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Experiments at Very Low Pressures

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In the years since World War II, developments in experimental techniques have taken place that have made it possible to achieve and to measure pressures three to four orders of magnitude lower than those previously possible. Based in part on the work I have briefly described as well as on the important pioneering work of W. B. Nottingham, P. A. Anderson, L. Apker, and others, a new technology has been evolved for the region of pressures below 10^{-8} mm-Hg, a range which I think it is reasonable to call ultrahigh vacuum. The extension of the range of pressures attainable at room temperatures was motivated largely out of requirements in the fields of (i) physical electronics, in which it is now possible to study reactions with atomically clean surfaces, and (ii) gaseous electronics, in which it is the partial pressure of impurities rather than the total pressure that must be kept in the ultrahigh-vacuum range. M. A. Biondi (*1*) of Westinghouse Research Laboratories has shown that it is possible to prepare gases with an impurity content of less than one part in 10^9.

In this article I have reviewed very briefly some aspects of ultrahigh vacuum technology that have grown up as a result of continued interaction among various workers at our laboratories. I have been very brief because much of this material has been described in publications during the course of the past 3 years (*2, 3*). Thereafter I have described, at least by title, a number of studies that have been either made possible or tremendously improved by the advent of these very low pressures.

Basic Developments and Techniques

Some of the basic developments underlying the new technology are (i) an ionization gage to measure pressures down to 10^{-11} mm-Hg; (ii) an all-metal vacuum valve for manipulative and gas-handling systems; (iii) "ion pumping" to evacuate systems to pressures below 10^{-8} mm-Hg; (iv) new approach to design and engineering of vacuum systems; and (v) demountable systems. In a paper by R. T. Bayard and D. Alpert (*4*), it was shown that the standard ionization gage has a lower pressure limit of about 10^{-8} mm-Hg. The limitation is caused by a current to the ion collector that is produced by soft x-rays formed when the ionizing electrons strike the grid. The x-rays in turn release photoelectrons from the ion collector that produce a current completely independent of the pressure but of the same sign as ions arriving at the collector. By greatly reducing the solid angle available to x-rays, we showed that it was possible to lower the limit of measurable pressures by a factor of approximately 1000. A second development was the all-metal vacuum valve (*5*) capable of high-temperature bakeout. Such valves make it possible to seal off one part of a system from another, or to transfer gases with less than one one-thousandth of the contamination introduced by standard grease stopcocks. Third, we showed that it was possible to use the ionization gage as an ion pump to evacuate to very low pressures. Empirically, one finds that positive ions formed in the grid volume of a gage are, more or less, permanently removed from the volume after they have struck negatively charged surfaces. Fourth, we have adopted an entirely new approach to the design of vacuum systems for experiments in physical and gaseous electronics. Principles of design and engineering have been introduced into a field that has included much conjecture and has been more of an art than a science. Finally, it has been shown that it is possible to design ultrahigh-vacuum systems containing demountable joints. I have not listed some other very useful developments such as a bakable absolute manometer for the measurement of higher pressures and special vapor traps (*6*) with unusual characteristics that I have described in a subsequent paragraph.

Using these means, it has been possible to achieve working pressures as low as 10^{-10} mm-Hg in a routine and straightforward way with no refrigerants or chemical getters of any kind. We have some 17 to 20 systems of this type in use in our laboratories at the present time, and many of us feel that it is easier to obtain pressures of 1 or 2×10^{-10} mm-Hg in such systems than it used to be to produce pressures hundreds of times greater with conventional means. A crucial requirement for any such system is that the entire system should be capable of high-temperature bakeout. Figure 1 shows a system in which the vacuum valves, ionization gages, and gas source are ready for assembly on a series of module units, each 16 inches square, which also form the bases for our standard-sized furnaces. To increase the size or complexity of our systems, we simply bolt down another module and attach the additional vacuum system with a simple vertical seal. Figure 2 shows our new standard furnaces in place. Each unit covers a single module and with this design we can vary the size of the system in either the horizontal or vertical direction. As previously indicated, we have found it possible to make demountable ultrahigh vacuum joints capable of repeated bakeout using gold gaskets squeezed flat between stainless steel or Monel flanges (*7*). Figure 3 shows a steel vacuum tank (10-liter volume) assembled with four such demountable joints for use in studies of breakdown at atmospheric pressures (*8*). I should like to call attention to two features of the system shown

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The author is manager of the physics department of the Westinghouse Research Laboratories, East Pittsburgh, Pa. This article is based on a paper that was first presented at the Berkeley meeting of the AAAS, 30 Dec. 1954, when Dr. Alpert received the Newcomb Cleveland prize.

in Fig. 3: (i) A vacuum valve is very often incorporated in our systems to isolate at will the system from the oil diffusion pump. In the region of pressure of 10^{-7} mm-Hg, such pumps become a source rather than a sink for contamination; by isolating the pumps completely, it is possible to attain ultrahigh vacuum through the use of ion pumping alone. (ii) The pumping speed of the system shown is extremely low; it is only of the order of 0.1 liter per second, although the working pressure of the system is 10^{-9} mm-Hg. Ordinary vacuum techniques would call for pumps hundreds of times greater in size and would at best attain ultimate pressures hundreds of times greater.

Another type of demountable joint, this one developed by Pattee (*9*) at Stanford University, is shown in Fig. 4. By utilization of a replaceable copper gasket, two portions of a system may be joined or electrodes may be inserted into a system by clamping the gasket between stainless steel flanges. The flanges have knife-edged ridges, as shown; when clamped, they form a vacuum-tight and flexible seal.

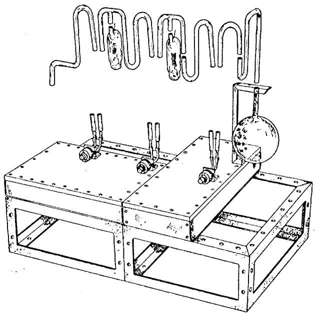


Fig. 1. Vacuum valves, ionization gages, and gas source ready for assembly on a series of module units.

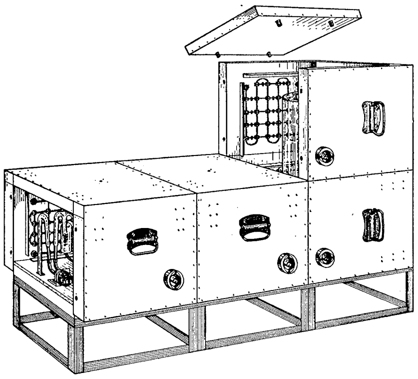


Fig. 2. Standard furnaces in place.

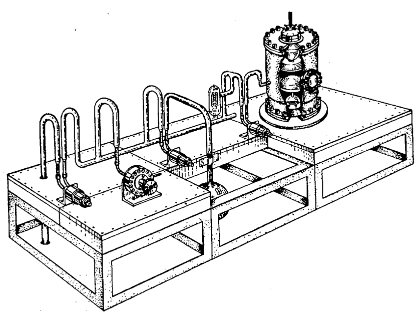


Fig. 3. Demountable breakdown chamber for very pure gases.

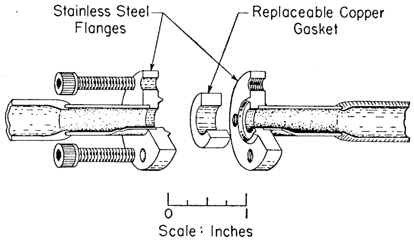


Fig. 4. Pattee demountable vacuum joint.

With these techniques, it has been possible to carry out experiments in a number of areas of physics that until recently have been both literally and figuratively "dirty" physics. One whole field of activity has grown directly from the ingenious field-emission microscope invented by Erwin Müller in 1937 (*10*). The device maps the cold electron emission pattern from a very fine metallic point with a tip of the order of 10^{-4} to 10^{-5} centimeter in diameter. By accelerating the electrons to a large fluorescent screen, one obtains a linear magnification as high as 1 million. Pattee and others have used the emission from such a tip in very interesting applications involving the production of very small x-ray spots. A large number of other workers, including W. P. Dyke, J. Becker, and R. Gomer, have used this idea in conjunction with the newly available ultrahigh-vacuum techniques to open up investigations in the fields of surface migration, chemisorption, field emission, and in various studies of gas and surface reactions on solids. It is well known that the characteristic field emission pattern in a Müller tube is remarkably altered by extremely small quantities of gas. And how much is extremely small? Well, the experts are still arguing (rather inconclusively) about whether it is possible to see a single adsorbed molecule. And when you consider that at 10^{-6} mm-Hg a whole monolayer of adsorbable gas is deposited in 1 second, you realize why it is essential to get pressures down to 10^{-10} mm-Hg and even lower if possible.

Another field that requires very low pressures and in which great strides have been made in recent years involves the interaction with solid surfaces of atomic particles such as ions, metastables, and light quanta. An example is the work of H. Hagstrum (*11*) at Bell Telephone Laboratories, who has measured the coefficient, γ_i, for the ejection of electrons from metals by incident positive ions. He has shown that most of the results of the past two or three decades in this field are subject to serious question because γ_i is very sensitive to the condition of the metal surface. In the case of tungsten, it has been found that even when the metal is baked out at 1000°C, it acts as if a layer of oxygen or of nitrogen is still attached to the surface. The effect disappears only when the metal is baked out at even higher temperatures. Such fields as gaseous electronics, or analytic mass spectrometry are ones in which ultrahigh vacuum techniques are uniquely applicable.

Limitations to Production

A number of interesting researches have grown out of our attempts to understand the limitations on the production of very low pressures. For example, although the x-ray limit of our ionization gage is approximately 10^{-11} mm-Hg, we had until recently never measured pressures in a sealed-off portion of a system below 3 to 4×10^{-11} mm-Hg even with the ionization gage running and therefore pumping continuously. We examined all sorts of possibilities for the causes of this limitation. First, we showed that the gage was linear over its usable range and calibrated it absolutely. Next, we measured the equivalent pressure reading owing to tungsten atoms that originate at the hot filament of the ionization gage and pass through the grid on the way to the glass envelope. In the process, we demonstrated a simple and straightforward way to get an approximate value for the vapor pressure and an accurate value for the heat of vaporization of refractory metals. The experiment showed that the equivalent pressure due to tungsten atoms evaporating from the

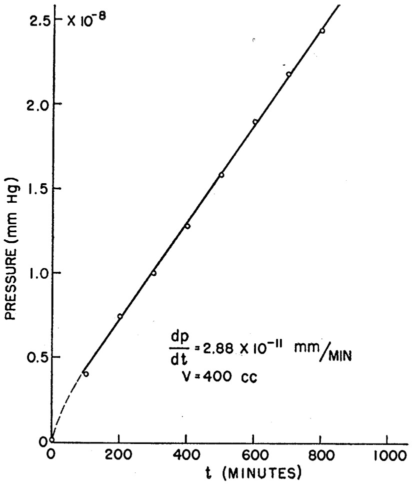


Fig. 5. Rate of rise of pressure in a typical vacuum system.

filament of the ionization gage was approximately 10^{-12} mm-Hg. But these results did not give insight into the reasons for the residual pressure.

Information concerning the source of residual gas in sealed-off systems was first obtained from measurements of the rate of rise of pressure in such systems. If in a sealed-off system all pumping action is eliminated, we find that no matter how carefully the vacuum system has been prepared, we observe an easily measured residual rate of rise as shown in Fig. 5. This rate of rise depends, of course, on the volume and surface area of the vacuum systems; for a typical system it was of the order of 2 or 3×10^{-11} mm-Hg per minute. This is not a very large leak; it corresponds to a rate of rise of 1 micron per century, but it could very readily be measured and was found to continue linearly for at least 75 days. Even after many days of such a rise, however, there was no indication of an adsorbable gas within the system. From these observations, we inferred that an inert gas, probably a noble gas, came from outside the system, possibly diffusing through the glass walls of the enclosure. From rather sketchy data, we found that the rate of rise was not inconsistent with the hypothesis that the gas was helium, which is present in the atmosphere to only a few parts in a million. But since there was a large discrepancy among various measurements of the permeation rate for helium in Pyrex, it was not possible to rule out other sources.

We therefore proposed a simple experiment to determine the answers to the question: Does the gas come from outside the system and, if so, what is the mechanism involved? The experiment consisted of enclosing a carefully sealed-off ionization gage within another vacuum system. Then, if at time $t = 0$ the outer pressure were reduced to zero, the rate of rise in the inner system should vanish. The data of Fig. 6 show that it did vanish, but that it took almost 60 days to do so. This strongly indicated a diffusion process, and a thoroughgoing consideration of the data showed that we could get not only the permeation rate k, but also the diffusion coefficient D and the solubility S. The permeation rate k is, of course, equal to the product of D and S. From the curve in Fig. 6, we obtained values for D and S, as well as k, and would have liked to compare them with existing data. We found that no measurement of D had ever been made and that S had been measured only once, at a temperature above 500°C. We then proposed a new experiment to measure k, D, and S for helium in Pyrex and to check the nonstationary diffusion equation for this process (*12*). The experiment is shown schematically in Fig. 7. Two ultrahigh vacuum systems were separated by a Pyrex diaphragm of thickness d and area a. At time $t = 0$, helium at a known pressure, P_A, was introduced on one side of the diaphragm and the pressure in the receiving volume, P_R, was measured as a function of time. I do not have space to describe the experiment in detail, but I show in Fig. 7 the usual diffusion equations and an approximation that is excellent at small times. By plotting the data in the form suggested by this equation, we were able to get from the slope of a semilogarithmic plot the values of the diffusion coefficient D, and from the intercept a value for the solubility S of helium in Pyrex glass. We checked the values of D and S with those for the unknown gas in the glass walls of our vacuum systems and thus obtained a conclusive confirmation of the helium hypothesis. We verified the diffusion mechanism for this process and obtained very interesting data on the variation of the diffusion constants with temperature.

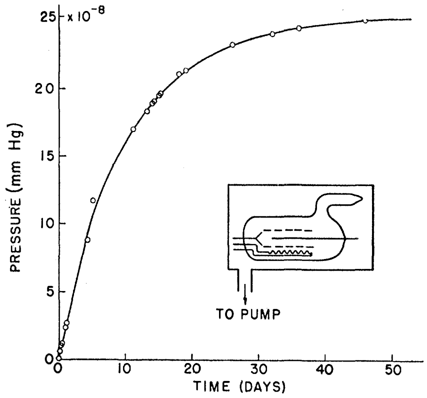


Fig. 6. Sealed-off ion gage in a vacuum.

To return to my original question, we have by this and other methods identified the incoming gas as helium. The question that remains is this: Does this process account for the entire residual pressure of 3 to 4×10^{-11} mm-Hg found in a typical system? From the ordinary equation for the pumping speed of a system, the rate of change of pressure is given by

$$\frac{dp}{dt} = -\frac{S}{V}p + r, \qquad (1)$$

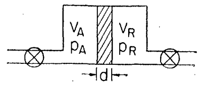
where S is the pumping speed of the system, V is the volume of the system, and r is the total rate of pressure rise in the system. The ultimate equilibrium pressure is obtained when the rate of change of pressure vanishes and the equilibrium pressure p_e, is given by

$$p_e = rV/S = r\tau, \qquad (2)$$

where $\tau = V/S$ is the characteristic time required to pump the system down to $1/e$ of its original pressure. Now the residual rate of rise r, has been measured to be about 3×10^{-11} millimeters per minute; τ is easily evaluated and for a typical system has been measured to be approximately 1 minute. Thus the expected residual pressure is equal to the product of r and τ and is equal to 3×10^{-11} mm-Hg. The entire residual pressure can be accounted for as the result of the diffusion of pure helium into the system. Under good conditions, we have indications that the nonhelium contamination is less than 10^{-13} mm-Hg.

Many people would be happy with this kind of vacuum; but in a number of experiments even this value of equilibrium pressure, as well as corresponding rate of rise, is altogether too high. In the diffusion experiment, in experiments on the adsorption of gases on surfaces, and in a number of other researches, one would like to reduce the ultimate pressure to even lower values. From Eq. 2, it is clear that one way to reduce p_e is to reduce or eliminate r. Varnerin and White (*13*) have done this by enclosing one vacuum system completely within another and sealing both to a kovar tubulation as shown in Fig. 8. In this way, pressures have been obtained that have been estimated to be below 10^{-11} mm-Hg. Under such conditions, we can no longer measure pressures and we need a new type of gage.

Another way to reduce the ultimate pressure would be to increase the pumping speed of the system and thus to reduce τ. We have known for years that at pressures below 10^{-7} mm-Hg an oil diffusion pump constitutes a source of contaminating vapors. On the other hand, we have also known that oil diffusion pumps retain their pumping efficiency at pressures far below 10^{-7} mm-Hg despite the manufacturers' literature, which usually indicates that the speed of the



DIFFUSION EQUATIONS:

$$\frac{V_R}{A}\frac{dp_R}{dt} = -D\left.\frac{\partial n}{\partial x}\right|_{x=d} \qquad \frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2}$$

APPROXIMATE SOLUTION FOR SMALL t·

$$\sqrt{t}\,\frac{dp_R}{dt} = Cp_A S e^{-\frac{d^2}{4Dt}}$$

WHERE:

D IS THE DIFFUSION COEFFICIENT
S IS THE SOLUBILITY OF HELIUM IN PYREX

Fig. 7. Schematic diagram of diffusion experiment.

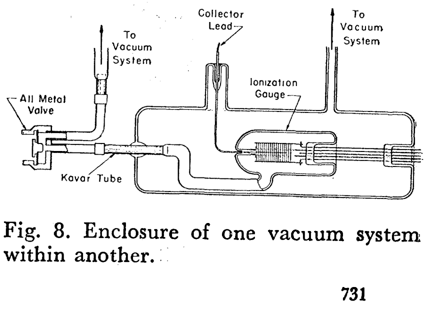


Fig. 8. Enclosure of one vacuum system within another.

pump goes to zero in this range. We felt that if we could design a trap that would prevent the backstreaming of oil vapor but not restrict the pumping action of the pump, we might be able to use the increased speed of the pumps to reduce our ultimate pressures. The trap used has been described in the literature (*6*) and is shown at *a* in Fig. 9. It consists of a standard reentrant glass trap into which corrugated copper has been inserted so that the trap contains a large number of fine copper straws. This trap design was originally proposed to solve the usual problem encountered with a refrigerated reentrant trap, that is, as the liquid refrigerant evaporates, the cold level drops and the gas that had previously been adsorbed is reevaporated into the system. In this design, it was intended to utilize the high thermal conductivity of the metallic insert so that the entire trap surface remained cold despite large fluctuations in the liquid level. The trap also affords an extremely high ratio of length to diameter without greatly sacrificing the speed of the system. It worked extremely well and eliminated the effect of variation of the liquid level. We used these traps for some time before we found that the trap worked very efficiently even when the liquid level dropped to zero. Since then, many of our traps have been designed for use without refrigeration, as shown in Fig. 9*c*, in a nonreentrant portion of the system. We then carried out an experiment in which such a trap was inserted between the system and a standard oil diffusion pump. After careful bakeout of the system, helium was introduced to a pressure of the order of 10^{-7} mm-Hg and the valve to the pumps was opened. The data of pressure versus time are shown in Fig. 10. They demonstrate that the oil diffusion pump continued to evacuate to a pressure below 10^{-10} mm-Hg with a constant pumping speed. The characteristic pumping time, τ, was measured to be 3.3 sec, equivalent to the computed conductance of the vacuum system. The corresponding pumping speed is 20 times that for an ionization gage. This higher speed did not result in even lower pressures because the rate of rise in this system was 1.2×10^{-9} mm-Hg, or 40 times the usual residual rate of rise. With smaller rates of rise, values of less than 10^{-11} mm-Hg have been obtained using standard oil diffusion pumps. To my knowledge, this is the first direct demonstration of the pumping efficiency of diffusion pumps in this range of pressures and constitutes another method for achieving pressures below our present range of measurement.

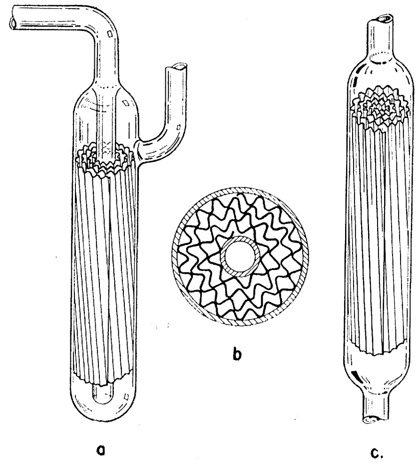


Fig. 9. Copper foil trap.

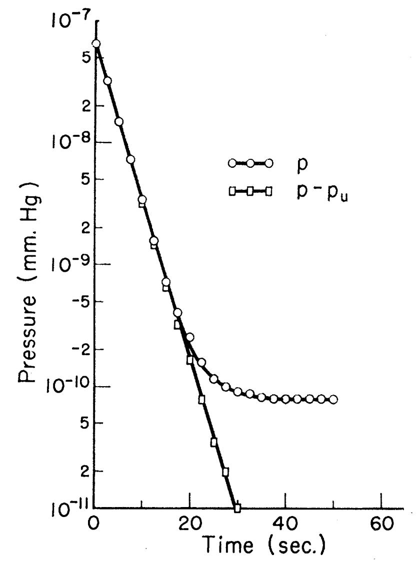


Fig. 10. Pump-down of helium by oil diffusion pumps.

Ion Pumping

I should now like to outline some of our most recent experiments designed to further understanding of the mechanism of ion pumping. I have previously described the studies directed toward obtaining an understanding of the rate of rise in our vacuum systems. We have felt that an understanding of the electrical pumping mechanisms might also be of great interest. Superficially, the ion pumping mechanism is very simple: ions formed in the volume of the ionization gage are driven into the negatively charged ion collector with an energy of 100 volts and are permanently removed from the volume (*14*). If every ion attached permanently to the surface, the resulting τ would be of the order of 1 minute, which is, in fact, the measured value of τ. But under some conditions, it has been found that for each ion that strikes the ion collector, two or even more atoms are removed. In fact, it is found that when a voltage is applied to the accelerating grid, atoms may be removed even when the ion collector potential is such as to repel ions. The answer to this question is relatively simple. Many ions are formed not only within the grid volume of the gage but also between the grid and the glass envelope of the gage. In this case, a little investigation shows that the glass walls may float at a negative potential so that the ions are driven largely into the glass envelope of the gage and, apparently, are permanently removed. But here again we are faced with a quandary because, if the gas is helium—and we obviously think it is—and if the ions are driven into the surface a few angstroms deep, we know from our recently attained knowledge of the diffusion coefficient that the helium atoms should diffuse out of the glass in a characteristic time of approximately 1 microsecond. That is, the gage should pump for only a few microseconds and then stop. As far as we have been able to determine, however, the gage pumps helium for an indefinite time. The answer to this problem was not readily forthcoming. Finally, L. J. Varnerin, one of my laboratory colleagues, demonstrated the answer in a very simple experiment (*15*) after he suddenly realized that the envelope of the gage was not glass at all, but consisted of a very fine layer of evaporated and sputtered metal transferred during the outgassing of the grid. Thus if his conjecture were true, there should be no pumping action with an absolutely clean ionization gage; if the glass walls were then covered with a deposit by outgassing of the grid, one might expect to obtain a pumping action. Figure 11 shows the results. Curve 1 was taken with a new gage direct from the production line. After the system had been prepared, the gage was turned on and pressure was measured as a function of time. After the first few minutes, it was found that the characteristic pumping time τ, was measured to be thousands of times greater than the normal value. After a slight outgassing, which presumably deposited a metallic film so thin that no measurable light absorption was present, curve 2 was

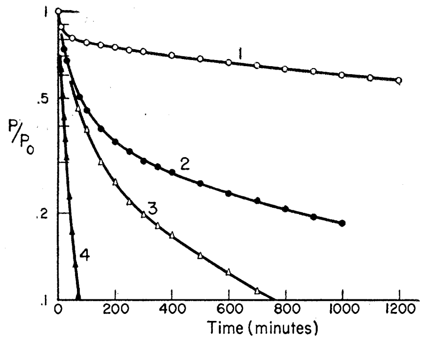


Fig. 11. Ionic pumping of helium by an ion gage after increasingly intense outgassing.

obtained with a very appreciable reduction in the time constant. After a little more outgassing and with a metallic film thickness estimated to be 10 angstroms thick, curve 3 resulted; and after a relatively heavy outgassing resulting in a film thickness of the order of 50 to 100 angstroms, the characteristic time had been reduced to its normal value of the order of a minute. This simple experiment clearly indicated that the helium ions are driven into the metallic deposit at the surface and that the pumping efficiency is strongly affected by the surface material. Very preliminary data would indicate that if the process of reemission of gas from the metallic surface could be described by a diffusion process, the diffusion coefficient would be approximately ten orders of magnitude less for helium in metals than for helium in Pyrex glass. Actually, Varnerin has shown in preliminary experiments that the reemission of such gas after it has been driven into the surface cannot be described by a simple diffusion process, so that we are not in a position to give diffusion constants for this material. Nevertheless, it is of interest to mention that we thought we were opening a new area in utilizing ultrahigh vacuums for the study of diffusion of helium in glass; we have now begun to investigate processes that are perhaps 10 orders of magnitude slower. Experiments are in progress that are intended to enable us to gain insight into the physical mechanisms by which excited or ionized gas may be attached to the surface of various types of solids.

Conclusion

With the description of these various fields of research, I have tried to outline a broad range of experiments that are greatly facilitated by the availability of a pressure range 3 or 4 orders of magnitude lower than that previously attainable. At the same time, I have indicated that there are a number of experiments for which even these new pressures are too high. I believe that we can produce significantly lower pressures than we can measure and that we need a pressure gage for the new range of pressure. I believe that the researches which are now being carried out at very low pressures will have interesting consequences for many areas of future scientific investigation.

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Patent Work in a Small Company

Theodore C. Browne

It sometimes happens that a large industry has a gap in its technology. That industry may make a product that receives wide acceptance, but the public may be utterly unaware that any manufacturing difficulties exist; nevertheless, the manufacturers are continuously harassed by their efforts to skirt around a technological hiatus.

When an inventor outside the industry finds a way to plug the gap, founds a company, and plans to service the industry with the element that had previously been missing, the best laid plans for an orderly development of the new company may go awry. Research men necessarily become production engineers, treasurers, packaging engineers, traffic experts, customer service men, product improvers, capital raisers, and experienced salesmen simultaneously. Things happen so fast and customers' demands become so pressing that the truly creative minds in the organization have little time to work with patent counsel, to build an ordered plan of protection, or to secure sound foreign patents. Then, too, there is no time for these men to study the art, learn its direction, study newly developed materials, and be made aware of the trends that they must know.

So, I would say to a young man: "If you have a faith in the idea, an urge to help a business grow, and if you are well trained in patent soliciting and the techniques of research, even if the enterprise is tiny, join it, and found its patent department; the growth of a company you know you have helped to grow will be your reward."

I will assume that you have been a junior in a patent law office or an examiner in Washington. As soon as you become a member of the new organization, the environmental change will be nearly overwhelming. If you have been an examiner, you have always been met in patent matters by a *fait accompli.* The story came to you complete, and if you are like most examiners, you read the claims before you read the patent specification and therefore you knew how the detective story would come out. If you have been a junior in a law office, you have had the inventor sit at your elbow, explain his idea, show you photographs of his machine or samples of his product, and here also you were met by a completed technological accomplishment. True, you might have spent a day or two at your client's plant, studying the process or watching the operation of the machine. You might have dug into books to inform yourself on possible ranges of equivalents. You might have asked for further tests and more detailed information, but ultimately there came a time when you realized that neither your client nor you could afford to spend any more time on the problem and that you had to write the best specification possible from the information already at hand.

In the new organization, you will have no such advantages. Your associates will be out of the laboratory more frequently than they are in it. You will have to catch their ideas and suggestions as they drift

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Mr. Browne is patent attorney of Dewey and Almy Chemical Company, Cambridge, Massachusetts. This article is based on paper presented at the meeting of the American Chemical Society in New York, 13 Sept. 1954.