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Radiation-Induced Swelling of Stainless Steel

Breeder reactor performance will be affected by swelling of structural material.

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All technologically advanced countries are now engaged in the development of sodium-cooled fast breeder reactors, reactors that will generate significantly more fissionable material than they consume (*1*). The core of such reactors provides a unique environment for structural materials. The two main features of this environment are the presence of liquid sodium and the high flux of fast neutrons. Compatibility of the stainless steel structural material with sodium is satisfactory in the temperature range of 380° to 600°C (700° to 1100°F) now being used. However, the high flux of fast neutrons produces changes in the stainless steel that have never been observed before.

Small voids form and grow, giving rise to swelling of the steel at an ever-increasing rate. This swelling phenomenon has been found to depend on temperature and neutron dose. The change in volume is only a few percent in the prototype fast reactors now in operation, but could be 10 percent or more under the conditions required in an economical breeder reactor. Such swelling will decrease the breeding ratio (that of fissionable material generated to fissionable material consumed) because additional free space must be put into the core to accommodate the swelling. Other problems arise from the core warping, which is due to differential expansion in different parts of the core. The differential expansion is the result of nonuniform temperature and flux distribution in the reactor core and could cause difficulties in reactor operation beyond a certain dose. The actual economic penalty resulting from swelling is significant but not yet clear.

The problem cannot be avoided simply by going to other metals or alloys, since voids will still form. Up to now, work on stainless steel shows that the extent of the swelling varies with alloy composition, heat treatment, and plastic deformation, although in ways poorly understood at this time. Reproducible reductions in swelling of a factor of 3 would have great economic value and seem to be in the realm of possibility.

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Experimental Observations

The swelling of stainless steel was first reported by Fulton and Cawthorne in 1967 (*2*). Since then the main characteristics of the swelling have been established. Figure 1 shows the voids that give rise to the swelling. They are a few hundred angstroms in diameter and are distributed rather uniformly throughout the specimen. There is some helium present in the alloy, but these are not helium-filled bubbles because, when the alloy is annealed at a higher temperature after radiation, the voids shrink and largely disappear. Helium-filled bubbles would expand slightly in such an annealing process because helium is insoluble in stainless steel.

Swelling occurs only in a limited temperature range. When the amount of swelling of stainless steel is plotted against temperature, the resulting bell-shaped curve falls off sharply outside the temperature range 400° to 600°C. In general, voids form between 0.3 and 0.5 of the absolute melting temperature in metals irradiated in a fast reactor. This temperature range cannot be avoided for stainless steel because, at higher temperatures, the strength is too low; but if the temperature of the sodium is lower, the loss in efficiency of the turbines is unacceptable.

Figure 2 shows the variation of swelling with the total number of fast neutrons passing through the sample, that is, the fluence. The slope of this line is greater than unity, an indication that the percent volume (V) change ($\Delta V/V$) varies between linearly and parabolically with time in the reactor. Figure 2 shows the fluence that the designers desire for minimum fuel-cycle cost in a commercial breeder reactor. No experimental data exist at this fluence of 3×10^{23} neutrons per square centimeter and above. In fact, almost no data exist above 1×10^{23} neutrons per square centimeter.

The neutrons formed by nuclear fission have an average kinetic energy of 2 megaelectron volts. In a breeder reactor, no effort is made to decrease the speed of the neutrons, and the mean energy of a neutron when it is again captured in the core is roughly 0.2 Mev. In this range of 2 to 0.2 Mev, the fission cross section of uranium or plutonium is much lower than it is for thermal neutrons. As a result, the neutron flux in a breeder reactor core is orders of magnitude higher than it is in a thermal reactor. The fast neutrons flying through the structural members of the core occasionally collide with a lattice atom. In this collision, roughly 1 percent of the neutron's kinetic energy is imparted to the lattice atom. This is enough to tear it from its lattice site and send it bounding through the lattice. The main result of this collision is the production of a diffuse cluster of roughly 100 vacant lattice sites, and the atoms ejected from their former positions end up in interstitial sites. The higher flux and mean energy of these neutrons result in a rate of production of such displacements that is roughly 10^3 times higher in a fast breeder reactor than in a thermal reactor.

Given this high rate of production of point defects, under what conditions can it lead to the growth of voids? Two conditions are needed: (i) the supersaturation of vacancies must be sufficient to overcome the surface tension forces that tend to shrink the voids, and (ii) a significant fraction of the interstitials and vacancies must be removed at sinks, instead of recombining with each other.

Under steady-state conditions, the rate of defect production is equal to the rate of annihilation. For vacancies, this balance can be written in the form

$$\alpha\phi = \beta D_i N_i N_v + \gamma_v p_s N_v D_v \qquad (1)$$

where production is equal to mutual recombination plus annihilation at sinks.

The production rate is proportional to the flux, ϕ. Mutual recombination occurs at a rate proportional to the product of the average vacancy concentration, N_v, the average interstitial concentration, N_i, and the diffusion coefficient of the more rapidly moving defect, the interstitial, D_i. The rate of annihilation of vacancies at sinks is proportional to the sink concentration, p_s, the vacancy diffusion coefficient, D_v, and N_v; α, β, and γ_v are the constants of proportionality. Solving for N_v gives the concentration of radiation-produced vacancies

$$N_v = \frac{\alpha\phi}{\beta D_i N_i + \gamma_s p_s D_v} \qquad (2)$$

Both D_i and D_v increase exponentially with temperature, while α, β, γ_s, and p_s are independent of temperature at the low temperature of interest here. Thus for a given flux, N_v increases rapidly, if the temperature falls. The total concentration of vacancies is that given by Eq. 1 plus the concentration at thermal equilibrium (N_v^e),

$$N_v^e \simeq \exp(-H_v/RT) \qquad (3)$$

where H_v is the energy required to form a vacancy, R is the gas constant, and T is temperature. The vacancy supersaturation is the ratio

$$S = \frac{N_v^e + N_v}{N_v^e} \qquad (4)$$

Now consider the two requirements for swelling: first, supersaturation and second, recombination instead of annihilation of sinks.

1) The supersaturation can be high only if $N_v \gg N_v^e$. As the temperature drops, N_v^e falls while N_v rises. Thus there is a crossover temperature above which $N_v^e > N_v$ and below which the vacancy concentration rises rapidly above N_v^e. The actual crossover point depends on the flux and sink concentration, but comes at about half the melting temperature. In Fig. 3 the vacancy concentration is plotted against the temperature estimated for stainless steel in a fast reactor core.

2) Figure 3 shows that the number of vacancies per unit volume in the steady state rises rapidly with falling temperature. Equations similar to Eqs. 2 and 3 exist for interstitials, so the interstitial concentration, N_i, also rises parallel to N_v. In Eq. 1, the rate of recombination increases as $N_v N_i$, whereas the rate of annihilation of vacancies at sinks is proportional to N_v (for interstitials it goes as N_i). Thus, as the temperature drops, the concentration of point defects rises, and recombination becomes the dominant process for eliminating point defects. Qualitatively, below some temperature so many vacancies occur that essentially all of the diffusing interstitials bump into vacancies before they come to a sink.

The limited temperature range where voids can form lies roughly between 0.3 and 0.5 of the melting tempera-

Table 1. Reactions producing helium in type 304 stainless steel.

Fast neutrons	Helium produced* (%)
$Ni^{58} + n^1 \rightarrow He^4 + Fe^{55}$	37
$N^{14} + n^1 \rightarrow He^4 + B^{11}$	21
$Fe^{56} + n^1 \rightarrow He^4 + Cr^{53}$	13
$Cr^{53} + n^1 \rightarrow He^4 + Ti^{50}$	10

* Produced in type 304 stainless steel (≃ 250 parts per million of nitrogen, 18 percent chromium, 10 percent nickel) in EBR-II [after Dudley *et al.* (*11*)].

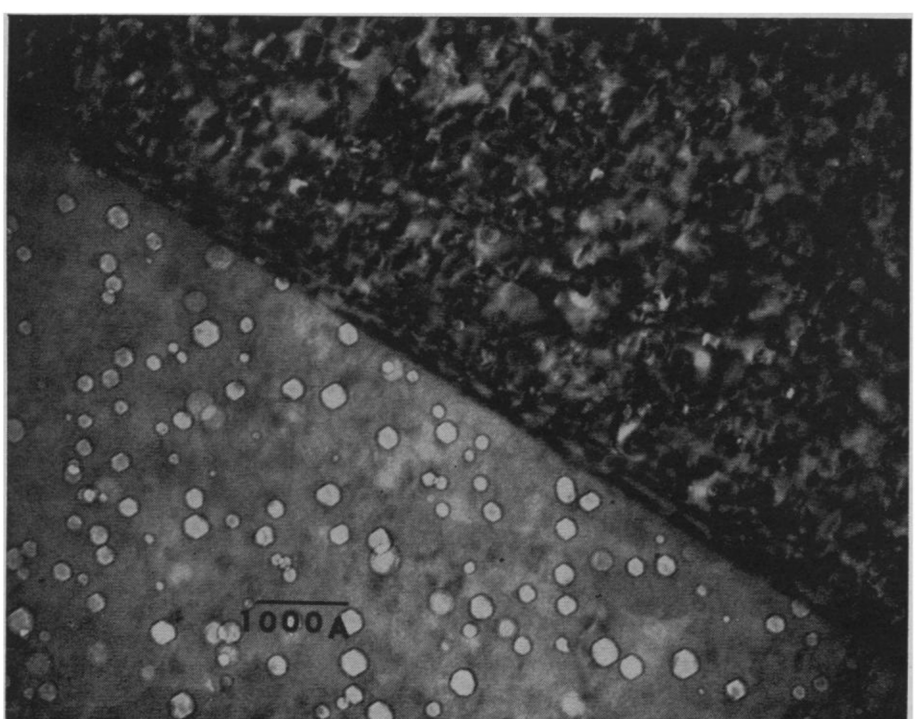


Fig. 1. Photograph of type 304 stainless steel taken in transmission with the electron microscope. Two grains are shown; the contrast conditions are adjusted in the darker one to show the high density of dislocation loops generated throughout the metal by the fast flux. In the lighter grain, only the voids show. [Courtesy of S. Harkness, Argonne National Laboratory]

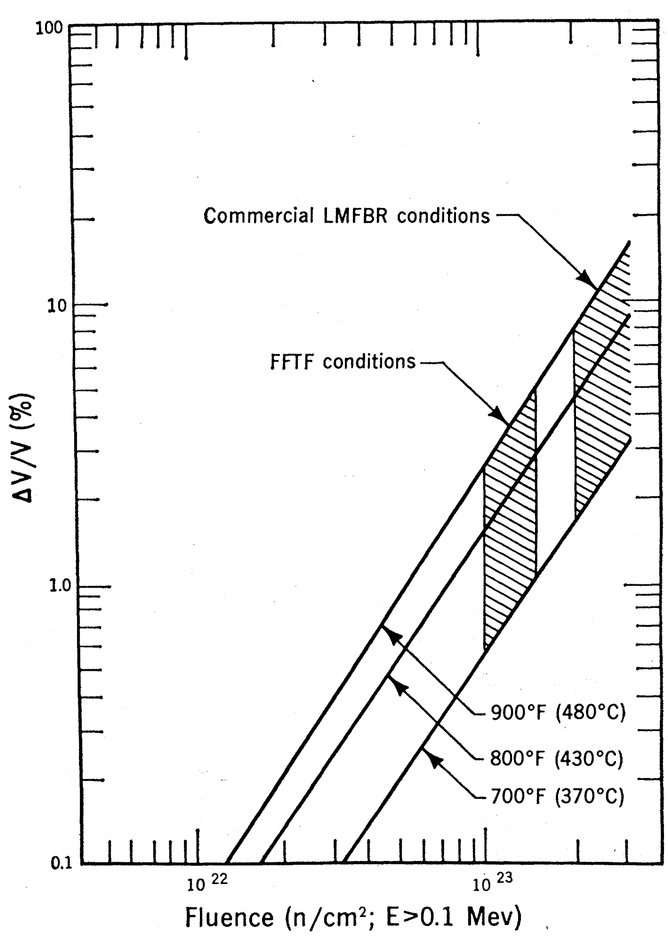
ture [400° to 600°C (750° to 1100°F) for stainless steel]. Above this range the vacancy supersaturation is inadequate; below this range recombination would play a dominant role.

This reasoning explains why voids *do not* form outside a limited temperature range. However, it doesn't explain why they do form in this range. Two related questions remain before we can complete our qualitative understanding of the phenomenon. (i) Why do the vacancies condense as three-dimensional voids instead of two-dimensional disks that would grow into a dislocation loop? The answer probably stems from the fact that helium is formed by fast neutrons through (n,α) reactions with the components of stainless steel (see Table 1). At equilibrium, helium is insoluble in stainless steel, so that these helium atoms will become trapped in clusters of vacancies and stabilize them as small voids. (ii) Since vacancies and interstitials are formed in equal numbers, why don't they diffuse to voids in equal numbers? Or, where do the excess interstitials go? The answer is that they go to dislocations. The main sink for interstitials and vacancies is dislocations. Both are attracted to dislocations by elastic forces, but, because the interstitial strains the lattice much more than the vacancy, the attraction between interstitials and the dislocation is stronger and longer range. Thus if voids and dislocations both exist in the metal, fewer interstitials and more vacancies will make it past the dislocations to the voids (*3*).

The factors determining the rate at which voids are formed (that is, the nucleation rate) are not well understood. Experiments indicate that the helium formed aids nucleation, as do interstitial impurity atoms dissolved in the metal. However, other factors influence the nucleation rate, but they are not yet identified. Harkness and Li (*4*) have given a kinetic treatment of void nucleation and growth that is consistent and complete. They evaluate several constants in their equations empirically, but within physically reasonable limits. They have made predictions about the dependence of $\Delta V/V$ on fluence, dislocation density, and precipitate density, among other things. Where data are available, their semiempirical theory works well.

What Can Be Done about It?

The impact of swelling on the design of the nuclear core of fast reactors is not yet clear, but the effect will be significant no matter what design changes are made. The uncertainty of the swelling under the higher fluence needed for economical fast reactors provides a substantial economic incentive in the search for cladding and structural materials that minimize the swelling.



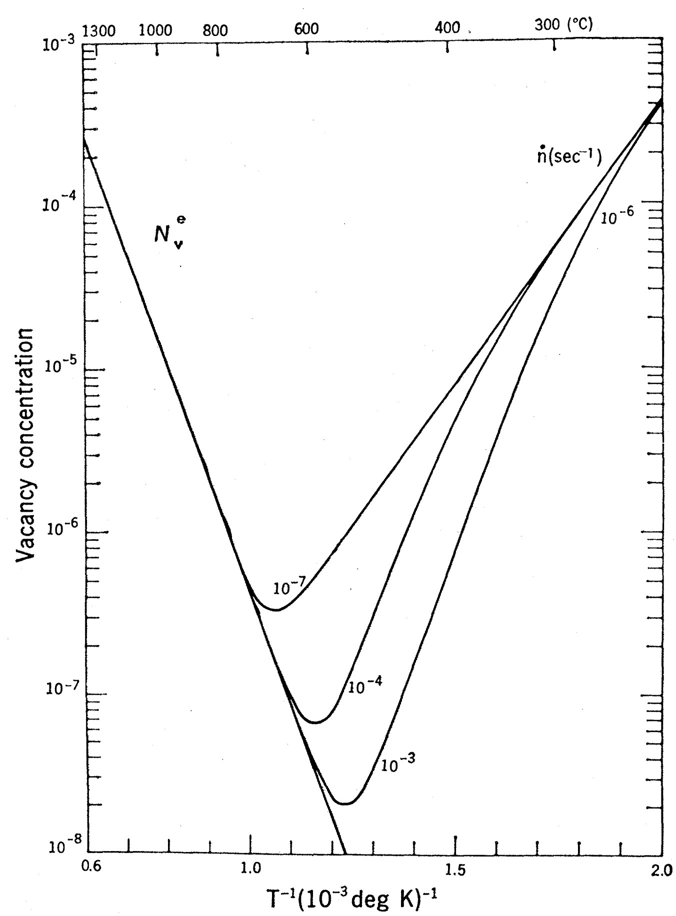


Fig. 2 (left). Estimates of swelling produced in cold-worked (20 percent) type 316 stainless steel. The data forming the basis for these curves lie below 10^{23} neutrons per square centimeter—much of it well below this value. Thus the lines are uncertain in the range of interest for a commercial liquid-metal fast breeder reactor (LMFBR). Fig. 3 (right). Vacancy concentration plotted against temperature estimated for stainless steel under fast reactor conditions; that is, 10^{-6} atomic displacements per second. The various curves on the right reflect differing sink concentrations ranging from annealed material (10^{-7}) to heavily cold-worked (10^{-3}). [After H. Wiedersich, North American Science Center]

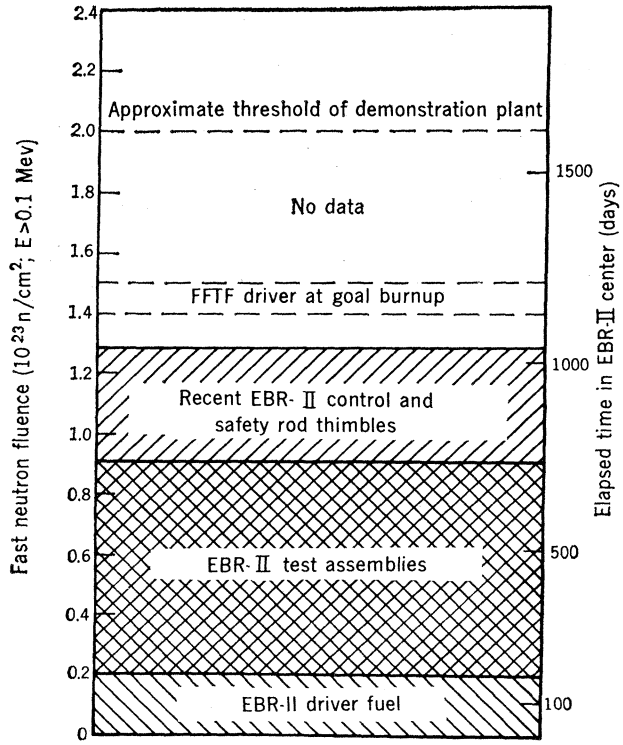


Fig. 4. Fast neutron fluence and time in EBR-II required to reach these levels are shown. Levels reached by material available to date are indicated in the hatched area. Above this are the levels projected for reactors being designed or built now.

This search for low-swelling materials is starting along two avenues: (i) for a different base metal and (ii) for a different composition or thermomechanical treatment of austenitic stainless steel. The first approach is not now being actively pursued in the United States. Studies of a wide range of metals have shown that all irradiated metals form voids, with the possible exception of the hexagonal close-packed metals zirconium and titanium (*5*). The British for several years have been studying molybdenum as a backup cladding material. Molybdenum might be used to avoid swelling problems, since coolant temperatures are below one-third of its melting point (~700°C or 1300°F). In the United States and Germany, appreciable work has been done on vanadium alloys, which swell less than stainless steel. However, at the present time the reactor industry would rather proceed with the familiar stainless steel in order to see how it really behaves than go through the substantial problems involved in establishing the experience needed to build a large plant with a more expensive new material.

Cold-working of the metal, heat treatment, and minor changes in composition all significantly affect the volumes of the fast neutron-induced voids. For example, the fluences required for $\Delta V/V$ to be 0.1 percent are an order of magnitude higher in commercially pure nickel than in high-purity nickel (*6*). Stainless steel that has been cold-worked 10 to 20 percent swells significantly less than annealed material, in the temperature range prevalent in test reactors (400° to 500°C or 750° to 930°F) (*7*). The addition of 0.2 percent titanium to type 304 stainless steel significantly decreases the swelling at lower fluences when the alloy is in the annealed condition, but does not affect it if the carbide is precipitated before irradiation (*8*).

These and other observations indicate that small changes in composition or microstructure can change the magnitude of swelling by a factor of 2 or more. If a reduction of even a factor of 2 could be attained *at higher fluences*, the economic benefits would be approximately $400,000 per year in one large (1000-megawatt electric) plant (*9*). When a significant fraction of the U.S. electrical energy is provided by the breeder reactor, the annual savings would run to eight figures.

The main problem in a systematic study of how these microstructural factors influence swelling is the long time needed to attain the necessary fluence in the available test reactors. Figure 4 shows the fluence attained in various parts of EBR-II, the only fast breeder reactor in operation in the United States. The time necessary to attain these fluences under the present operating conditions is shown on the right. Also shown are the fluences expected in the cladding of the next U.S. breeder reactor, the FFTF (fast flux test facility at Hanford, Washington), and in the projected power demonstration plant. These are at a fluence where no data now exist. If someone put a new set of test specimens in EBR-II today, it would take over 2 years to reach a fluence of 1×10^{23} neutrons per square centimeter, even with the higher power and higher plant factor that have recently been attained.

Thus considerable interest has developed in the use of heavy-ion accelerators to simulate the damage processes in fast reactor cladding. These machines can accelerate substantial currents (1 to 2 microamperes) of ions through voltages of 1 to 10 Mev. In a narrow region a few microns thick, these beams can produce displacement damage at a rate of 10^2 or 10^3 times greater than that caused by neutrons in EBR-II. (Reference here is only to the U.S. test reactor, but the flux is, within a factor of 2, the same as in the British fast reactor at Dounreay or in the French reactor at Cadarache.) Although the processes occurring in the accelerator target must differ in some ways from those in the reactor, there are some similarities. Experiments so far have shown that voids can be formed with the accelerator. The accelerator provides an opportunity to perform experiments in which conditions of temperature, purity, microstructure, dose, and the like can be systematically varied. This should allow us to obtain information that will aid in the development of an accurate model and help select the alloys to be studied in more detail in the fast test reactor (*10*).

Conclusion

Significant swelling (1 to 10 percent) due to small voids have been found in stainless steel when it is exposed to fast neutron doses less than expected in commercial fast breeder reactors. The main features of this new effect are: (i) the voids are formed by the precipitation of a small fraction of the radiation-produced vacancies; (ii) the voids form primarily in the temperature range 400° to 600°C (750° to 1100°F); and (iii) the volume increases with dose (fluence) at a rate between linear and parabolic. The limited temperature range of void formation can be explained, but the effects of fluence, microstructure, and composition are determined by a competition between several kinetic processes that are not well understood.

This swelling does not affect the feasibility or safety of the breeder reactor, but will have a significant impact on the core design and economics of the breeder. Preliminary results indicate that one cannot eliminate the effect, but cold-working, heat treatment, or small changes in composition can reduce the swelling by a factor of 2 or more. Testing is hampered by the fact that several years in EBR-II are required to accumulate the fluence expected in demonstration plants. Heavy-ion accelerators, which allow damage rates corresponding to much higher fluxes than those found in EBR-II, hold great promise for short-term tests that will indicate the relative effect of the important variables.

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12. Work performed under the auspices of the U.S. Atomic Energy Commission.

Maximum Principles in Analytical Economics

Paul A. Samuelson

The very name of my subject, economics, suggests economizing or maximizing. But political economy has gone a long way beyond home economics. Indeed, it is only in the last third of the century, within my own lifetime as a scholar, that economic theory has had many pretensions to being *itself* useful to the practical businessman or bureaucrat. I seem to recall that a great economist of the last generation, A. C. Pigou of Cambridge University, once asked the rhetorical question, "Who would ever think of employing an economist to run a brewery?" Well, today, under the guise of operational research and managerial economics, the fanciest of our economic tools are being utilized in enterprises both public and private.

So at the very foundations of our subject maximization is involved. My old teacher, Joseph Schumpeter, went much farther. Instead of being content to say economics must borrow from logic and rational empirical enquiry, Schumpeter made the remarkable claim that man's ability to operate as a logical animal capable of systematic empirical induction was itself the direct outcome of the Darwinian struggle for survival. Just as man's thumb evolved in the struggle to make a living—to meet his economic problem—so did man's brain evolve in response to the economic problem. Coming 40 years before the latest findings in ethology by Konrad Lorenz and Nikolaas Tinbergen, this is a rather remarkable insight. It would take me away from my present subject to more than mention the further view enunciated by Schumpeter (*1*) in launching the new subject of econometrics. Quantity, he said, is studied by the physicist or other natural scientist at a fairly late and sophisticated stage of the subject. Since a quantitative approach is, so to speak, at the discretion of the investigator, all the more credit to the followers of Galileo and Newton for taking the mathematical approach. But in economics, said Schumpeter, the very subject matter presents itself in quantitative form: Take away the numerical magnitude of price or barter exchange-ratio and you have nothing left. Accounting does not benefit from arithmetic; it is arithmetic—and in its early stages, according to Schumpeter, arithmetic is accounting, just as geometry in its early stages is surveying.

I must not leave you with the impression that analytical economics is concerned with maximization principles in connection with providing vocational handbooks for the practicing decision-maker. Even back in the last generation, before economics had pretensions toward being itself useful to practitioners, we economists were occupied with maxima and minima. Alfred Marshall's *Principles of Economics*, the dominating treatise in the 40 years after 1890, dealt much with optimum output at the point of maximum net profit. And long before Marshall, A. A. Cournot's 1838 classic, *Researches into the Mathematical Principles of the Theory of Wealth*, put the differential calculus to work in the study of maximum-profit output. Concern for minimization of cost goes back a good deal more than a century, at least back to the marginal productivity notions of von Thünen.

It is fashionable these days to speak of identity crises. One must not make the mistake attributed to Edward Gibbon when he wrote his *Decline and Fall of the Roman Empire.* Gibbon, it was said, sometimes confused himself and the Roman Empire. I know in these days of the living theater—and I ought to add on this occasion, of the theories of quantum mechanics—the distinction often becomes blurred between observing audience and acting players, be-

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This article is the lecture he delivered in Stockholm, Sweden, 11 December 1970, when he received the Nobel Prize in Economic Science. Minor corrections and additions have been made by the author. The article is published here with the permission of the Nobel Foundation and is included in the complete volume of *Les Prix Nobel en 1970* as well as in the series Nobel Lectures (in English) published by the Elsevier Publishing Company, Amsterdam and New York.