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Effect of Antimony Impurity on Self-Diffusion of Silver*†

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Coefficients for diffusion of Ag^{110} into single crystals of alpha silver antimony were measured as a function of temperature and concentration, over the range 550–900°C and 0–$1\frac{1}{2}$% antimony concentration. In addition, a number of measurements were made of the diffusion of Sb^{124} into similar alloys. The activation energy for silver self-diffusion was found to decrease by $1\frac{1}{2}$ kcal per percent added antimony. Effects of impurity were appreciably less for solute diffusion than for solvent diffusion. The results are in qualitative agreement with theories of Overhauser and Lazarus, and indicate that effects due to changes in vacancy concentration are smaller than those resulting from changes in mobility energy.

INTRODUCTION

COMPARISON of pre- and postwar data for the diffusion of antimony into silver[1] demonstrated considerable differences in results, probably due in part to the large gradients and solute concentrations necessitated by the earlier techniques. The existence of these large discrepancies indicated the desirability of a fundamental investigation of both impurity and gradient effects, using modern tracer methods.

It had been proposed by Seitz[2] that the role of vacancies in diffusion processes might be studied by enhancing the density of vacancies in the lattice. Small amounts of dissolved impurity, it was suggested, might cause such an enhancement.

Previous studies of the effects of impurities on diffusion had been made[3,4] and increases of diffusivity noted. Within the past few months, Hoffman, Turnbull, and Hart[5] have reported additional measurements on polycrystalline samples of AgPb and other silver alloys over a range of 700–900°C. The present investigation was designed to make measurements on alloy single crystals over a larger temperature range, in order to determine the existence and magnitude of changes, due to impurities, of the activation energy Q and frequency factor D_0, both defined by the equation

$$D_{\mathrm{Ag}}=D_0\exp(-Q/RT), \tag{1}$$

where D_{Ag} is the self-diffusion coefficient of silver in the alloy, R is the universal gas constant, and T is the absolute temperature.

EXPERIMENTAL

In order to preclude grain boundary diffusion in low-temperature measurements, single crystals were used for all specimens diffused below 850°C. These were prepared from 99.99% pure vacuum-cast silver and 99.9% pure antimony. The metals were placed in a National Carbon Co. A.U.C. grade graphite crucible, which had previously been cleaned by boiling in aqua regia, leaching in hot distilled water, and baking in vacuum at 1000°C. The filled crucible was sealed in Vycor at a pressure of 10^{-5} mm Hg, and the contents mixed by repeated tipping at a temperature above the melting point of silver. Following this, the sealed container was removed to a Bridgeman-type furnace, where the single crystal was grown. A gradient of 100°C per inch was maintained in the furnace by water cooling the lower end. It was possible to obtain crystals with an antimony concentration up to $1\frac{1}{2}$% by lowering the charge through the gradient at a rate of about one inch per hour.

Methods of preparation and diffusion of the individual specimens have been described previously.[6,7] Most of the diffusion coefficients were determined by standard sectioning techniques, using a precision lathe to obtain cuts of $\frac{3}{4}$ to 3 mils thickness.

An attempt was made to extend the temperature range down to 450°C by use of a precision grinding machine which permitted removal of sections 3 microns in thickness.[8] These latter data were unfortunately less reliable due to macroscopic voids in the alloy crystals used. Metallographic examination showed these voids to be roughly spherical, 5–20 microns in diameter, and of varying sizes in different specimens. Thus the apparent diffusion coefficients in grinder samples, where the total penetration, $4(Dt)^{\frac{1}{2}}$, was less than 2 mils (50) microns), could easily have been 10–20% high, as the results indicated.[9] For this reason, low-temperature results are not included here. However, the data reported, in the range above 550°C, do not suffer from this source of error, since penetration depths were invariably greater than 10 mils. It should be noted that such voids have not been observed in pure silver or

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[1] Slifkin, Lazarus, and Tomizuka, J. Appl. Phys. **23**, 1405 (1952).

[2] F. Seitz, Acta Cryst. **3**, 355 (1950).

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[7] Slifkin, Lazarus, and Tomizuka, J. Appl. Phys. **23**, 1032 (1952).

[8] Letaw, Slifkin, Portnoy, Rev. Sci. Instr. **25**, 865 (1954).

[9] E. Sonder, Ph.D. thesis, University of Illinois, 1955 (unpublished).

copper crystals which are grown more slowly and in a continuously pumped rather than sealed vacuum.

The chemical composition of the alloy specimens was determined, after the diffusion measurements had been completed, by the Detroit Testing Laboratory. The method used consisted essentially of separation of the silver and antimony by precipitation and filtration and subsequent volumetric titration of the antimony against potassium bromate to a methyl orange end point. The analyses showed that specimens originating from the same ingot differed less than 15% in composition, indicating that segregation in the grown crystal ingots was small, and that the maximum variation in composition in any particular diffusion sample was less than 2%, since none of the samples were longer than $\frac{1}{8}$ the length of the original ingot.

A summary of the results of 21 measurements between 500 and 900°C appears in Table I. The coefficients given were calculated by a least squares method from the raw data, shown plotted in Figs. 1–4. To permit consideration of these results in terms of activation energy, the diffusion coefficients for each concentration range have been normalized to the same concentration and are shown plotted logarithmically as a function of $1000/T$ in Fig. 5. Also included in Fig. 5 and shown dotted are curves for the diffusion of antimony into pure silver as well as for self-diffusion of silver. The antimony line is from reference 6, while the silver self-diffusion line has been obtained from preliminary results of a re-evaluation of the activation energy for this process.[10]

TABLE I. Experimental data.

Tracer	Atom% Sb in alloy	Diffn. coeff. (cm²/sec)	Temperature (deg C)
Ag	0.54	1.17×10^{-11}	629.2
Ag	0.56	9.66×10^{-11}	716.9
Ag	0.67	2.27×10^{-9}	882.3
Ag	0.67	3.20×10^{-9}	899.8
Ag	0.92	2.71×10^{-12}	568.6
Ag	0.92	2.67×10^{-12}	568.6
Ag	0.90	1.06×10^{-10}	716.3
Ag	0.88	2.46×10^{-9}	875.7
Ag	0.85	2.84×10^{-9}	890.4
Ag	1.36	3.50×10^{-12}	567.8
Ag	1.43	1.74×10^{-11}	629.3
Ag	1.33	1.38×10^{-10}	716.5
Ag	1.38	6.23×10^{-10}	792.7
Ag	1.42	2.94×10^{-9}	875.3
Ag	1.45	3.80×10^{-9}	890.6
Sb	0.72	2.09×10^{-11}	567.7
Sb	0.72	1.96×10^{-11}	567.7
Sb	0.73	5.54×10^{-10}	714.7
Sb	0.73	5.89×10^{-10}	714.7
Sb	2.73	7.15×10^{-10}	709.9
Sb	2.73	7.07×10^{-10}	709.9

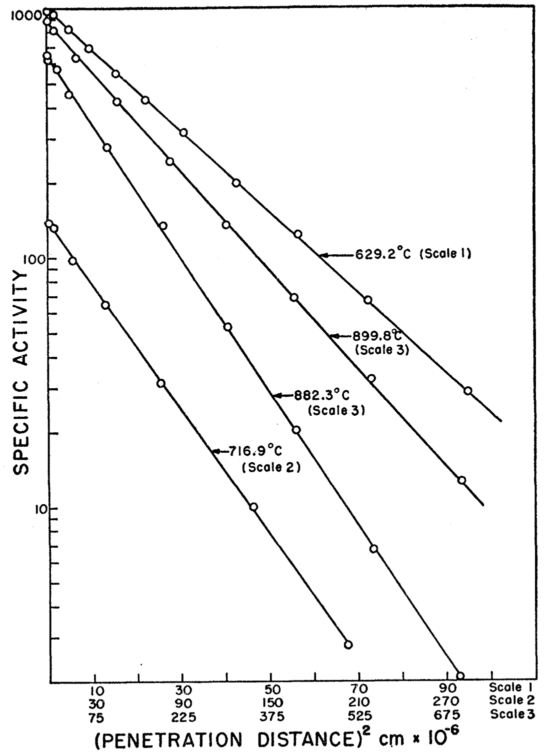

FIG. 1. Penetration curves, 0.53% Sb alloy, silver tracer.

The diffusion coefficients determine, within experimental error, straight lines. The activation energies obtained from these by a least squares method are listed in Table II, together with the frequency factors, D_0. The results may be summarized by the relations: $Q(c)-Q(c=0)=1.5c$, and $D_0(c)/D_0(c=0)=0.25c$, where c is the antimony concentration in atom percent and Q is in kilocalories.

Exploratory results indicate that, for diffusion of antimony in the same alloy system, impurity effects are appreciably smaller. Four measurements on 0.7% antimony samples, indicated by filled triangles in Fig. 5, show no difference from diffusion in pure silver. However, in a 2.8 atomic percent antimony polycrystalline sample, a small but significant increase (20% above the value for pure silver) was noted. That point is shown by a filled circle. It might be observed that the total amount of antimony soluble in silver, 7%, is only slightly more than twice the 2.8% in the sample showing increased diffusion.

An estimate of the accuracy of the data was made from the reproducibility of repeat measurements and from the standard deviation of the data from the Arrhenius plots, both being approximately 6%. In-

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[10] Upon connecting diffusion coefficients at the same temperature but different composition by smooth curves, it was found that extrapolation to zero Sb concentration indicated appreciable difference from published values (reference 7) for self-diffusion of pure silver. Since one of the purposes of the present investigation was to determine the change of activation energy with impurity concentration, it was deemed of critical importance to have a very accurate value of Q for the slef-diffusion of silver. A redetermination of the temperature dependence of self-diffusivity was thus begun. Partially completed results are given by $D=0.4\exp(-44.1/RT)$ cm²/sec.

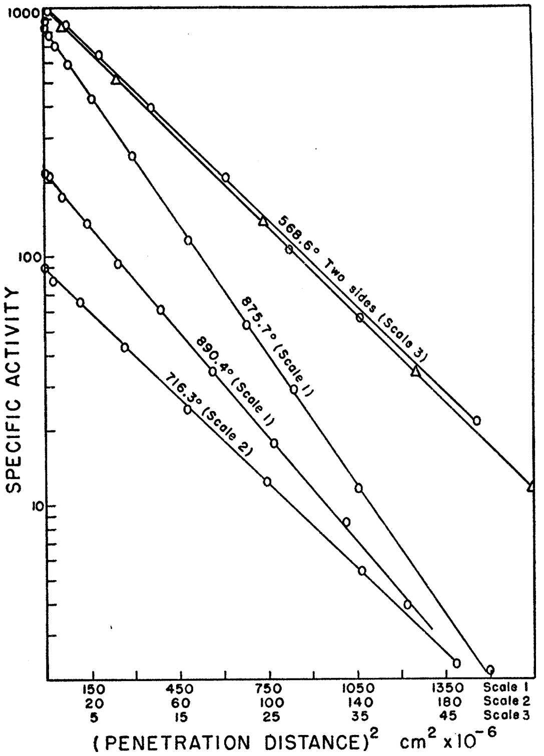

FIG. 2. Penetration curves, 0.89% Sb alloy, silver tracer.

cluding a possible 2° error in temperature calibration, one would estimate the probable error in D_0 and Q to be 15–20% and about 0.8% respectively.

DISCUSSION

A. Comparison with Prewar Data

As mentioned previously, pre- and postwar measurements of the diffusion of antimony into silver yielded inconsistent results.[1] Diffusion coefficients differed by as much as a factor of ten; the activation energies differed by 100%. The present experiment shows that these discrepancies are not due to the higher antimony concentrations in the prewar measurements. The diffusion couples of these early experiments consisted of pure silver and a 3% antimony alloy. According to the present results, the maximum change in diffusion coefficient ascribable to a 3% antimony concentration is about 50%; changes in activation energy should not exceed 10%. It therefore seems that the inconsistencies are caused by gradients in concentration or by the poor sensitivity of the prewar techniques.

TABLE II. Experimental results showing change of activation energy, Q, and frequency factor, D_0, due to added antimony.

	Pure silver	0.53% Sb	0.89% Sb	1.42% Sb
Q	44.05	43.5	42.6	42.0
D_0	0.403	0.382	0.302	0.275
ΔQ		0.55	1.45	2.05

B. Possibility of Large Changes in the Number of Vacancies

The fact that reasonably constant slopes were obtained from plots of log D as a function of $1/T$ indicates that the impurity atoms cause little increase, if any, in the concentration of vacancies in the lattice. A large number of impurity-created vacancies would probably evidence itself by a diminished activation energy at low temperatures, where the number of thermally activated vacant sites would become smaller than the more or less constant number accompanying the impurity atoms.

C. Possible Changes in Mobility Energy

It is well known that solution of an impurity may change the lattice spacing of a metal.[11] Since the mobility energy of diffusion seems to be quite sensitive to interatomic spacing, it has been proposed by Overhauser[12] and later by Lazarus[13] that impurity effects

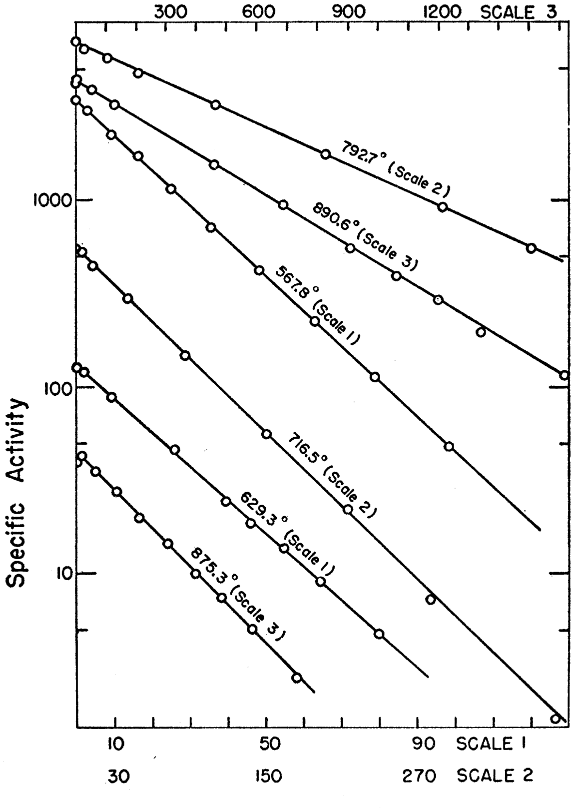

FIG. 3. Penetration curves, 1.4% Sb alloy, silver tracer.

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[11] See, for instance, Hume-Rothery, Lewin, and Reynolds, Proc. Roy. Soc. (London) **A157**, 167 (1936).

[12] A. Overhauser, Phys. Rev. **90**, 393 (1953); **91**, 246(A) (1953).

[13] D. Lazarus, "*Impurities and Imperfections in Metallic Diffusion*," American Society of Metals, Chicago Meeting, 1954 (unpublished).

may be viewed in terms of changes of the mobility energy.

Overhauser considered the impurity atoms as sources of strain in a continuous medium. Assuming a Born-Mayer repulsive potential between atoms, $W=K\times\exp(-r/\rho)$, where r is the nearest neighbor distance and K and ρ are constants, Overhauser calculated the change in diffusion barrier height as a function of strain at any point. Subsequent averaging over the strain field permitted derivation of an expression for the change in mobility energy,

$$\Delta E=RTX\left[\frac{128\pi}{45}\left(\frac{b}{r_0}\right)^3\left(\frac{gk}{RT}\right)^2+\frac{32\pi\gamma}{3}(1-3\lambda)\left(\frac{gk}{RT}\right)\right],$$

where

$$k=\frac{Kb\sqrt{\frac{3}{2}}}{\rho}\exp\left(-\frac{b}{\rho}\sqrt{\tfrac{3}{8}}\right),$$

$$\lambda=\exp\left[-\left(\frac{2-\sqrt{3}}{2\sqrt{2}}\frac{b}{\rho}\right)\right],$$

$$\gamma=2(1-2\mu)/(1+\mu).$$

μ is Poisson's ratio, b is the lattice constant, X is the fraction of impurity atoms, g is a numerical constant proportional to the strain discontinuity introduced by the impurity atom, and r_0 is a cut-off parameter of the order of the lattice spacing, introduced in the averaging process to prevent the integral from diverging at the origin. Using the present data for the silver antimony system, Hume-Rothery's measurements for the expansion of the silver lattice,[11] and a value of 0.20 A for the constant ρ, we have calculated r_0 to be 4.04 A, a value which differs little from the lattice constant of the silver lattice, 4.08 A. The fact that the r_0 calculated from these data does approximate the lattice constant would indicate that an approach like Overhauser's can very well account for the small changes observed, i.e., that the changes in Q may very well be due to changes in mobility energy for vacancies.

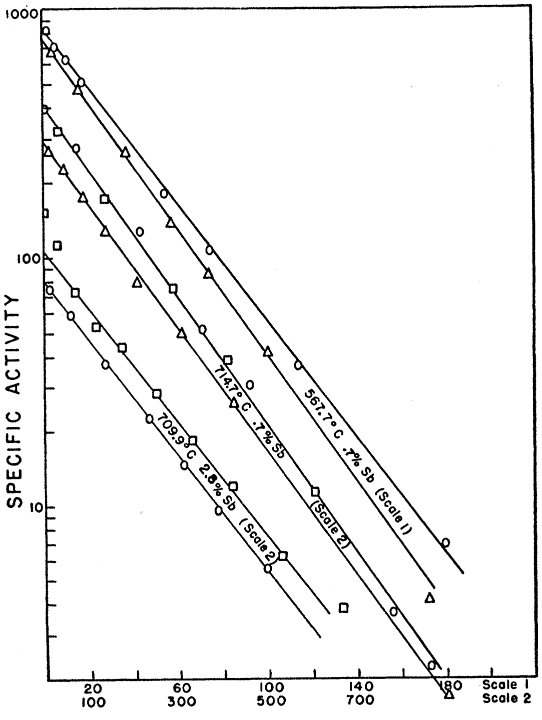

FIG. 4. Penetration curves, 0.7% 2.8% Sb alloy, antimony tracer.

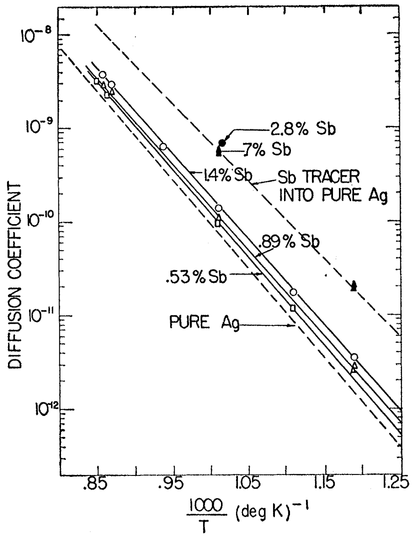

FIG. 5. Temperature dependence of diffusion coefficients.

A more quantitative calculation has been presented presented by Lazarus, who based his calculation on a model in which a diffusion jump is viewed as a unit shear of the lattice cell containing the diffusing atom and a vacancy. The change in mobility energy is thus equal to one-half the change in the atomic 110 shear modulus, which can be calculated for a uniform expansion of the lattice by the method of Fuchs.[14] Localized effects were taken into account separately by assuming that a solvent atom that is adjacent to both members of an impurity vacancy pair will be able to shear into the vacancy with no higher mobility energy than the impurity atom. The resulting expression for the ratio of jump probabilities in the impure (p^i) to that in the pure (p^0) lattice is given by

$$p^i/p^0=1-4X+4X\exp(-\Delta E_{mi}/RT), \tag{3}$$

where ΔE_{mi} is the difference in mobility energy between the solvent and solute atoms diffusing in the pure lattice.

Including also a small effect due to a slight increase in the vacancy concentration, Lazarus arrived at the following expression for the ratio of self-diffusivities in

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[14] K. Fuchs, Proc. Roy. Soc. (London) **153**, 622 (1936).

TABLE III. Comparison of experimental results and values calculated on the basis of Lazarus' model.

Theoretical	$\rho(A)$	0.15	0.20	0.25
	$D_0/(D_0)_{\text{pure}}$	0.50	0.72	1.02
	ΔQ(kcal/mole)	1.3	1.2	1.1
Experimental				
	$D_0/(D_0)_{\text{pure}}$	0.73		
	ΔQ	1.5		

an impure (D^i) and pure (D^0) lattice,

$$\frac{D^i}{D^0}=\left[\exp\left(\frac{C\alpha r}{R}-\frac{1}{RT}\right)\left(E_m{}^i-E_m{}^0\right)\right]\times\left[1-X+X\exp-\frac{\Delta E_{vi}}{RT}\right]\times\left[1-4X+4X\exp-\frac{\Delta E_{mi}}{RT}\right], \quad (4)$$

where α is the linear coefficient of thermal expansion, r is the nearest neighbor distance, $E_m{}^0$ and $E_m{}^i$ are the mobility energies in the pure and impure lattice calculated on the basis of uniform expansion, C is a constant of the order of 3, and ΔE_{mi} and ΔE_{vi} are the differences of mobility and vacancy creation energies between diffusion of the solvent and solute. The sum of these last two, $\Delta Q=\Delta E_{mi}+\Delta E_{vi}$, can be obtained from diffusion measurements of solvent and solute in the pure lattice.

Since the Born-Mayer exponent, ρ, which appears as a parameter in the theory, is not accurately known, effective activation energies, Q, and intercepts, D_0, have been calculated for three values of ρ, 0.15, 0.20, and 0.25. These effective values were obtained by calculating diffusion coefficients for temperatures of 700, 800, 900, and 1000 deg K and then fitting them to an Arrhenius equation, as had been done for the experimentally determined diffusion coefficients. Ratios of values of D_0 for a 1% alloy and pure silver as well as differences in activation energy, Q pure $-Q1\%$ impurity, are compared with the experimental results in Table III. It might be pointed out that the theory does not wholly account for the observed changes, although qualitative agreement is excellent.

D. Jump Frequency Formalism

In connection with their data on Pb, Cu, Ge, and Al impurities in silver, Hoffman, Turnbull, and Hart[5] have presented a formalism in which diffusion coefficients for solvents and solutes in pure and impure material are written in terms of three jump frequencies, those of the solute, pure solvent, and a solvent atom in a zone around an impurity. They have neglected effects due to the overall expansion of the lattice, but have derived an expression that takes into account short-range effects from all sources, i.e., changes in mobility as well as in vacancy concentration. The self-diffusivity, in an impure solvent in which the impurity diffuses faster than the solvent, is given by

$$D_1=(1-aX)D_1{}^0+aXD_2, \quad (5)$$

where $D_1{}^0$ is the self-diffusivity of the pure solvent, D_2 is the diffusion coefficient for the solute in the solvent, and a is the number of effective solvent vacancy exchanges during the time the solute exchanges once with the vacancy. This number cannot be greater than the total number of solvent atoms in the region strained by the impurity, since additional jumps could not be classed "effective."

It is interesting to compare this result with the expression derived by Lazarus [Eq. (3)] under much more restrictive assumptions. He assumed that the mobility of only those four atoms that can be nearest neighbors to both the impurity and the vacancy will be enhanced, hence the four in Eq. (3). It might seem reasonable to assume as did Hoffman, Turnbull, and Hart that other atoms in the region may also diffuse more easily; hence substitution of a number greater than four would seem justified. The present data suggest that a value in the range of six or seven is needed for agreement.

SUMMARY

1. Measurements of self-diffusion coefficients of silver as a function of antimony concentration and temperature show that in the range 550–900°C the activation energy decreases by $1\frac{1}{2}$ kcal per mole per percent added antimony, and that the frequency factor decreases by 25% for each percent added antimony in the 0–$1\frac{1}{2}$% antimony range.

2. The effect of impurities on solute diffusion is appreciably smaller than that on self-diffusion.

3. Impurity effects are small and can therefore not be the major cause of discrepancies between tracer and nontracer results.

4. Qualitative agreement exists between these data and theories of Overhauser and Lazarus, both of which ascribe the effects mainly to changes in mobility energy. The lack of any great amount of curvature in the Arrhenius plots indicates small changes in the vacancy concentration due to impurity additions.

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