CI.—*On Active Nitrogen. Part II. Reactions with Gases.*

By Eric John Baxter Willey and Eric Keightley Rideal.

In a previous communication (J., 1926, 1804) evidence was presented for the assumption that active nitrogen represents a metastable molecule with the low mean energy content of *ca.* 43,000 cals./g.-mol. Experiments are now described upon the addition of gases—elementary, compound, and mixed—to the afterglow, and the bearing of these observations upon the energy content of active nitrogen is discussed.

The considerations underlying the various possible types of interaction between atoms and electrons noted by Franck, Klein, and Rosseland (*Z. Physik*, 1922, 4, 41) have been extended by Franck and his co-workers to the case of interaction between excited atoms and molecules. In applying these considerations to the case of active nitrogen, the following possibilities are open :

(1) If the least radiation potential of the added gas be less than the energy of active nitrogen, the former may be stimulated to the

production of an excited molecule with the subsequent emission of its characteristic spectrum. Moreover, if its critical increment for dissociation, reaction, or decomposition also be less, chemical action may occur.

(2) If the lowest radiation potential of the added gas be greater than the energy of active nitrogen, the luminescence of the latter should be quenched to an extent depending on the nature and amount of the added gas. The excitation of certain spectra of metals, the dissociation of hydrogen examined by Franck (*Z. Physik*, 1922, **11**, 16), and the quenching of fluorescence with various gases examined by Wood (*Physikal. Z.*, 1912, **13**, 353) for mercury atoms excited by the line $\lambda = 2537$ are well-known examples of these cases.

Certain other possibilities, however, are present.

(3) The active nitrogen may react with the added gas or vapour to form a nitride, the necessary energy of activation for formation being less than the energy content of active nitrogen. If the resulting nitride be stable and its formation exothermic, the energy set free (which includes the heat of formation and the original energy content of the active nitrogen) may be dissipated as radiation—the phenomenon of chemiluminescence.

(4) Finally, reaction may take place between active nitrogen and molecules excited as in (1) to form an endothermic nitride which may subsequently undergo decomposition with the emission of radiation.

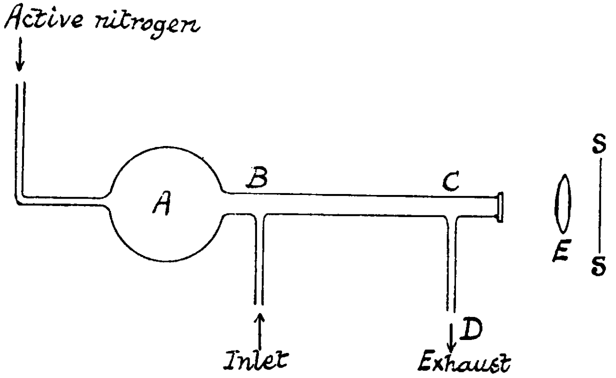
By applying these data upon the critical energy increments to observations of the effect of other gases upon the afterglow and the chemical reactions effected, we should be able to determine approximately the energy content of active nitrogen. The experiments show that with gases of critical energy increments below 55,000 cals./g.-mol. chemical action is always traceable, but it is only strong where the critical energy increment is *ca.* 43,000 cals. and under. Reliance has been placed upon chemical reaction rather than spectroscopic observations, the employment of the latter being inadvisable in view of the presence of so many possible disturbing factors, as has already been pointed out by one of us (*Nature*, 1926, **118**, 735). The latter value agrees closely with that put forward in our first paper.

EXPERIMENTAL.

Active nitrogen was led from the discharge tube through the bulb, A (Fig. 1), to the tube, BC, which was some 25 cm. long. About 2 cm. along this tube a second tube was provided for the admission of the gases whose effects were to be studied, and the mixture was drawn to exhaust at D. The end of BC remote from the active-nitrogen inlet was ground flat, and by means of a lens, E, the light in it could be focussed on the slit, SS, of a Hilger spectrometer. A series of condensing traps immersed in liquid air was placed in the exhaust line for the collection of any condensable products of the reactions taking place. The results are now given according to the considerations already advanced.

(a) *Hydrogen.* This gas is of interest in that its heat of dissociation is *ca.* 75,000—80,000 cals./g.-mol., and that it is readily activated or dissociated by collision with mercury atoms excited by the line $\lambda = 2537$. In agreement with Lord Rayleigh (*Proc. Roy. Soc.*, 1911, *A*, **85**, 219) we find that pure hydrogen has no appreciable effect upon the glow. Examination of the gases condensed by cooling in liquid air after a run of 10 hours failed to show any trace of ammonia. Since, however, the evidence for the formation of ammonia on the admixture of nitrogen and activated hydrogen is conflicting,* the nitrogen–hydrogen mixture was

FIG. 1.



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* The experiments of Wendt, Venkataramaiah, and Hirst all indicate that active hydrogen, produced either by the discharge or by Franck's method with excited mercury atoms, yields appreciable quantities of ammonia on interaction with nitrogen. On the other hand Bonhoeffer (*Z. physikal. Chem.*, 1924, **113**, 199) and Taylor (*Trans. Faraday Soc.*, 1925, **21**, 562) have failed to detect ammonia formation with active hydrogen. We have satisfied ourselves that if a stream of nitrogen at 10 mm. pressure be led into a stream of hydrogen at a point 150 mm. away from the end of the discharge tube through which hydrogen is flowing at the same pressure, appreciable quantities of ammonia are formed.

Mr. A. Caress, working in this laboratory, has recently obtained experimental evidence in support of the view that hydrogen atoms react with nitrogen to form ammonia at a catalytic metal surface but not in the homogeneous gas phase, a reaction which can be made to take place on excitation by electron collision.

passed over iodine, arsenic and sulphur (compare Wendt and Landauer, *J. Amer. Chem. Soc.*, 1922, **44**, 510), and also, after admission of oxygen, over phosphorus pentoxide in a weighed tube. In no case was any evidence obtained for the production of an active variety of hydrogen.

(b) *Oxygen.* This readily extinguished the luminescence with the production of heat. No evidence for the formation of nitric oxide or ozone was obtained. Also, with hydrogen–oxygen mixtures in various ratios, no indication of water formation over periods of 10 hours was obtained.

(c) *Carbon monoxide.* This gas merely dilutes the glow, behaving in this respect like nitrogen or hydrogen, as might be anticipated from the close similarity between carbon monoxide and nitrogen.

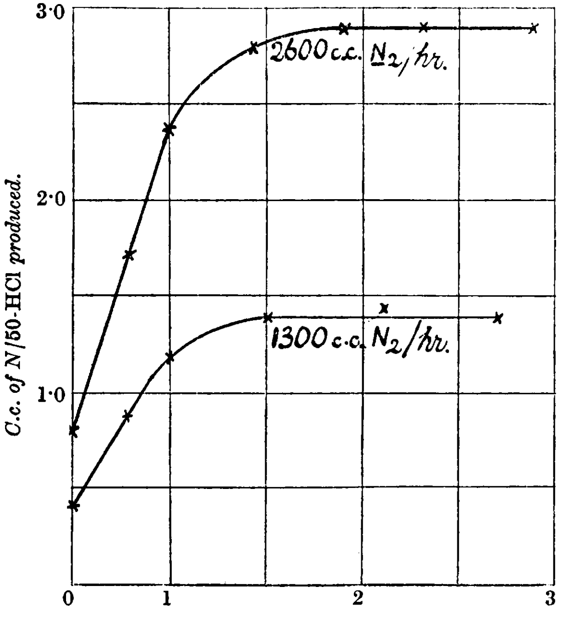
(d) *The halogens.* The characteristic blue luminosity of iodine is readily excited (compare Rayleigh, *loc. cit.*). The same holds true for bromine, the colour being brick-red. In the case of chlorine, the effect on the afterglow is much less marked; this, however, may be due in part to the fact that the spectrum of chlorine in the visible region overlaps the spectrum of the afterglow. The dissociation energies of the three halogens (in cals./g.-mol.) are: Iodine, 34,500; bromine, 46,200; and chlorine, 55,000.

In no case could any condensate containing nitrogen and halogen be obtained by cooling with liquid air (compare Noyes, *J. Amer. Chem. Soc.*, 1921, **43**, 1774).

The effect of admitting a mixture of hydrogen and a halogen to the afterglow was examined for the production of hydrogen halides, but the results were negative with both bromine and iodine. With chlorine, however, the production of hydrogen chloride, together with minute traces of ammonium chloride and small quantities of a substance giving the characteristic reactions of chloroamine, was observed. Since this was the first instance of a chemical reaction being brought about by active nitrogen, similar to a hydrogen–oxygen reaction brought about by active mercury atoms, the case was examined in some detail.

When a mixture of hydrogen and chlorine was admitted to a stream of active nitrogen and the mixture drawn to exhaust through a U-tube cooled by liquid air, the gases which condensed gave a strongly acid solution in water, even when examined so rapidly as to preclude the formation of hydrogen chloride by reaction between the chlorine and the water. An absorption tube was then constructed in such a manner that the inlet tube terminated about 3 cm. above the bottom, and 10 c.c. of 15% neutral solution of potassium iodide were frozen into it. It was then immersed in liquid air and employed as a condenser as before. At the end of the experiment, this tube was filled with nitrogen whilst still connected to the apparatus, sealed off, and warmed to allow the chlorine to be absorbed. It was then opened and the contents were washed out and titrated with neutral *N*/50-sodium thiosulphate until the iodine was removed, after which phenolphthalein was added and the whole titrated to neutrality with *N*/50-alkali, several c.c. being required. The presence of free hydrochloric acid was also proved (*a*) by titrating with *N*/50-sodium thiosulphate after addition of potassium iodide and iodate, and (*b*) by means of the hydrogen electrode.

FIG. 2.



Bubbles of 1 : 1 H_2–Cl_2 *mixture per second.*

Blank tests in which all conditions were the same as in the actual experiments, except that the nitrogen was not activated, gave no trace whatever of hydrogen chloride.

With constant nitrogen flow and constant composition of the hydrogen–chlorine mixture, the yield of hydrogen chloride was constant, and a few quantitative studies of its production were made. The results (Fig. 2) show that with a 1 : 1 mixture of hydrogen and chlorine the yield of hydrogen chloride increases with the quantity of the mixture added, but a limit is reached after which no further combination takes place.

The formation of hydrogen chloride may be ascribed to three causes: (*a*) Reduction *in situ* by the hydrogen of an unstable nitrogen chloride. (*b*) Photochemical combination of chlorine and hydrogen under the influence of ultra-violet light emitted during the decay of the active nitrogen, probably with the formation of long chains to account for the relatively high yields of hydrogen chloride. (*c*) The production, by second-type collisions, of active chlorine molecules excited to a level sufficiently high to enable them to combine with hydrogen.

The first of these is contrary to the fact that Noyes (*loc. cit.*) was unable to prepare any nitrogen chloride by the action of active nitrogen upon chlorine even under the most varied conditions of flow speeds, etc. Decomposition of an unstable halide should be prevented by the addition of a large excess of chlorine.

In the absence of measurements of the absolute intensity of the active nitrogen luminosity, little can be done directly to prove or disprove the second hypothesis. Such a determination would give the total number of quanta emitted per second per unit volume of active nitrogen. A knowledge of the intensity of the part of the afterglow spectrum which is of wave-length short enough to bring about this synthesis, relative to the whole series of bands, would then give the number of quanta available for the reaction. Application of this value to the known data for the combination of hydrogen and chlorine would give an approximate estimate as to the probable yield of hydrogen chloride.

The third hypothesis is to a certain extent capable of analysis. It is possible, upon the assumption that every collision between molecules of active nitrogen and chlorine results in the formation of hydrogen chloride through the intermediate production of an active chlorine molecule, to calculate the probable yield of the acid. The number of collisions per c.c. per second is given by

$$n = 2\nu_1\nu_2(\sigma_1 + \sigma_2)^2\sqrt{2\pi kT(m_1 + m_2)/m_1m_2}$$

where ν_1 and ν_2 represent the number of molecules entering per second of active nitrogen and chlorine, respectively, σ_1 and σ_2 their diameters, and m_1 and m_2 their masses, and k and T have their usual significance. In a typical experiment a flow speed of 2600 c.c./hr. of nitrogen at *N.T.P.* was maintained, 1·5% of active nitrogen was present, and a 1 : 1 mixture of hydrogen and chlorine was admitted at the rate of $6{\cdot}2 \times 10^{-3}$ c.c./sec. 3·04 C.c. of *N*/50-hydrochloric acid were obtained in 30 minutes.

$$\text{Hence } \nu_1 = 1{\cdot}5 \times 10^{-2} \times 2{\cdot}7 \times 10^{19} \times 2600/3600 = 2{\cdot}9 \times 10^{17};$$
$$\nu_2 = 3{\cdot}1 \times 10^{-3} \times 2{\cdot}7 \times 10^{19} = 8{\cdot}3 \times 10^{16};$$
$$\sigma_1 + \sigma_2 = 6 \times 10^{-8};\ k = 1{\cdot}37 \times 10^{-16};$$
$$m_1 = 1{\cdot}66 \times 28 \times 10^{-24};\ m_2 = 1{\cdot}66 \times 71 \times 10^{-24}.$$

Substituting in the equation, we obtain $15{\cdot}2 \times 10^{24}$ collisions/sec. between molecules of active nitrogen and chlorine.

Since the number of chlorine molecules entering per second is $8{\cdot}3 \times 10^{16}$, we see that every one will be hit several times every second; hence we may assume that all the chlorine molecules present are activated at least once.

The number of collisions between the hydrogen and chlorine molecules is similarly calculated to be $6{\cdot}2 \times 10^{24}$/sec.

Hence the number of collisions between the active nitrogen and chlorine molecules and between the chlorine and hydrogen is sufficient to warrant the assumption that yields of hydrogen chloride comparable with the concentration of active nitrogen should be obtained. This is the case, since the yield observed gives $2{\cdot}05 \times 10^{16}$ molecules/sec., whereas the active nitrogen flow is $2{\cdot}9 \times 10^{17}$ molecules/sec.

Hence we have considerable evidence that the production of hydrogen chloride is due to the formation of excited molecules of chlorine.

In searching for a reason why hydrogen chloride should be produced whilst neither hydrogen bromide nor iodide is formed, we may note that we are dealing with the stimulation only of the halogen to form an excited molecule, a condition comparable with the photochemical union between hydrogen and the halogens rather than with the thermochemical union. The photochemical union of the halogens is conditioned either by the heat evolution of the reaction $X + H_2 = HX + H$, as postulated by Nernst, or by that of the reaction $X_2' + H_2 \longrightarrow XH + H + X$, if the view be taken that the excited halogen molecule (X_2') is the reactive molecule. It is well known that the photochemical combination of hydrogen with chlorine, but not that of hydrogen with bromine or iodine, takes place at the ordinary temperature when the halogens are excited only to their threshold values for reaction, *i.e.*, in the visible portion of the spectrum. The fact that the halogens on excitation with active nitrogen yield banded rather than line spectra lends support to the hypothesis that the primary chemical reaction in the photochemical combination of a halogen with hydrogen is a reaction between an excited molecule of the halogen and hydrogen rather than the dissociation of the excited molecule into atoms with subsequent reaction. It does not, however, distinguish between the two possible reactions (1) $X_2' + H_2 \longrightarrow HX + HX'$, and (2) $X_2' + H_2 \longrightarrow HX + H + X$, although, from analogy with the thermal combination of hydrogen and bromine and from the existence of chains in the hydrogen–chlorine reaction, the reaction (2) appears more plausible than (1).

(e) *The hydrogen halides.* The halides HI, HBr, HCl form an interesting series in that the energies of activation for decomposition rise from the iodide to the chloride. From Bodenstein's data (*Z. Physik,* 1899, **29**, 295), the energy of activation for the thermal decomposition of hydrogen iodide can be computed as $E_{2HI} =$ 45,700 cals. For the other reactions, such data are not available, but it may be noted that hydrogen bromide decomposes in the homogeneous gas phase quite rapidly over the temperature range 400—750° K., which would indicate an energy of activation of about 40,000—50,000 cals./g.-mol. For hydrogen chloride, much higher temperatures are necessary (*ca.* 1400° K.) which would yield a value of $E_{2HCl} =$ *ca.* 90,000. If we compare the threshold radiation wave-lengths at which the percentage decompositions for the three halides are approximately identical, we obtain $\lambda = 4000$, 2800, and 2200 Å. for the iodide, bromide, and chloride, respectively. Since $E_{2HI} = 45{,}700$, those of the others must be of the order $45{,}700 \times 40/28$ and $45{,}700 \times 40/22$ or 65,000 and 83,000, respectively. We may assign values of the order of $E_{2HI} = 45{,}700$, $E_{2HBr} = 50{,}000$, $E_{2HCl} = 90{,}000$ without serious error. We should anticipate that both hydrogen iodide and hydrogen bromide might suffer decomposition, but not hydrogen chloride. This is found to be the case; the typical spectra of iodine and bromine were noted, whilst in the liquid-air trap both free halogen, ammonium halide, and traces of halogeno-amine were obtained. The reaction was *much* less marked with hydrogen bromide than with hydrogen iodide.

(f) *The oxides of nitrogen.* Both nitric oxide and nitrous oxide are of importance in this connexion. As has already been indicated (Part I, *loc. cit.*), the critical increment of nitric oxide is certainly below 55,000 cals., and in consequence the gas reacts with active nitrogen, undergoing decomposition to nitrogen and oxygen. In the case of nitrous oxide, we can, from the data of Hunter (*Z. physikal. Chem.*, 1905, **53**, 441) and of Hinshelwood (*Proc. Roy. Soc.*, 1924, **106**, 284) for the homogeneous bimolecular reaction, calculate an energy of activation of 60,300 cals./g.-mol. This gas was examined in the present experiments and did not affect the glow of active nitrogen. Moreover, when the gases, after admission of the nitrous oxide, were mixed with nitric oxide below the point where the afterglow ceases to be visible, no evidence of the formation of nitrogen peroxide in the liquid-air trap was found, indicating that no decomposition of the nitrous oxide had taken place

We have noted that hydrogen chloride, hydrogen, and nitrous oxide, with energies of decomposition of the order of 90,000, 85,000, and 60,000 cals./g.-mol., respectively, do not affect the afterglow, and we may therefore conclude that the energy of active nitrogen is below these limits. Other gases of relatively large critical energy increments were likewise examined for their effect on the afterglow; these included water vapour, carbon dioxide, and carbon monoxide, with energies of activation of the order of $E_{2CO_2 \rightarrow 2CO + O_2} = 120{,}000$ cals./g.-mol. and $E_{2H_2O \rightarrow 2H_2 + O_2} = 110{,}000$ cals./g.-mol. In neither case was any effect other than a dilution observed.

Careful search for oxygen (by the admission of nitric oxide) and for cyanogen compounds in the former case, and for water and formaldehyde in a carbon monoxide–hydrogen mixture, revealed no evidence of chemical reaction.

We have seen that among the gases which are raised to a chemically reactive state we may include the halogens, and in the case of chlorine, of which the lowest critical increment for reaction with hydrogen is some 55,000 cals./g.-mol., only a part of the active nitrogen appears to be effective in promoting chemical action. This would set 55,000 cals. as the upper limit for the energy content of active nitrogen, whilst the experiment with nitrous oxide indicates that 60,000 cals. is well above the maximum.

Adopting a value of 150,000 cals. for the latent heat of evaporation of carbon (Thiel and Ritter, *Z. anorg. Chem.*, 1923, **132**, 151), we obtain for the linkage C–H (Fajans, *Ber.*, 1920, **53**, 643) a value of *ca.* 80,000 cals.; we should accordingly anticipate that methane would not be affected by active nitrogen. Lord Rayleigh (*Proc. Roy. Soc.*, 1915, **91**, 317) was of the opinion that methane underwent slight decomposition, a view to which König and Elöd (*Ber.*, 1914, **47**, 516) could not subscribe. Since small traces of other hydrocarbons readily react with active nitrogen, it is necessary to ensure their absence from the gas, and we have accordingly prepared pure methane from carbon monoxide and hydrogen by passage over a diatomaceous earth–nickel catalyst. This gas, which, after seven fractionations from liquid air, was free from carbon monoxide, did not affect the glow of active nitrogen, and no hydrogen cyanide could be detected in the gases after admixture of the methane. It may be observed that methane will undergo decomposition with a critical increment of only 55,000 cals. on a hot platinum wire (Schwab and Pietsch, *Z. physikal. Chem.*, 1926, **121**, 189) and a surface reaction between active nitrogen and methane is thus not impossible under the right conditions.

Ammonia is readily decomposed by active nitrogen into nitrogen and hydrogen; the critical increment here is probably quite low.

Conclusions.

In all the cases so far examined, chemical action as a result of second-type collisions, either between active nitrogen and the gas introduced or else as a "sensitised" reaction, occurs only when the critical increment of the second gas for the appropriate reaction is below 55,000—60,000 cals./g.-mol., and is strongest when this is about 45,000 cals./g.-mol. This is obviously a measure of the energy of active nitrogen, and is not incompatible with the view that in the afterglow we probably have a species of statistical equilibrium among three types of active molecules, some above, some below, and the majority upon the 2-volt level, an opinion which is supported by the spectroscopic evidence upon the afterglow. The three series of bands into which the true afterglow spectrum can be divided have intensities roughly in the ratio 1 : 2 : 1 for the red, yellow, and green, respectively, and the upper limit of the last-named bands coincides well with that observed for the limiting increment for reaction with active nitrogen (55,000—60,000 cals./g.-mol.). Moreover, if, as a first approximation, we regard these intensities as giving the relative concentrations of the three species, we see that with a gas of critical increment of, say, 55,000 cals./g.-mol., the extent of the reaction should be about one-fourth of that observed, all other conditions being left constant, with a gas for which the critical increment is 43,000 cals./g.-mol. and below. In the case of hydrogen and chlorine the yield of hydrogen chloride is about 1/14th of the active nitrogen concentration, and while the point cannot for obvious reasons be stressed, this observation is nevertheless significant.

These reactions are of course selective in nature and do not directly give a mean value for the energy of the active nitrogen, such as is obtained by the calorimetric method. Making due allowance for other necessary considerations as indicated, we see that the value originally given for the energy of active nitrogen is amply confirmed.

It is also interesting to note that Aakeson (*Lunds Univ. Arsskr.*, 1916, **12**, No. 11) found that 1·7-volt electrons undergo inelastic collision with nitrogen molecules, and whilst this value is most probably not correct to ± 1 volt, since no correction was applied for initial velocity, the existence of a level in the molecule at about that to be expected from an evaluation of the energy of active nitrogen would appear to be established.

It would here appear advisable, in view of the criticisms which have been directed against our contentions as to the energy content and nature of active nitrogen, to restate our case *in extenso* and effect such agreement as is possible between our observations and the postulates of the spectroscopists (compare Johnson, *Nature*, 1927, **119**, 9).

In the preceding paper, on the assumption that one molecule of active nitrogen excites but one molecule of nitric oxide on reaction according to the schemes $N_2' + NO \longrightarrow NO'$ and $NO' + NO \longrightarrow N_2 + O_2$, it was shown that the calorimetric energy content of active nitrogen was equivalent to *ca.* 2·0 volts. In this paper, we have shown that chemical reaction is only effected by transfer of energy by second-type collisions from the active nitrogen to other gases when the requisite energy of activation lies below *ca.* 2·1 volts.

It is hoped to communicate similar conclusions from experiments on the catalytic decay of active nitrogen at the surface of metallic filaments, and from application of the Nernst heat theorem to the observations of one of us (Willey, *J. Soc. Chem. Ind.*, 1924, **43**, 260) on the iron nitride content of the vapours in an iron–nitrogen arc. It thus appears that for the purposes of chemical reaction active nitrogen only liberates energy equivalent to a 2·0-volt fall. We have regarded this as the total energy content of active nitrogen, for, as was pointed out in our first communication, there appears to be no reason why we should postulate the existence of several 2·0-volt falls in each molecule of active nitrogen. If, for example, the true energy content of active nitrogen is equivalent to 10 volts, then it will be necessary to postulate that one molecule can excite five nitric oxide molecules, transferring at each collision energy equivalent to *ca.* 2·0 volts. The same is true for the variety of chemical reactions recorded here : in no case do we find the active nitrogen transferring energy at one time equivalent to 4, 6, 8, or 10 volts, but always in 2-volt steps. Such steps in energy transfer apparently do not occur with excited mercury atoms, but if this suggestion for the reconciliation of spectroscopic and chemical data be true, it appears probable that the existence of successive 2-volt levels of some kind in the decay of active nitrogen should be capable of observation by spectroscopists.

THE LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE.
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