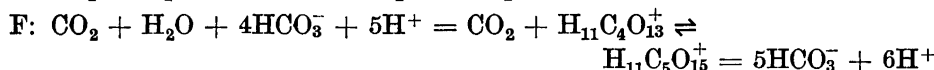
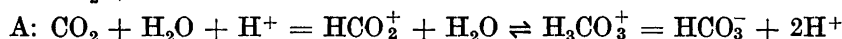
## THEORETICAL

The total turnover,  $s$ , in a net process which can take place by several routes is obviously the sum of the reaction rates by each of the routes:

$$s = s_A + s_B + s_C + \dots \quad (1)$$

Now, for each reaction scheme, X, we can design, we can calculate an expression for the dependence of the reaction rate  $s_x$  on  $\Delta\text{pH}$ . The eventual analysis of the experimental curves will consist of producing from such  $s_x$ -functions a linear combination which will reproduce the results with a satisfactory degree of accuracy.

For the present experiments it has turned out that we must combine five different reaction schemes: the Spontaneous reaction, the Base reaction, the Acid catalyzed reaction, the biCarbonate catalyzed reaction and the Fivefold acid catalyzed reaction:



In these schemes proton exchanges, polymerisations and depolymerisations are assumed to be very rapid reactions and are indicated by an equals mark (=), whereas the rate determining steps involving the establishment of a chemical bond to C in  $\text{CO}_2$  are marked with double arrows. We control the concentrations of the first and the last combinations of molecular and ionic species in each scheme. In between we have suggested such hypothetical intermediates as we find the most probable — or the least improbable. The velocity expressions refer exclusively to the first kind of species.

It is convenient to introduce the equilibrium velocities,  $v_x^0$ , which are the velocities of the forward reactions at equilibrium and hence also of the back reactions at equilibrium,  $v_{-x}^0 = v_x^0$ . Equilibrium values of the concentrations are marked  $[\text{OH}^-]_0$  and  $[\text{H}^+]_0$  and water concentration is taken into the constants. We derive the following:

$$s_s = v_s - v_{-s} = k_s[\text{CO}_2] - k_{-s}[\text{HCO}_3^-][\text{H}^+] = v_s^0 (1 - 10^{-\Delta\text{pH}})$$

since  $v_s^0 = k_s[\text{CO}_2] = v_{-s}^0 = k_{-s}[\text{HCO}_3^-][\text{H}^+]_0$

and  $[\text{H}^+]/[\text{H}^+]_0 = 10^{-\Delta\text{pH}}$ ;  $[\text{HCO}_3^-] = [\text{HCO}_3^-]_0$ ;  $[\text{CO}_2] = [\text{CO}_2]_0$

In the same way we derive

$$s_B = v_B - v_{-B} = k_B[\text{CO}_2][\text{OH}^-] - k_{-B}[\text{HCO}_3^-] = v_B^0 10^{\Delta\text{pH}} (1 - 10^{-\Delta\text{pH}})$$

$$v_B^0 = k_B[\text{CO}_2][\text{OH}^-]_0 = k_{-B}[\text{HCO}_3^-]$$

$$s_A = v_A - v_{-A} = k_A[\text{CO}_2][\text{H}^+] - k_{-A}[\text{HCO}_3^-][\text{H}^+]^2 = v_A^0 10^{-\Delta\text{pH}} (1 - 10^{-\Delta\text{pH}})$$

$$v_A^0 = k_A[\text{CO}_2][\text{H}^+]_0 = k_{-A}[\text{HCO}_3^-][\text{H}^+]_0^2$$

$$s_C = v_C - v_{-C} = k_C[\text{CO}_2][\text{HCO}_3^-] - k_{-C}[\text{HCO}_3^-]^2[\text{H}^+] = v_C^0 (1 - 10^{-\Delta\text{pH}})$$

$$v_C^0 = k_C[\text{CO}_2][\text{HCO}_3^-] = k_{-C}[\text{HCO}_3^-]^2[\text{H}^+]_0$$

$$s_F = v_F - v_{-F} = k_F[\text{CO}_2][\text{HCO}_3^-]^4[\text{H}^+]^5 - k_{-F}[\text{HCO}_3^-]^5[\text{H}^+]^6 \\ = v_F^0 10^{-5\Delta\text{pH}} (1 - 10^{-\Delta\text{pH}})$$

$$v_F^0 = k_F[\text{CO}_2][\text{HCO}_3^-]^4[\text{H}^+]_0^5 = k_{-F}[\text{HCO}_3^-]^5[\text{H}^+]_0^6$$

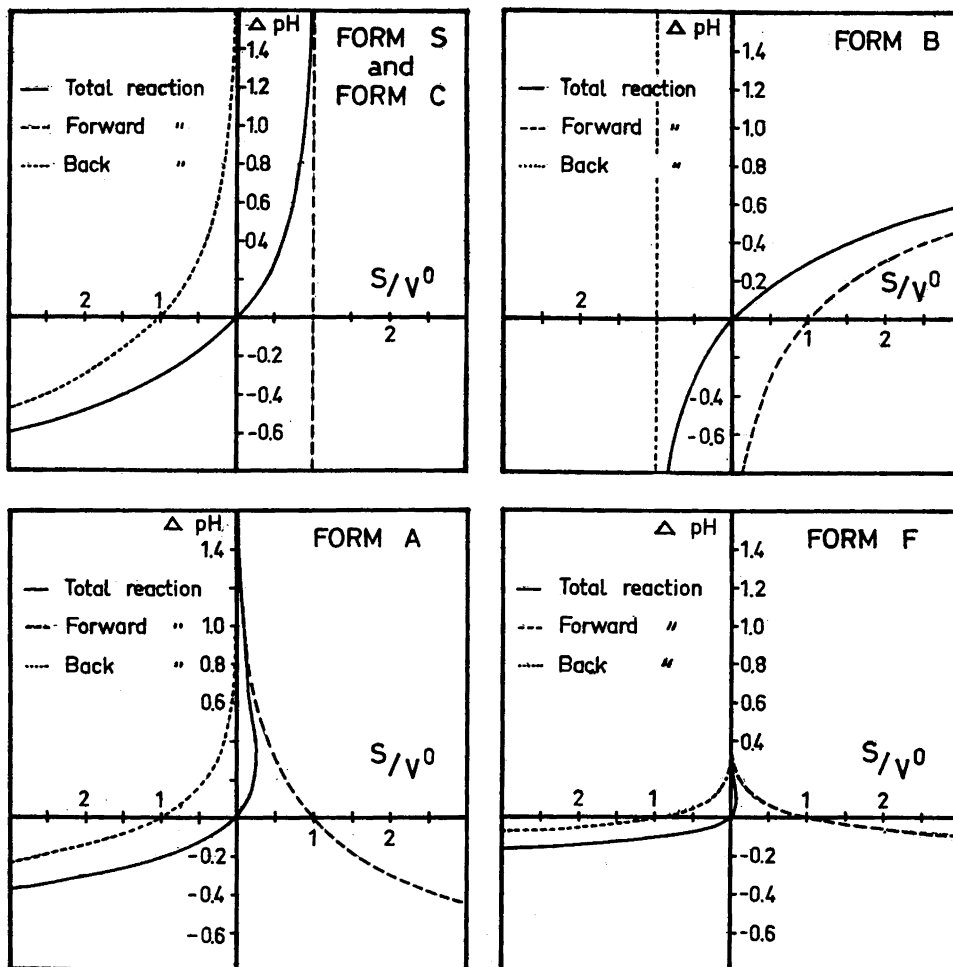


Fig. 2. The general patterns of the  $\Delta \text{pH}$  versus  $s$  curves that would be shown if each of the reactions could proceed separately. Drawn to such scales that forward and back reactions proceed with unit velocity at equilibrium ( $\Delta \text{pH} = 0$ ).

The patterns of the curves are shown on Fig. 2. For each of the schemes are plotted  $v_x$ ,  $v_{-x}$  and  $s_x$  to such a scale that  $v_x^0$  is put equal to one. Reactions S and C have the same form of curves, but  $v_c^0$  is proportional to bicarbonate concentration whereas  $v_s^0$  is independent of it.

Incidentally we notice that these plots are also affinity-velocity plots for these reactions, since for all the reactions:

$$A = -\Delta G = \mu(\text{CO}_2) + \mu(\text{H}_2\text{O}) - \mu(\text{HCO}_3^-) - \mu(\text{H}^+) = (RT \ln 10) \Delta \text{pH}$$

since  $\mu(\text{CO}_2) + \mu(\text{H}_2\text{O}) = \mu(\text{HCO}_3^-) + \mu_o(\text{H}^+)$   
and  $\mu(\text{H}^+) - \mu_o(\text{H}^+) = -(RT \ln 10) \Delta \text{pH}$

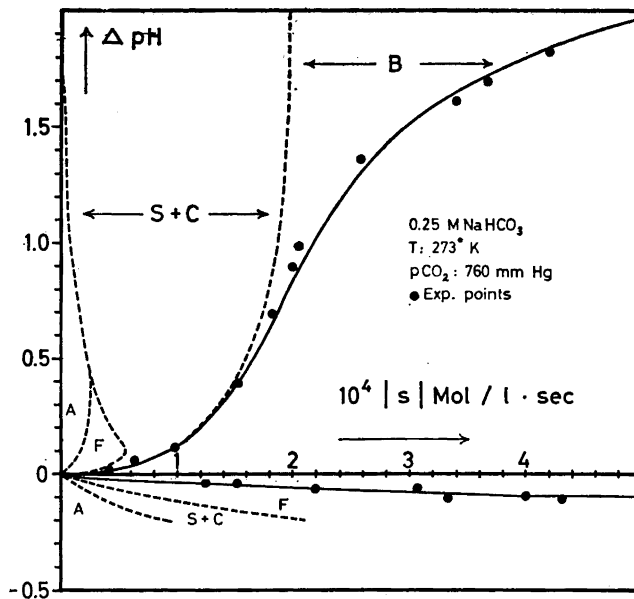


Fig. 3. Experimental results, series 1. Solution: 0.25 M NaHCO<sub>3</sub> + 0.50 M NaCl. CO<sub>2</sub> gas saturated with H<sub>2</sub>O at 0°C. pH<sub>0</sub> = 6.75. NaOH supplied at positive ΔpH, HCl at negative ΔpH. Full curve represents calculated values, dotted lines indicate contributions from the various reactions according to the chosen parameters (see Table 1).

In accordance with De Donder's theory we find, therefore, that all the curves go through the origin as continuous and differentiable functions; but proportionality between velocity and affinity is for reaction F certainly restricted to infinitesimal intervals. This curve is reminiscent of a voltage *versus* current plot for an electrical rectifier.

## RESULTS

The measured values are plotted in Figs. 3—5. To save space the numerical value of  $s$  has been chosen as abscissa, so that negative ΔpH corresponds to acid supply by the syringe and acid consumption by the reaction, which in the theoretical section were counted as negative values of  $s$ .

The full curves in these figures represent calculated values, derived from the above expressions with the choice of  $v^\circ$  values shown in Table 1 together with the corresponding values of the velocity constants. Values of  $v^\circ$  are estimated to about one significant figure only, and no attempt has been made to improve the fit by fine adjustment of the constants.

Also shown in the figures are the contributions from each of the reactions. Each abscissa value on the full curve is a sum of contributions from the five reactions and these contributions are represented by the length between consecutive pairs of the dotted lines, as indicated by the corresponding letters.

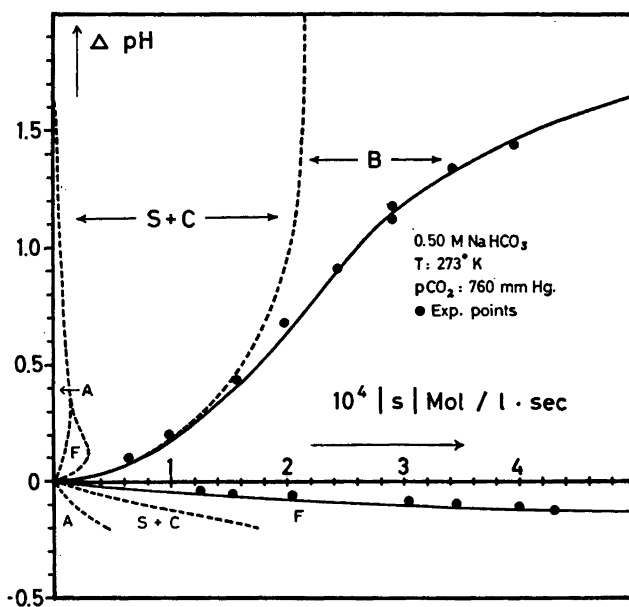


Fig. 4. Experimental results, series 2. Solution: 0.50 M NaHCO<sub>3</sub> + 0.25 M NaCl. pH<sub>0</sub> = 7.05. Otherwise as Fig. 3.

It is clear that all of the reactions are necessary to make up the total rate, each having its main influence in one particular range of  $\Delta\text{pH}$  with some variation according to bicarbonate concentration. It is the very unsymmetrical

Table 1. Experimental results. 0°C, ionic strength 0.75 M. Parameters used in drawing the curves in Figs. 3–5.

NaHCO <sub>3</sub>	NaCl	pH <sub>0</sub>	10 <sup>4</sup> v <sub>S</sub> <sup>0</sup>	10 <sup>4</sup> v <sub>B</sub> <sup>0</sup>	10 <sup>4</sup> v <sub>C</sub> <sup>0</sup>	10 <sup>4</sup> v <sub>A</sub> <sup>0</sup>	10 <sup>4</sup> v <sub>F</sub> <sup>0</sup>
0.25	0.50	6.75	1.8	0.033	0.2	1.0	6.0
0.50	0.25	7.05	1.8	0.066	0.4	0.5	3.0
0.75	0	7.23	1.8	0.10	0.6	0.33	2.0

$$[\text{CO}_2] = 0.062 \text{ M (Harned and Davies } ^6)$$

$$-\log K_w = 14.94 \text{ (Harned and Owen } ^7)$$

$$-\log f_{\pm} = 0.18 \text{ (estimated)}$$

$$k_S = v_S^0 / [\text{CO}_2] = 0.003$$

$$k_B = v_B^0 / [\text{CO}_2][\text{OH}^-]_0 = 5\,500$$

$$(\log [\text{OH}^-]_0 = \log K_w + \text{pH}_0 - \log f_{\pm})$$

$$k_C = v_C^0 / [\text{CO}_2][\text{HCO}_3^-] = 0.0013$$

$$k_A = v_A^0 / [\text{CO}_2][\text{H}^+]_0 = 6\,000$$

$$k_F = v_F^0 / [\text{CO}_2][\text{HCO}_3^-]^2[\text{H}^+]_0^2 = 1.7 \cdot 10^{33}$$

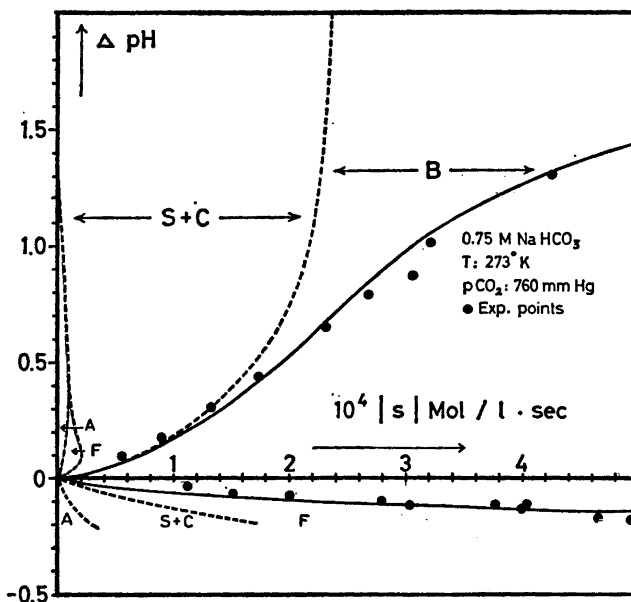


Fig. 5. Experimental results, series 3. Solution: 0.75 M NaHCO<sub>3</sub>. pH<sub>0</sub> = 7.23. Otherwise as Figs. 3 and 4.

behaviour towards acid and base that makes necessary the high power of hydrogen ion concentration in  $s_F$ , but if bicarbonate did not enter also to some high power, it would not be possible to fit the acid branches of the three curves with the same function. The contributions from reactions A and C are the least important and it would be possible to make a reasonable fit without them. That we have included these two reactions and not taken any further possible reactions into account is the result of a somewhat arbitrary estimate regarding what is reasonable in view of our experimental accuracy.

#### DISCUSSION

The method we have applied seems in many respects to be very well suited for the purpose, and from the results we have obtained it is not difficult to see why previous methods have been less satisfactory. All previous methods have allowed a drift of pH over a certain range during the reaction, and too many parameters are therefore changed at the same time.

The value of our  $k_s$  is in excellent agreement with Faurholt's<sup>1</sup> value ( $0.0013 \times 2.3 = 0.0030$ ) and with Ljunggren and Lamm's<sup>2</sup> value at 4°C (0.0044). The agreement with Roughton's<sup>3</sup> value (0.0021) is not quite so good.

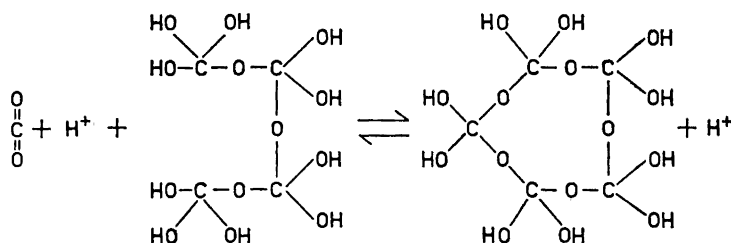
Our value of  $k_B$  is about six times that of Faurholt<sup>1</sup>. Experiments at lower carbon dioxide pressures must be made before this peculiar fact can be discussed.

In the acid reaction we have proposed the intermediate  $\text{HCO}_2^+$ , because this structure should be favourable for a bond formation to the carbon atom.

The base strength of  $\text{CO}_2$  has not been measured.  $\text{p}K$  is probably between  $-3$  and  $-6$  (cf. Hammett <sup>4</sup>).

The most remarkable feature in our results is the necessity of assuming a reaction like F. Whether the exponent to hydrogen ion activity is really five, or whether it might as well be four, six or seven cannot be said with certainty. We only know that it must be high and that it must be about one higher than that of the bicarbonate concentration.

The only reasonable explanation for this peculiar behaviour is that some polymeric carbonic acid is present and acts as a powerful catalyst. Tentatively we suggest that it might be structures like the following that describe the changes involved in the rate determining step of reaction F.



The existing evidence for polymerization of carbonic acids has been summarized by Rosotti <sup>5</sup>. Whether polymerization occurs through hydrogen bonds or through addition to the C—O double bond as assumed above cannot be decided. That boric acid, silicates and many other similar compounds polymerize in aqueous solution is too well known to need discussion.

Faurholt <sup>1</sup> has pointed out the difficulty in understanding why  $\text{H}_2\text{CO}_3$  is not a considerably stronger acid than formic acid. If most of the hydrated carbon dioxide exists in the form of very weak monomeric or polymeric orthoacids, true  $\text{H}_2\text{CO}_3$  may still be some ten to a hundred times stronger than it is now believed to be.

It is difficult, however, to tell through what kind of experiments crucial evidence could be obtained for these molecular species. We plan some measurements at reduced  $\text{CO}_2$  pressure, which will necessitate modification of the apparatus. Although we can only hope to provide circumstantial evidence in this way, it may still be worth while to learn more about this important reaction.

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