GENERAL ENGINEERING LABORATORY

VACUUM PROCESS EVALUATION

by

D. J. Santeler

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May 12, 1958

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TITLE

Vacuum Process Evaluation

ABSTRACT

Vacuum Process Evaluation is a new technique to: 1) determine the outgassing occurring within a vacuum system as a continuous function of time, and 2) Analyze the resulting curve to obtain information as to the source and nature of the outgassing. The report describes this technique and its application in determining the optimum combination of

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CONCLUSIONS

(cont.) of Abstract

such parameters as temperature, time, materials, restrictions, and pumps on such processes as hermetic volume exhaust and cellulose dehydration. Vacuum Process Evaluation has also been used to study such phenomena as the outgassing characteristics of insulating materials and vacuum gages, the flow of gasses through orifices and short tubes, and the gettering action of various materials. A digital computer and data reduction facilities have been incorporated to eliminate the detailed hand calculations and plotting. This has resulted in a rapid and inexpensive method for the study of vacuum engineering problems.

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TESTS MADE BY -----

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COMPONENT Mechanical Engineering Laboratory

VACUUM PROCESS EVALUATION

BY

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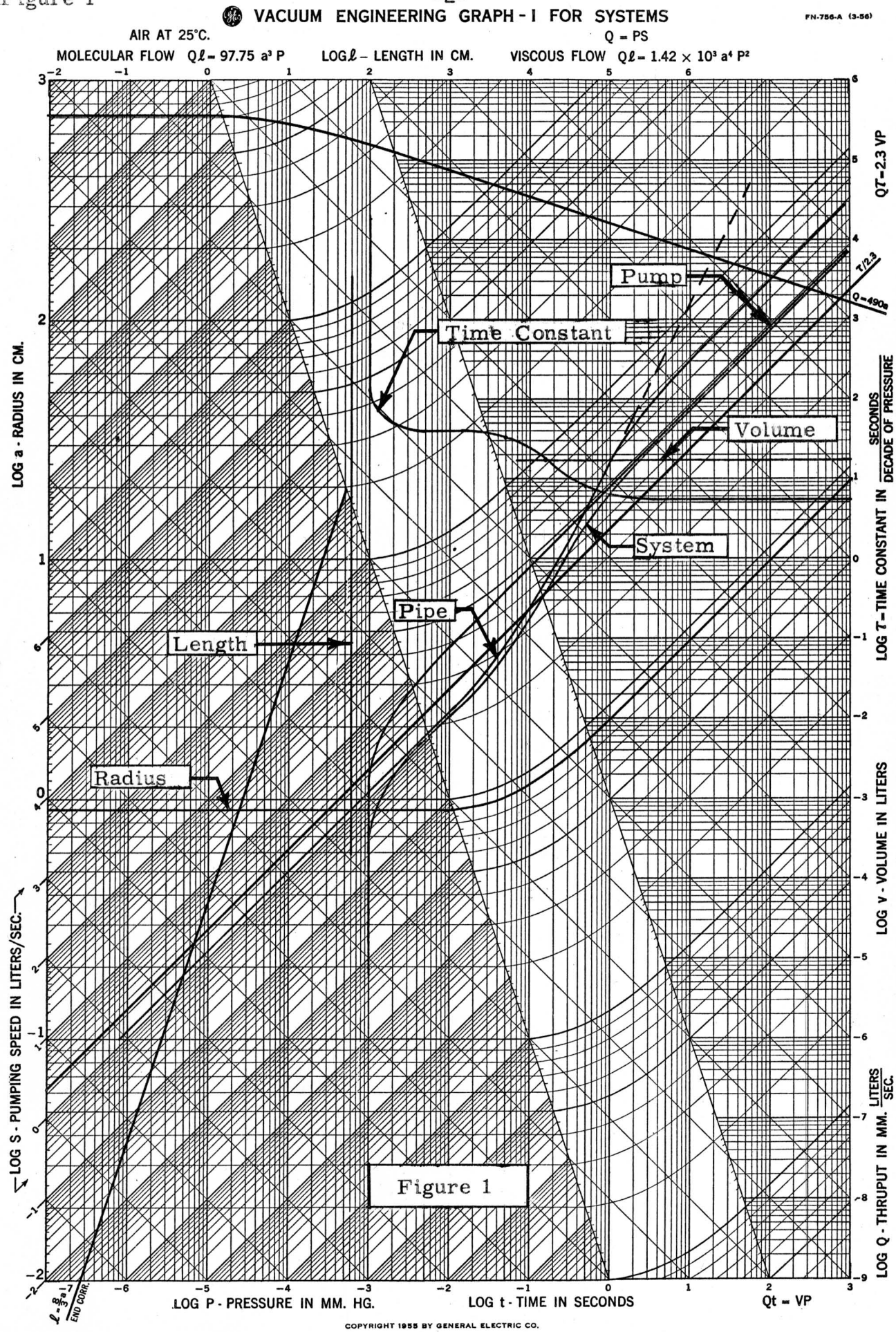
Figure 1

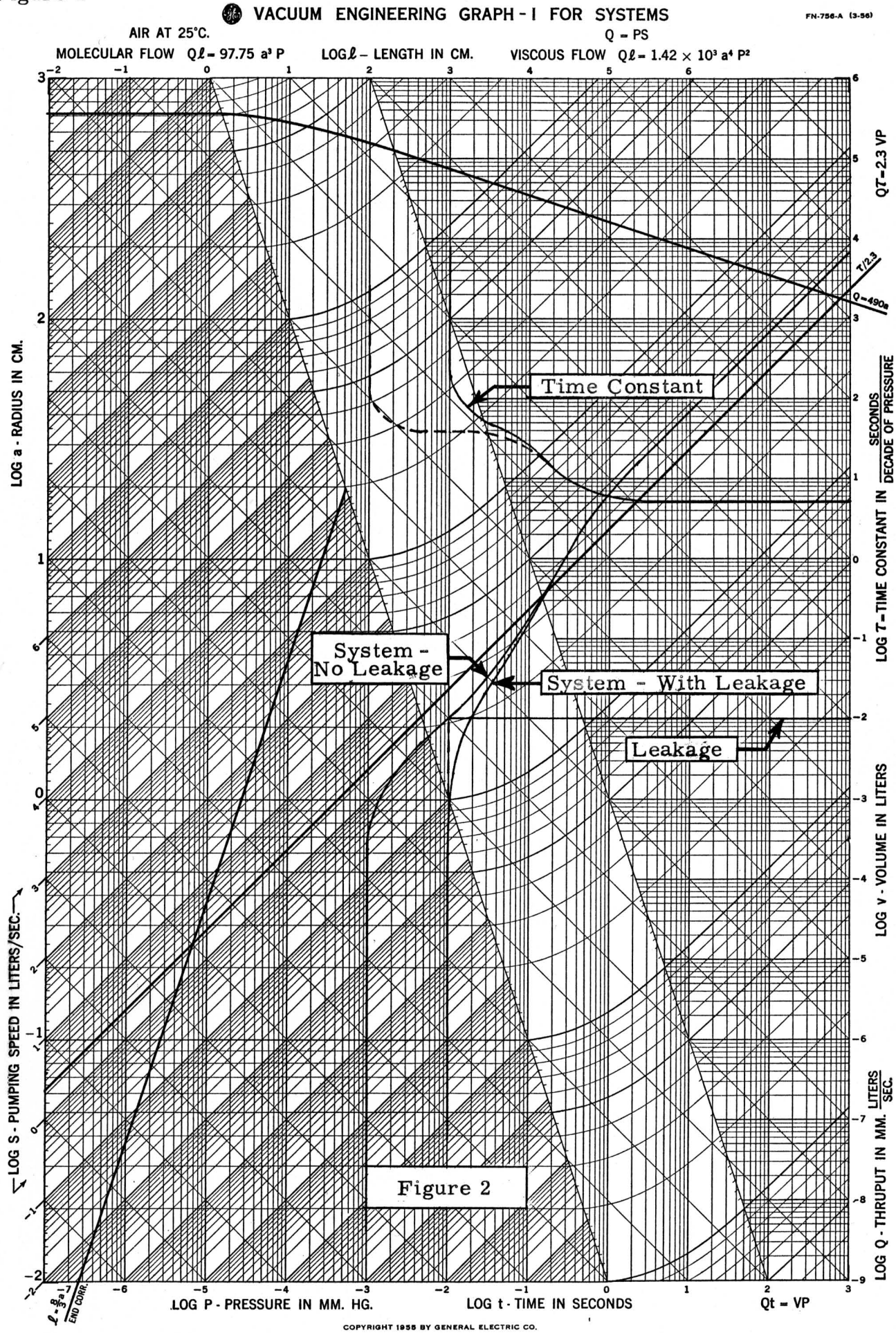


I INTRODUCTION

This report describes a new technique which was developed to study the nature of outgassing and the effect of certain parameters such as pumps, tabulations, and temperatures on the outgassing process. We call this technique Vacuum Process Evaluation. It is an application of vacuum engineering to produce a method which will: 1) Determine the outgassing occurring within a vacuum system as a continuous function of time, and 2) Analyze the resulting curve to obtain information as to the source and the nature of the outgassing. This technique has been used to study many different types of vacuum engineering problems dealing with outgassing and gas flow. Some of these applications will be discussed in the report.

The most common purpose of a vacuum system is to remove the gas from a given item in order to accomplish some primary purpose. When we think of removing the gas from a particular item, we must consider not only the gas in the gaseous state, but also that gas which is in the solid or liquid parts of the item. This additional gas may originate from capillaries, from the vapor of a liquid or solid, from the surface of various materials, from the interior of the materials, or from chemical decomposition. The removal of this gas is referred to as outgassing and it presents one of the most difficult problems in vacuum processes. For the simple case where only the gasses in the gaseous state are involved, the solutions for the gas flow or for the pressure-time relationship during evacuation are well established. A graphical technique (1) is available for those who do not desire to use the complex differential equations required for an exact solution or the simplified relations available for an approximate solution. Figure 1 illustrates

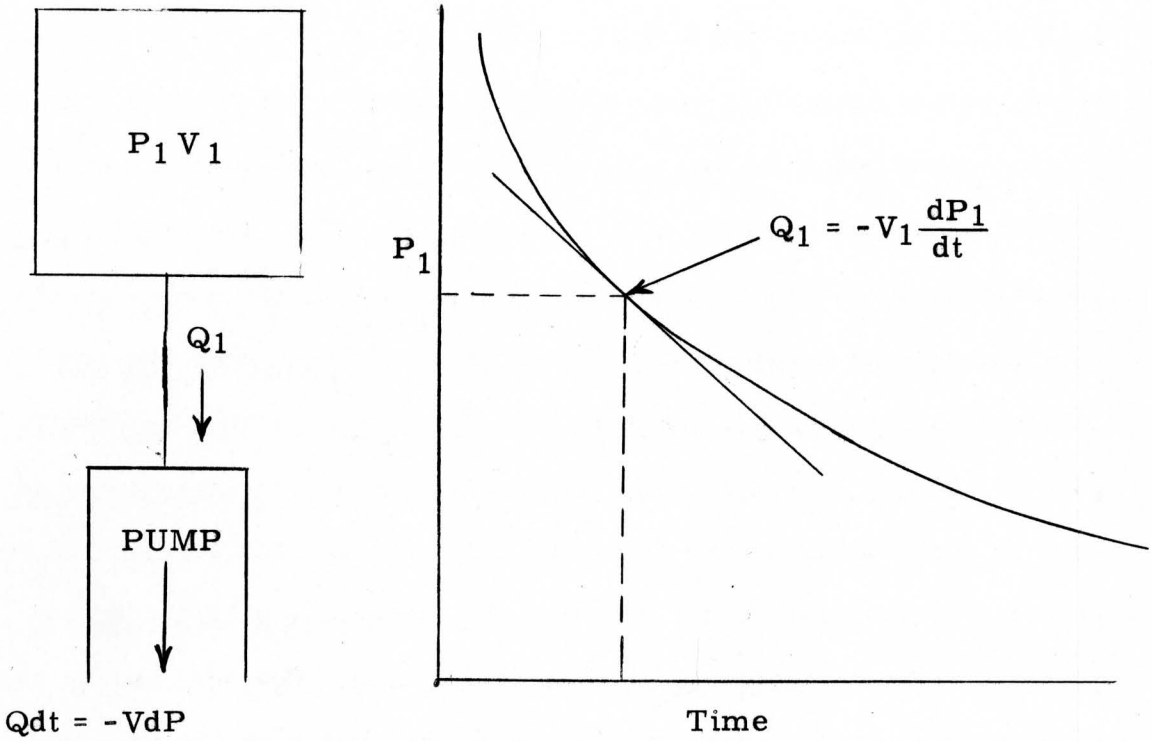
Figure 2



the graphical solution for a simple vacuum system consisting of a mechanical pump, an interconnecting line and a volume. From the time constant curve, we can accurately compute the relationship between the pressure in the volume and the time. The presence of a fixed leakage can easily be handled on the graph as illustrated in figure 2. The original characteristic curve still relates the pressure in the volume to the gas flow through the system, while the modified curve relates the pressure in the volume to the net gas flow out of the volume, that is, the VdP/dt part of the gas flow equation. The modified characteristic curve is used to construct the time constant curve used for the solution of pressure versus time in the volume. This technique will handle any constant leakage regardless of size or location. However, in the case of outgassing, we are dealing with "leakages" which may be pressure, temperature or time dependent. As long as this outgassing or variation leakage is unknown, it is practically impossible to predict anything about the pump down or degree of outgassing. Even in those cases where experience has dictated the time required for a particular outgassing process, it is almost a hopeless task to accurately predict the effect on the pump down which will result when various parameters are changed. The answer to such questions as: Will a bigger pump speed up the process?, Can I decrease the tabulation size?, Can I lower the temperature?, Do I have the optimum time cycle for my equipment?, Can I get to a lower outgassing level for the same time investment?, all depend on a knowledge of the outgassing which is occurring.

Early in the development, it became apparent that the detailed calculations required would be both expensive and time consuming. For this

Figure 3



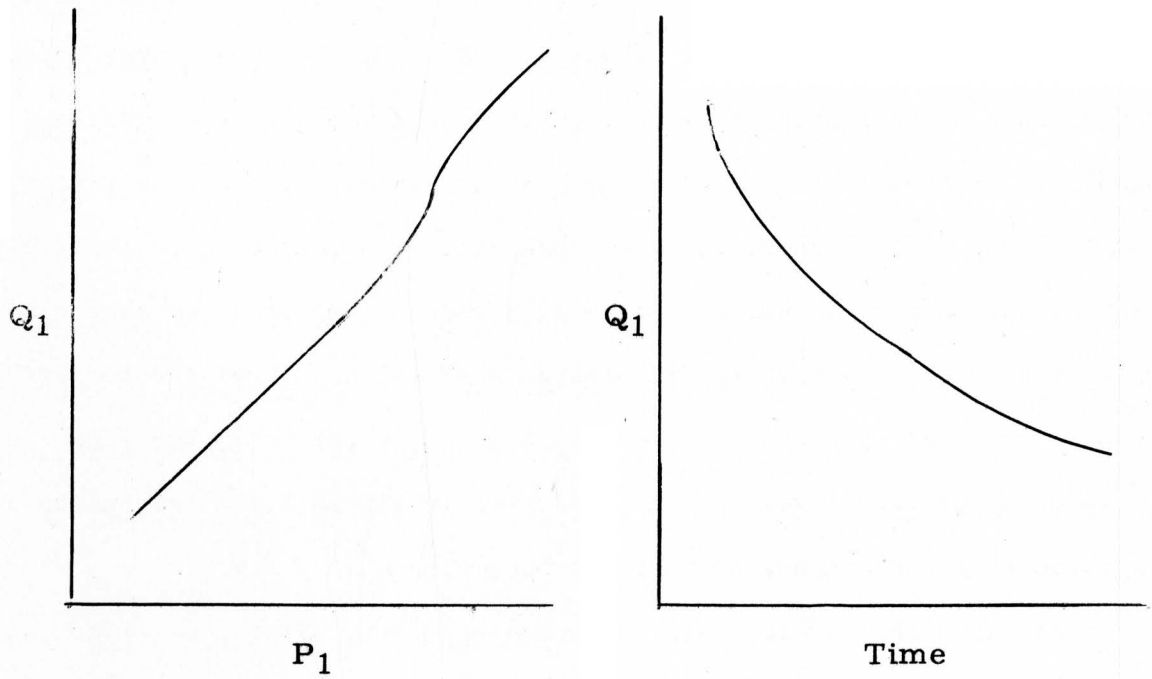


Figure 3 Pump Down - No Outgassing

reason the entire solution was programmed on a digital computer. We also found that data reduction facilities could be employed to still further reduce the cost. At present, all pressure data is taken on a recorder. This data is then directly processed to IBM cards which are run through a digital computer. The answer cards are then automatically plotted and the final curves given to the engineer for analysis. This combination has resulted in over a ten-fold reduction in cost and an improvement in accuracy. An even more desirable solution would be to utilize an analog computer and directly record the answers while the data is being taken.

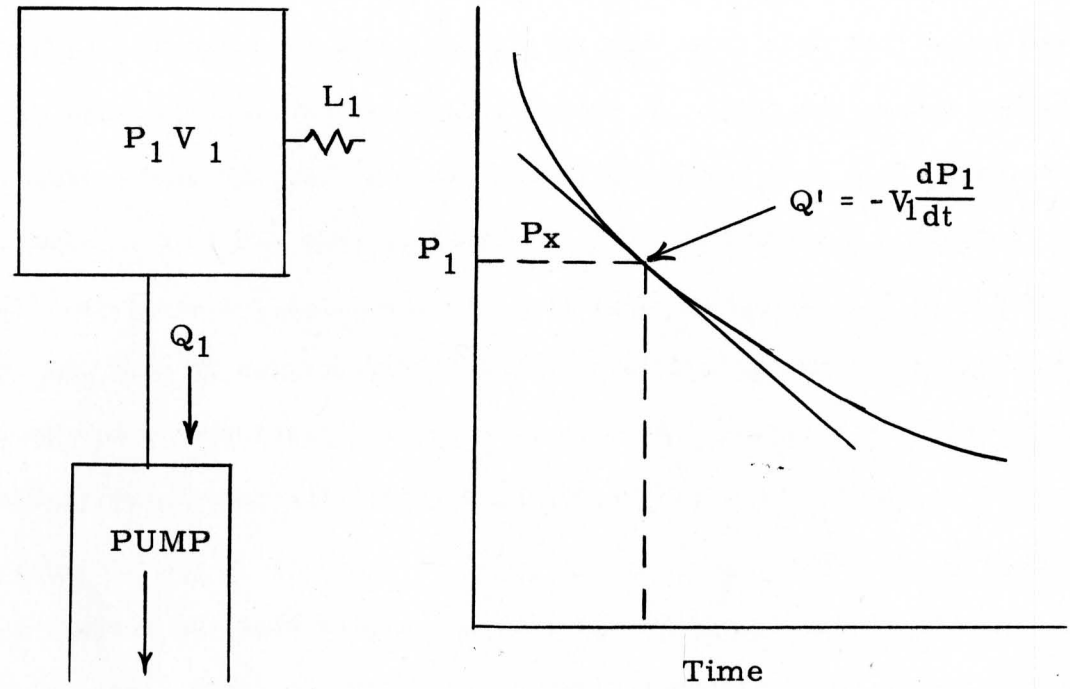
In the following report, it will be assumed that the reader is familiar with the basic nomenclature of the vacuum field.

II PRODUCTION OF THE OUTGASSING CURVE

We begin our discussion with the simplified vacuum system shown in figure 3. Here we have a pumping system and its associated restrictions connected to a volume V_1. We assume that the pressure P_1 in the volume can be directly measured. In the complete absence of outgassing, the differential equation $Q_1 = -V_1 dP_1/dt$ will apply. Let us therefore record the pressure versus the time during exhaust. At any point on the curve we can draw the slope of the curve, dP/dt, and hence compute the flow rate out of the volume at that instant of pressure and time. By repeating at a number of points on the curve the complete relationship between the pressure and the flow or between the flow and the time can be obtained.

Let us next consider that a certain unknown leakage L_1 is admitting gas to the volume. The differential equation changes to that shown on figure 4. The leakage may be a complex function of pressure, time and

Figure 4



$$Q_1 - L_1 = V_1 \frac{dP_1}{dt}$$

$$L_1 = f(P, t, T)$$

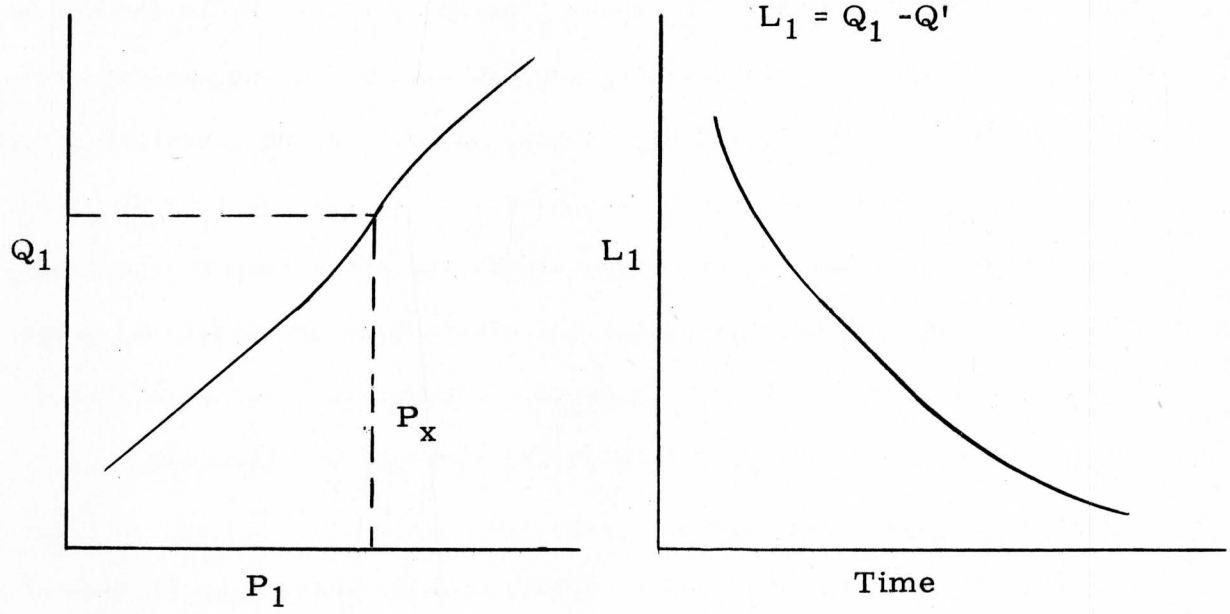


Figure 4 Pump Down - With Outgassing

temperature. We again plot out the pressure time curve. At a point on the curve, we compute the slope to determine the net gas flow out of the volume. Because of the leakage, the flow V dP/dt out of the volume is no longer equal to the flow through the pumping system, rather the difference between the two flows is equal to the leakage. We see then that we must have the characteristic curve of the system, that is, the relation between P_1 and Q_1. This can be obtained by taking a pump down on a thoroughly outgassed system, by graphical analysis, or by calibration with a series of known size leaks. At a given pressure, the difference between the flow computed from the slope of the pump down curve and the flow through the pumping system obtained from the calibration curve will be equal to the leakage at that instant of time for which we had the chosen value of pressure. This is then repeated at other values of time to produce the complete leakage curve or outgassing curve. Since the entire analysis is done on a rate of change of pressure at a pressure, there is a constant correction for the pump down of the gasses in the gaseous phase. If the analysis were to be made on the basis of what the pressure is relative to the time and then compared to what it would have been in the absence of outgassing, no such correction is applied. A common example of this is using the time to reach a given pressure as the criteria of the degrees of outgassing. While this is an extremely good monitor for an established process, it cannot properly be used to evaluate a process or predict the effect of changing parameters even though the experienced vacuum engineer can do some fairly accurate guess work using such data as a guide. Another advantage in using the rate of change of pressure is that all time constants are eliminated. If a transient square wave leak occurs, the analysis, within its accuracy,

Figure 5

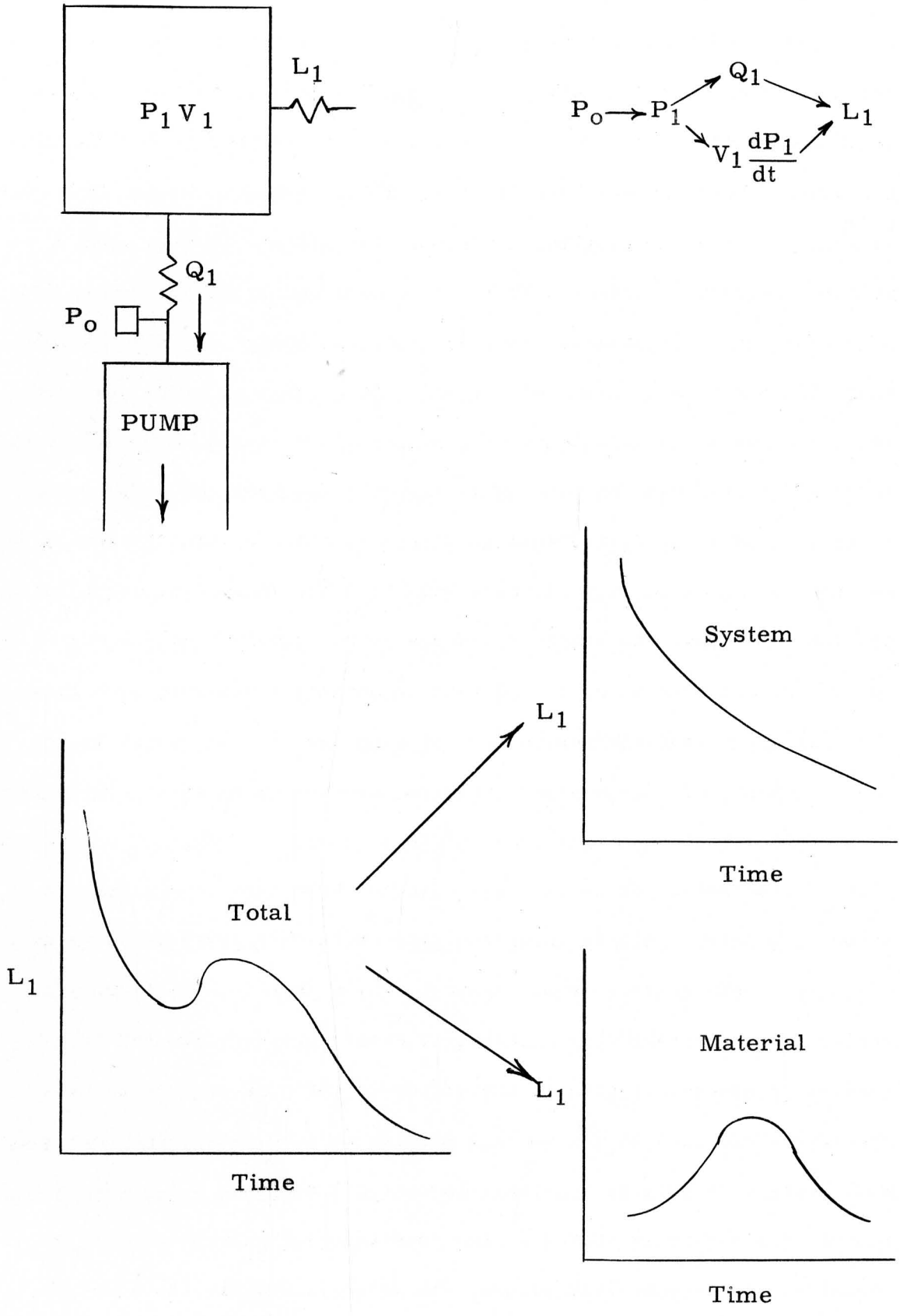


Figure 5 Outgassing

will show it as a square wave despite the fact that large volumes and small restrictions may be involved. This is true even in the cases to be discussed where the vacuum gage is located at a remote distance from the volume.

In many outgassing processes, high temperatures are involved and frequently it is not possible to locate the vacuum gage directly on the item under test. On figure 5, P_o represents the measured pressure at some known point between the volume and the pump. For this condition the relation between P_o and P_1 must be known. This can be obtained from the graphical solution or by direct calibration. The procedure is now as illustrated on the figure. That is, from measured values of P_o we convert to P_1. From P_1 in turn we obtain Q_1 and $V_1 dP_1/dt$. The difference between these yields the total leakage or outgassing curve. The resultant curve is the summation of all outgassing originating within the volume. Hence, if certain sources of outgassing are known, they can be subtracted off to yield the unknown sources. For example, if it is desired to study the outgassing of a given material, we must recognize that when the material is placed in a vacuum system both the material and the system are sources of gas. However, the separate outgassing of the system can be measured with the test material missing and then subtracted from the outgassing curve of the system plus the material. In similar fashion, if the overall outgassing curve of a complex system is being studied, it can in turn be broken up into the different sources and each studied separately by studying the materials separately. It is also true that the total outgassing curve is a summation of the different gasses present and each gas may be acting differently. This type of problem will be discussed later.

Figure 6

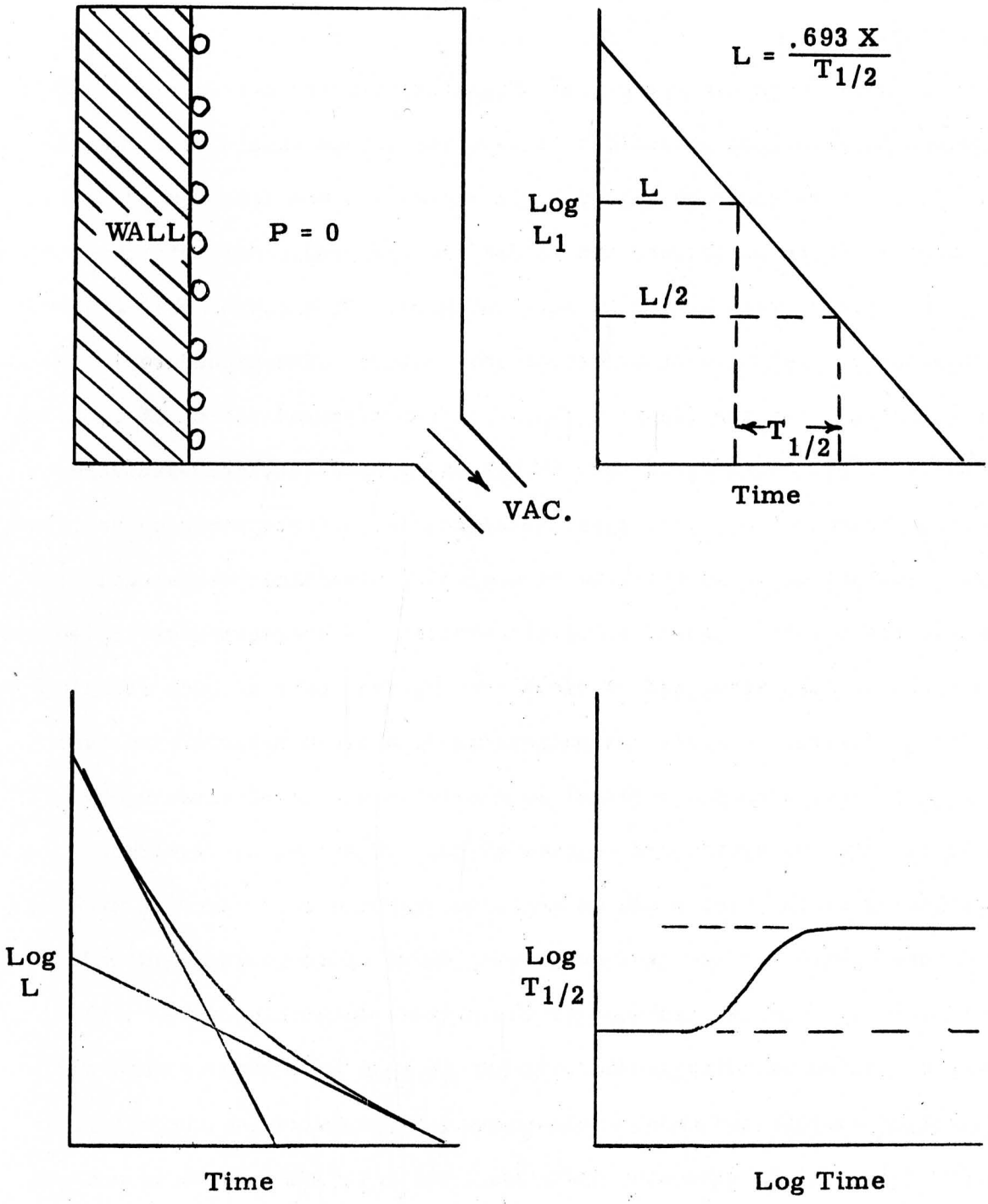
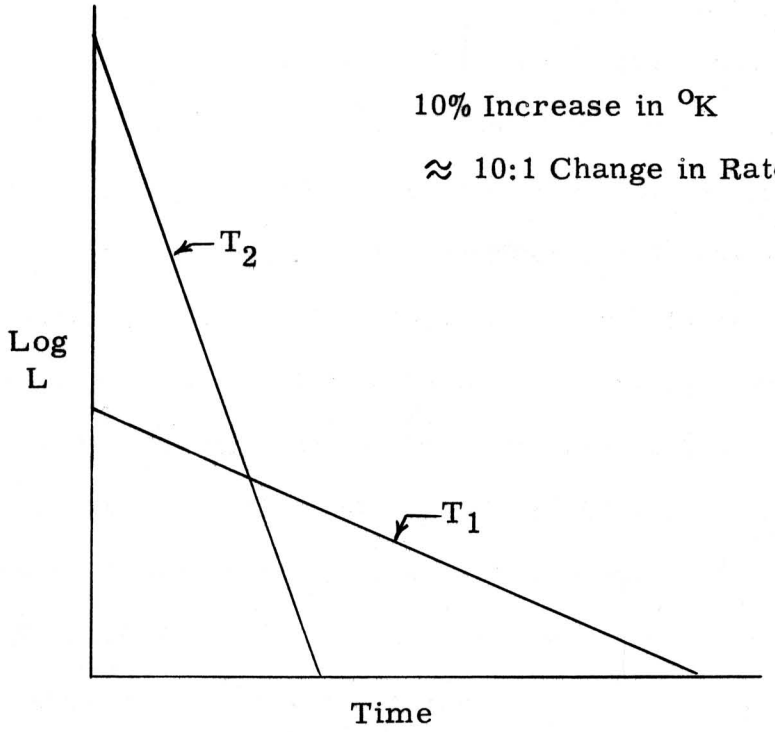


Figure 6 Adsorption and Half Life

III OUTGASSING AND HALF LIFE

The simple production of the outgassing curve is hardly enough for we also need a technique for its analysis. It is surprising how similar two outgassing curves will look despite the fact that they may represent two entirely different types of processes. To best explain the analysis, let us consider some of the simpler types of outgassing. First of all, we will look at an idealized case of adsorption where each moelcule occupies an individual site on the surface (see figure 6). In this case no surface gas molecule has any knowledge of the presence of its neighbors and will be removed only as a function of temperature dependent statistics. The diagram in the upper left of figure 6 shows the surface still in equilibrium with a gas. When the pressure is removed by means of a vacuum, equilibrium is lost and outgassing occurs. For our idealized case, the outgassing at a given temperature is a linear function of the number of molecules on the surface. When the surface coverage is reduced by one-half, the outgassing rate will be reduced by one-half. The resultant leakage curve is a logarithmic function as shown. This is analogous to the decay of a radioactive isotope. We define the half life in the conventional way of the nuclear physicist as being equal to the time to reduce the flow rate by a factor of 2 to 1. For this idealized case the half life is a constant and we can write the relation $L = .693\ X/T_{1/2}$ where X is the total quantity of gas left on the surface corresponding to the flow rate L. In such a situation the total gas remaining on the surface can easily be determined by computing the half life from the slope of the outgassing curve and observing the instantaneous rate of outgassing.

Figure 7



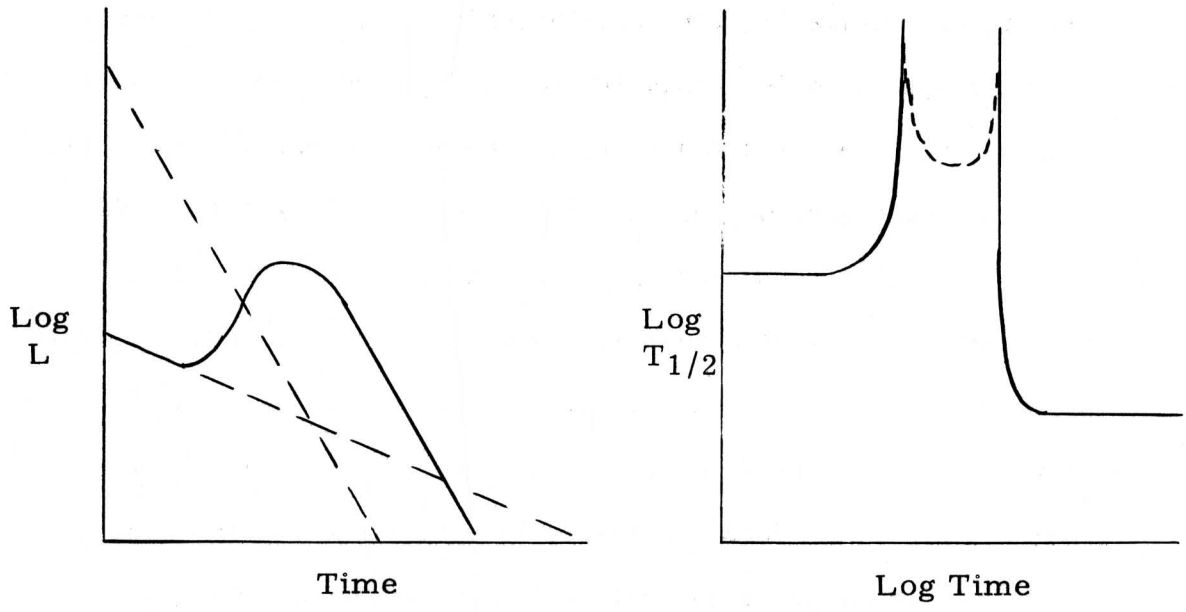


Figure 7 Temperature Dependency

Suppose that two different gasses or two different surfaces are taking part in an idealized adsorption reaction. The net outgassing curve which will be obtained is also illustrated in figure 6 and is dhown to be equal to the sum of two log functions.. If we compute the half life of the compound curve as a function of time, we obtain the half life curve shown on the right side of the figure. Such a curve would immediately indicate that the separate outgassing reactions were occurring.

Another effect of importance has to do with the temperature dependency of outgassing. This is illustrated in figure 7, still for our idealized adsorption condition. The curve labeled T_1 represents the outgassing at a certain temperature. If the temperature is increased, we increase the average energy of the surface molecules and hence their probability of escape. This results in a much higher initial outgassing rate and a faster reduction or shorter half life. We have observed that for most outgassing processes, and in fact for most all reactions from solid or liquid phase to gas phase that a 10% increase in <u>absolute temperature</u> will result in approximately a ten-fold increase in rate and a ten-fold reduction in the half life. This is equivalent to the chemist's rule of thumb for first order reactions that a $10^{o}C$ change will double the rate. By using the percentage relation the rule is valid over a much broader span of temperature. For example the vapor pressure of metals at elevated temperature will fit this generalization. As an example of the importance of this temperature dependency, we can consider the condition of adsorbed water. Around normal room temperatures, the half life of adsorbed water on many materials is approximately one hour. By simply raising the temperature to $90^{o}C$, the half life will be reduced to about

Figure 8

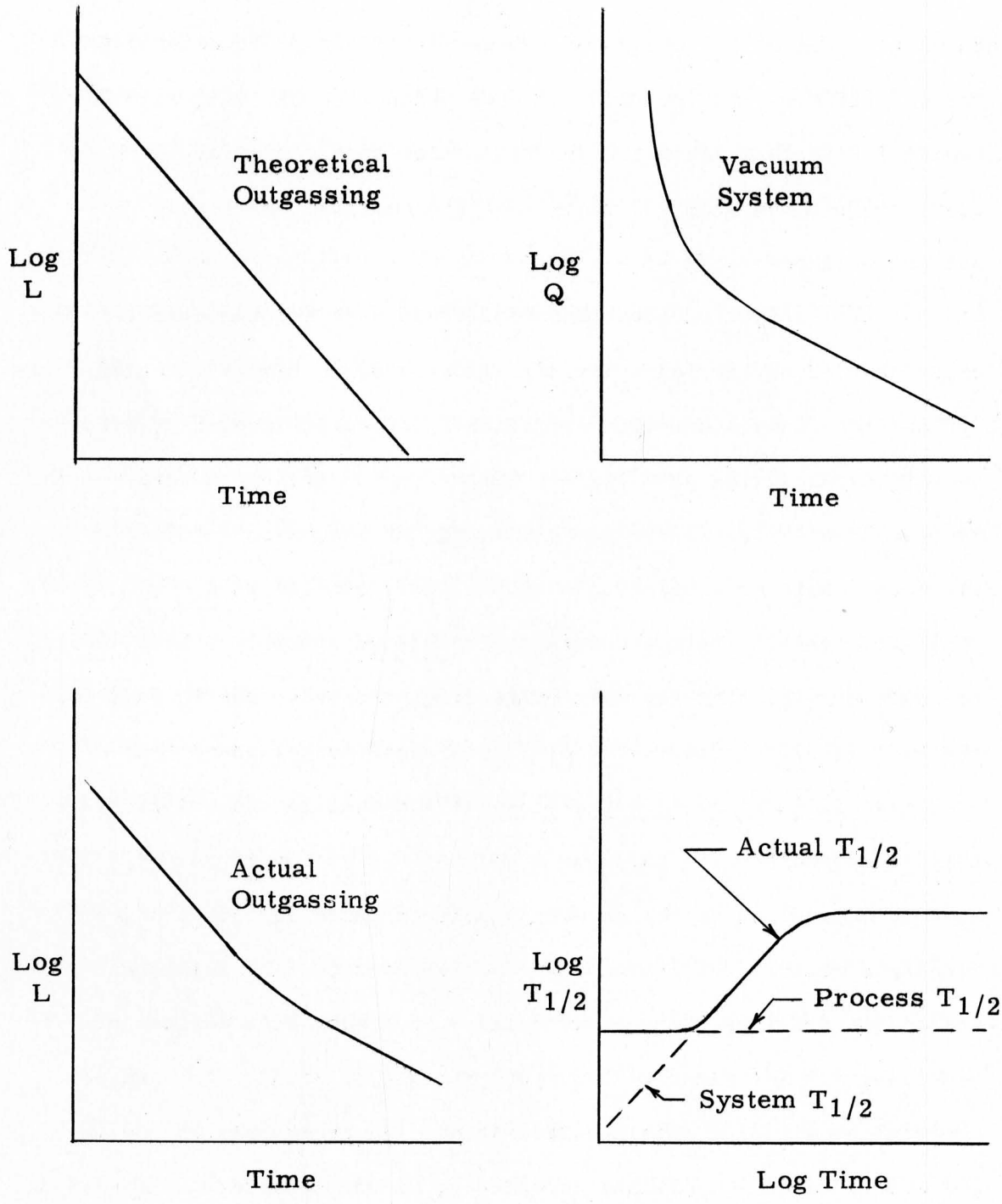


Figure 8 Pressure Dependency

one half minute and rapid surface clean up can be obtained. When the temperature changes from one value T_1 to a second T_2 we obtain the type of curve shown in the center of the figure. As the temperature increases, we see an increase in outgassing which eventually begins to decay as the surface becomes depleted. When temperature equilibrium is reached the outgassing curve will again follow a log function as shown. The half life of such a reaction is also illustrated.

To this point, we have been considering outgassing to a perfect vacuum. What happens when the pumping system or a limiting resistance is not capable of removing the gas fast enough to keep well ahead of the outgassing. It can be shown mathematically that in the presence of a pressure and for unity accommodation coefficient the outgassing will be reduced by the ratio $(P_E - P)/P_E$ where P_R is the instantaneous pressure the surface would like to be in equilibrium with and P is the actual pressure existing. If this ratio is a constant (a condition existing for a molecular flow limitation) the flow rate and half life curves will appear as though for a lower temperature. We see that this then poses a practical limit on the temperature for a given process. As the temperature increases, the half life will decrease only to that point where it is limited by the system restrictions. Further increases in temperature will fail to have any important effect on the outgassing. Rather the pressure will be almost in equilibrium with the surface and the process will be limited by how fast the gas is removed from the volume. In order to get a yardstick for this situation, we introduce the nomenclature of the time constant of a system as being the time to reduce the theoretical flow rate of gas out of the volume by a factor

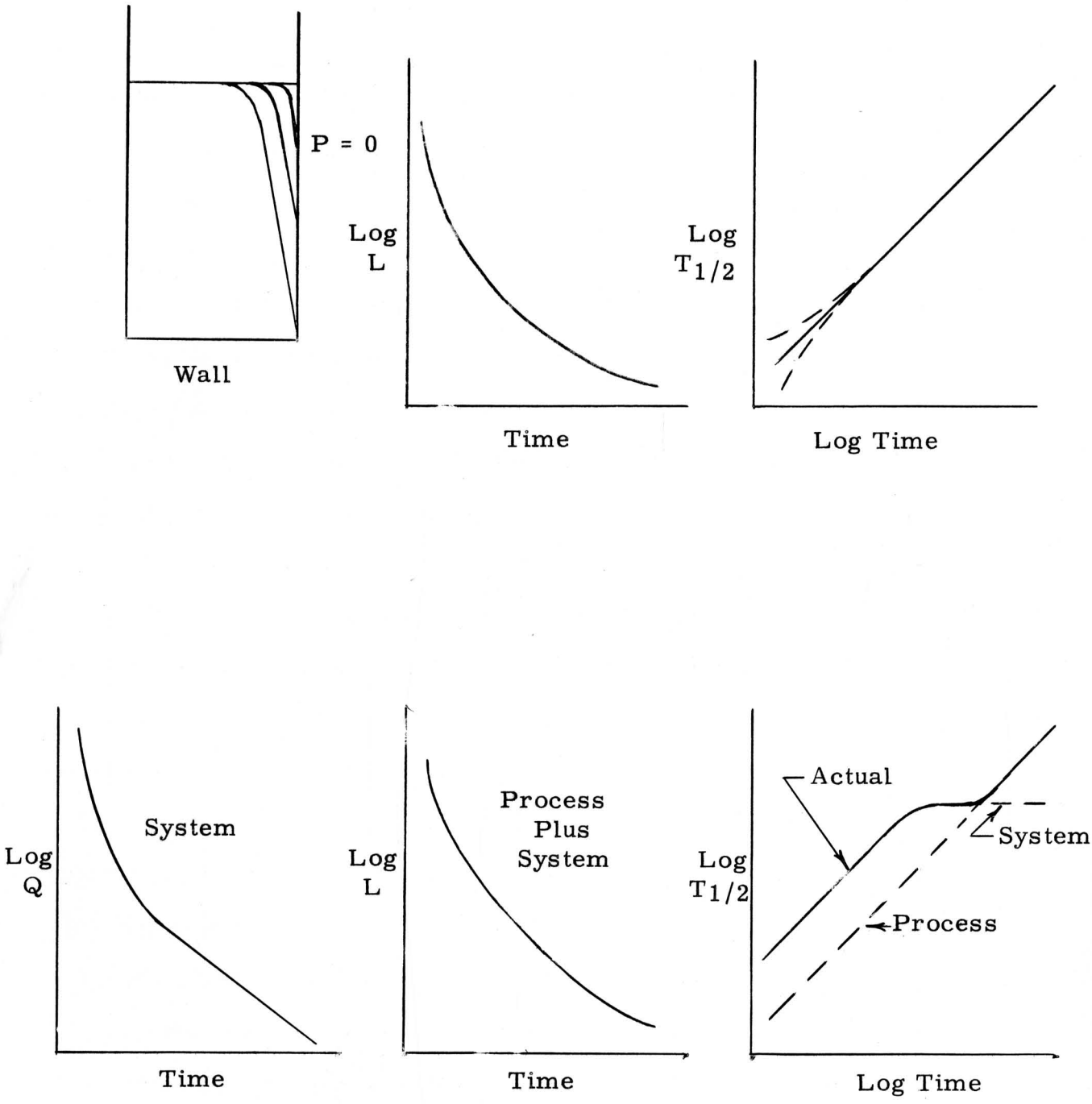


Figure 9 Absorption

of 2:1 in the absence of outgassing. Mathematically this is equivalent to $T_{1/2} = .693\ V/S$. Figure 8 illustrates some of these considerations. Here we have shown a theoretical outgassing curve plus the time dependent theoretical flow out of a particular system in which the outgassing is occurring. Because of the limitations of the system, the actual outgassing is slowed down as shown in the lower left of the figure. This can be more clearly seen by considering the half life plot on the lower right. Note that the system half life increases while in viscous flow and becomes constant in molecular flow where the speed is constant. The process half life is theoretically a constant value. However, the longest half life must predominate and hence the half life of the actual outgassing will follow the solid line shown. In practice the solid half life curve is obtained from the outgassing curve and is used to determine the effect of known or unknown restrictions on the process.

To further illustrate the value of the half life in the analysis of outgassing curves, let us consider a different type of reaction, that of absorption or diffusion. In the upper left corner of figure 9 we have illustrated the cross section of a piece of material containing a gas in solution. When a vacuum is applied to one side of the wall outgassing occurs and a diffusion gradient forms within the material. As time passes, the gradient moves deeper into the material and the outgassing decays as shown. Note, however, that in this case we do not obtain a straight line on a plot of the log of the leakage versus time. If we compute the instantaneous half life along the curve and then plot the log of the half life versus the log of the time we obtain

Figure 10

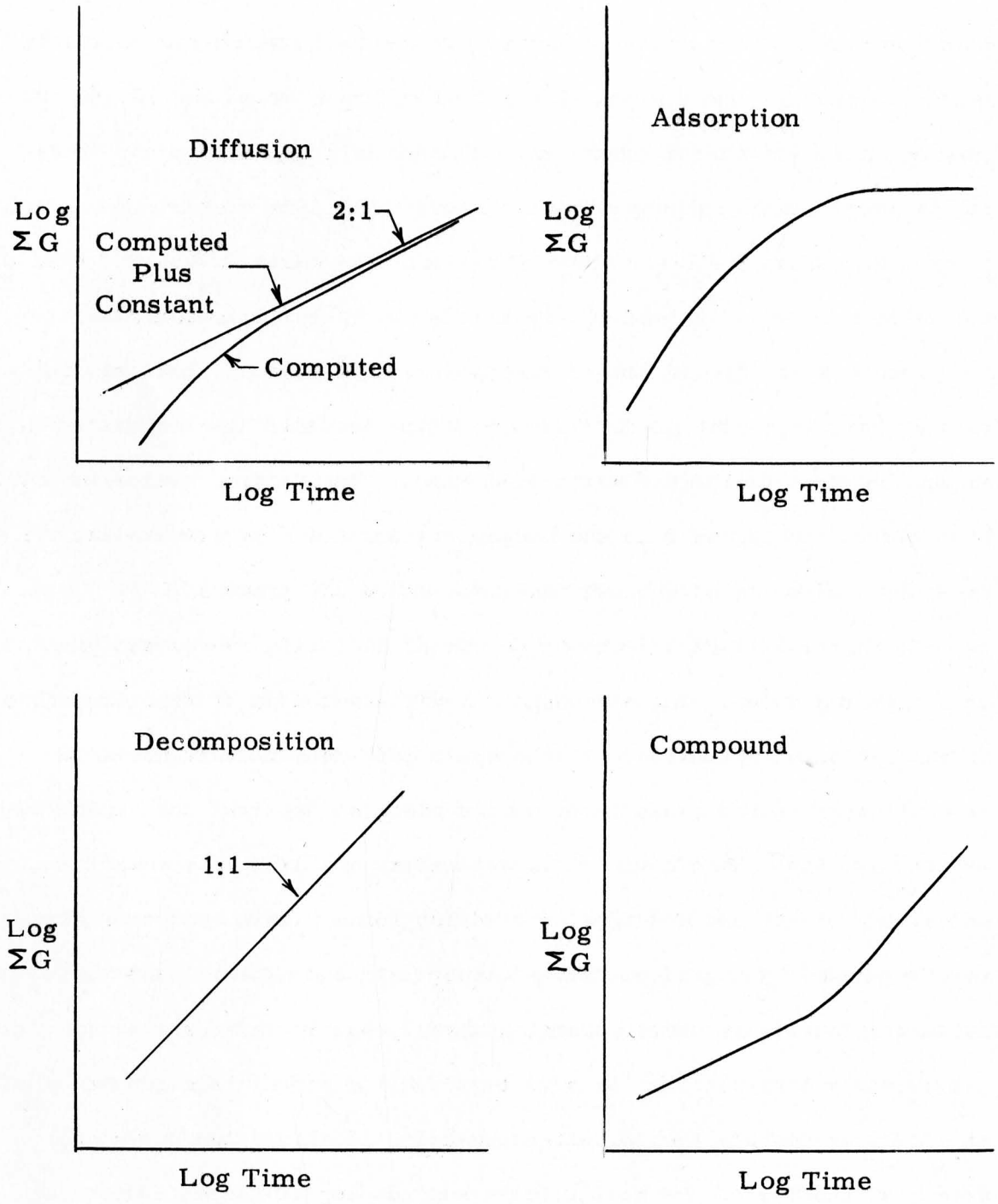


Figure 10 Total Gas

a 45° line indicating a linear relation between the two. Depending upon nonuniform gradients or errors in the reference zero time the curve may show as illustrated by the dashed lines. This can be used to study the effect or presence of previous outgassing processes. In the lower part of the figure, we again illustrate the effect of system limitations. The middle graph shows the actual outgassing curve which may be obtained in a given case when a diffusion type reaction is taking place in a material within a vacuum system. The curve looks very similar to the one above. Yet when the half life curve is computed and plotted, it is easy to see the effect of the system limitations. In this type of reaction the system is generally limiting early in the outgassing while the diffusion is limiting at the end. This is the reverse of what we observed for the idealized adsorption reaction. The temperature dependency fits the same generalization that a 10% change in the absolute temperature will cause a ten-fold change in the rate. Graphically, this is equivalent to a verticle shift in the 45° half life curve. The system part of the half life curve is only moderately temperature dependent.

The previous discussion has illustrated how the half life curve can be used to study outgassing, restriction and temperature dependencies, and their various interactions. Frequently these curves are quite complex due to multiple types or sources of outgassing. To aid in these studies further interpretive information is required. Fortunately, several other parameters are available. We will next discuss briefly the parameter of the total outgassing or ΣG (see figure 10). Mathematically this is equal to $\int L dt$ from T = 0 to a particular instant of time. If we compute the instantaneous value of ΣG and plot this as a function of

time on log log paper a number of interesting patterns can be observed. For example Dr. Benjamin Todd pointed out that the particular solution of Fickse law of diffusion for outgassing from a uniform concentration gradient involved the time to the one-half power. When we plot out the ΣG curves for this type of reaction we obtain a 2:1 slope as shown. Other reactions or groups of reactions have similar characteristic patterns which aid in the identification and analysis of the process. In taking outgassing data, it is almost impossible to obtain data at the start of the process due to the large flow of permanent gases out of the volume. By plotting the data as a log log plot, it is generally easy to recognize the missing gas. The figure shows an example of this condition where the total gas plot has been corrected by adding a constant to the Y axis. Also shown are typical patterns for adsorption, decomposition and a compound curve of diffusion and decomposition.

We next introduce threeadditional parameters which may be used to analyze the outgassing. To do so we must consider a special system, that of 2 volumes in series.

IV. THE TWO VOLUME PROBLEM

In many instances, it is found that a given vacuum system cannot be reduced to the simple condition of a volume, an interconnecting line, and a pumping system but rather must be considered as 2 volumes in series separated by a restriction plus the interconnecting line and pumping system. While there are limiting conditions which are easily solvable, the general solution, which would allow for a prediction of the pressure versus time in both volumes, has not been advanced, at least to the author's knowledge. However, we have found that we can

utilize a special condition of the two-volume problem to aid in the study of outgassing. Regardless of how complex the outgassing is, it could be simulated by the gas flow from a second volume through a variable conductance. This is illustrated in Fig. 11. To avoid depleting the supply of gas in the second volume we add a virtual variable leak. In the figure L_1, is the known system leakage which can be subtracted out. The unknown outgassing which we are studying is now represented by Q_2, the flow between the two volumes. If we assume a value for the virtual volume V_2, we can compute values for C, L_2 and P_2 and hence study how these virtual parameters vary with time. In the case of complex series restrictions, the process can be repeated on L_2 by the addition of another virtual volume. We are still studying the interpretation of the way these parameters vary with time. In addition, we hope to use this approach to study those processes which have variable temperatures during outgassing. It can be shown, for example, that if we allow the volume V_2 to vary with time in relationship with the temperature, the expansion and contraction of the volume will completely cancel out the temperature effects and the solution for C, P_2, and L_2 will be independent of the existing temperature. This then allows for a study of the basic outgassing process without the complications introduced by changing temperatures. This phase of the program is only beginning and a great deal of work is still necessary.

V. COMPUTER PROGRAM

Very early in the program, it became apparent that a great deal of computation is required for a complete analysis. For each pressure

Figure 11

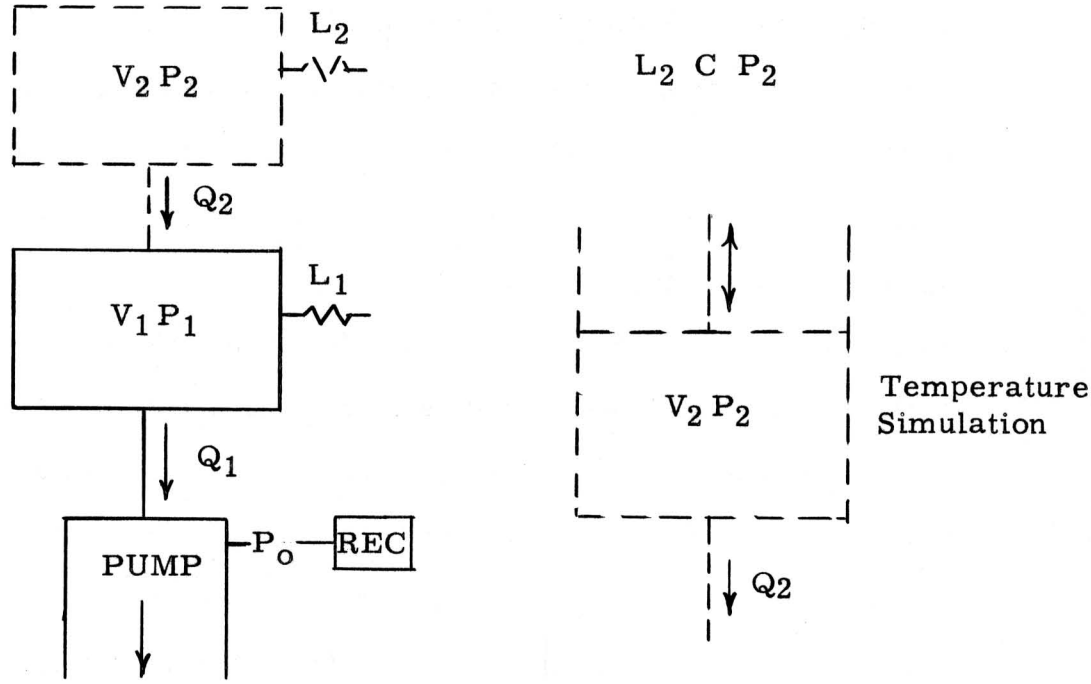


Figure 11 Other Parameters

Figure 12

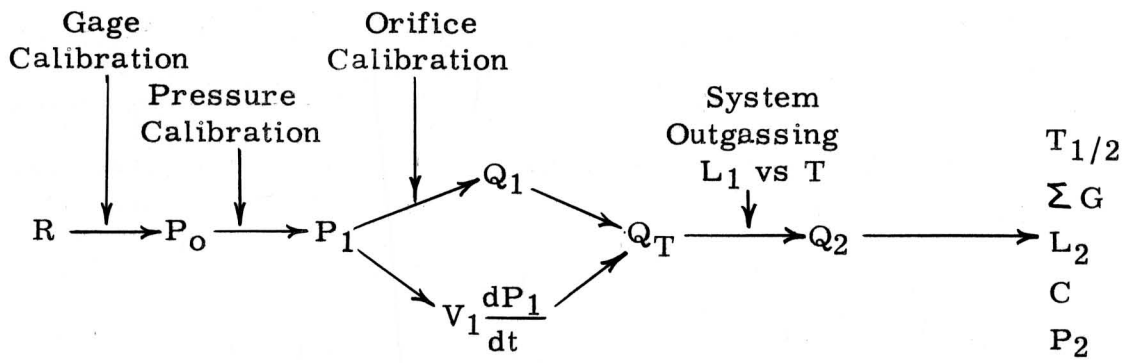


Figure 12 Computer Program

curve taken, it is necessary to compute the slope at anywhere from 20 to 200 points and then calculate the leakage. An equal number of derivatives of the log leakage curve are required to obtain the half life, and the curve must also be integrated point by point to obtain the $\lesssim G$ curve. Finally, there is the solution for the three virtual parameters of L_2, P_2, and C. Regardless of how laborious such a solution may be for an engineer, this is a simple problem for a digital computer. For this reason, we programmed an IBM 650 digital computer to handle the problem. An outline of the program is shown in Figure 12. Sufficient parameters and calibration tables were written into the program to allow for almost any possible condition. Two other tiresome operations were reading the pressure time data from the recorder sheets and later plotting the answers. To eliminate these chores, automatic data reduction and plotting facilities were incorporated. We now transcribe the data directly from the recording to IBM cards. After computation, the answers are plotted directly from the IBM answer cards. This results in a considerable reduction in both cost and time as well as an improvement in accuracy.

VI. EXAMPLES

This program was originally developed to study and analyze the complex outgassing problems which exist in the manufacture of many industrial products. Most outgassing cycles currently used are the result of trial and error, guesswork, or pure black magic. In many situations, little is known about the actual outgassing and what can be done to produce the best product at the lowest cost. To illustrate the application of Vacuum Process Evaluation, I would like to briefly

discuss two applications. First of all, consider the problem of producing well evacuated volumes. The volumes might range in size from a fraction of a cubic centimeter through hundreds of letters. Within the volume, we may find quite a variety of materials: glass, metals, ceramics, inorganic compounds and organic materials. Many pre-manufacturing processes are involved. Some add impurities while others are intended to remove them - such as acid washing of glass, hydrogen firing of metals, miscellaneous cleaning processes and air baking. In applying vacuum process evaluation, we first study the existing process by analyzing the outgassing at exhaust. From a study of the curves considerable information can be gained as to the source and nature of the outgassing and the amount of gas left in the volume. By varying the temperature cycle or by separately studying the individual components, further data can be obtained to arrive at the optimum cycle. This is also used to determine what materials are limiting the process and what can be done in the way of material selection. The next step is to evaluate the effect of the pre-manufacturing process. The answer to such questions as: What wash time and concentration of hydrofluoric acid should be used for glass?, How long an air exposure at what humidity is damaging to the process?, and what is the effect of various cleaning processes? All can be answered by deliberately varying the process in question and then comparing its outgassing, half life, etc., to the previous curves. In this way, quality control specifications can be established. As the parameters are varied, information is obtained as to the location of their effect on the outgassing curve. This information can then be used to diagnose for trouble when a sudden

siege of gassy product begins to show up. All that is required then, is to take a sample curve and compare it to the reference. Such information is also of advantage when designing a new product or when setting up a new process. Finally, the effect of the pumping system can be evaluated. This can be accomplished in two ways. First of all, the half life of the vacuum system is known and can be compared to the measured half life curve of the process to determine if the system is limiting at any point. This can further be evaluated by deliberately throttling the speed and studying the change in the half life, if any. Similar techniques are used to evaluate the effect of pinch-off restrictions. While it is difficult to make generalizations, it has been my observation that most pinch-off tubes on large equipments are far too small and most vacuum systems are far too big. It is sometimes surprising how small a vacuum system is required to adequately keep up with many of the outgassing processes.

The second application of wide industrial concern is that of cellulose outgassing, commonly used in various forms for insulation. It has long been recognized that several processes are acting in series. First, there is the outgassing of the micells and the fibers. This is followed by the restrictions of thickness and density of the cellulose material, wrapping tightness, product exhaust port and pumping equipment. The question, however, is which of these processes are limiting and at what time and temperature. Surprisingly enough, it is not possible to pick on a single culprit as being guilty. For example, the outgassing of free fibers at constant temperature is similar to a diffusion process in that the half life is a linear function of

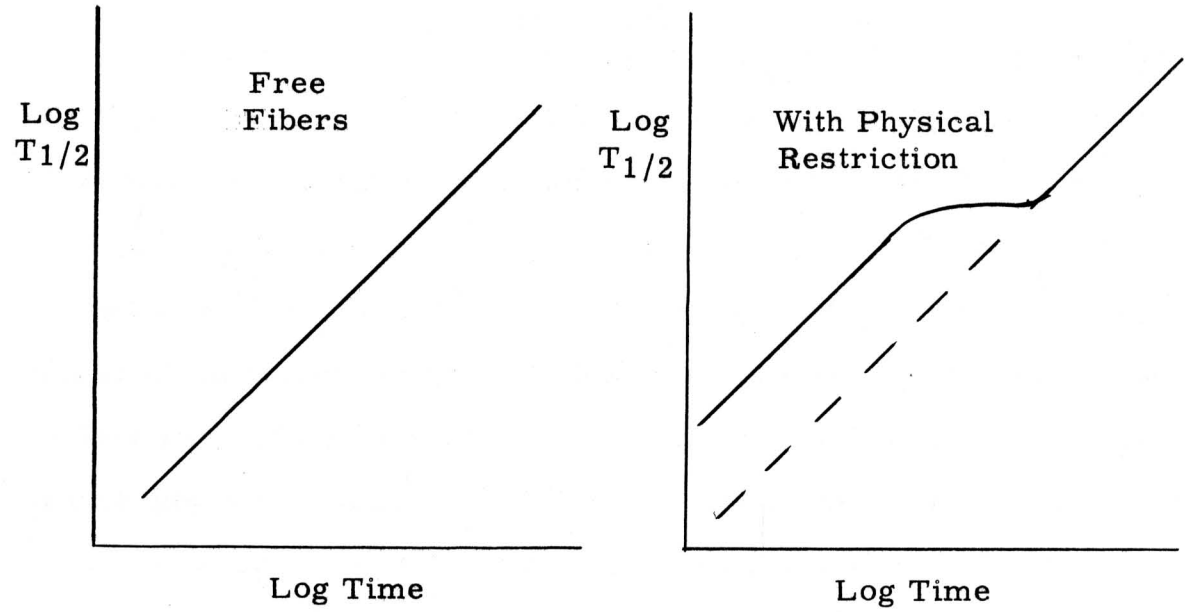


Figure 13 Cellulose Dehydration

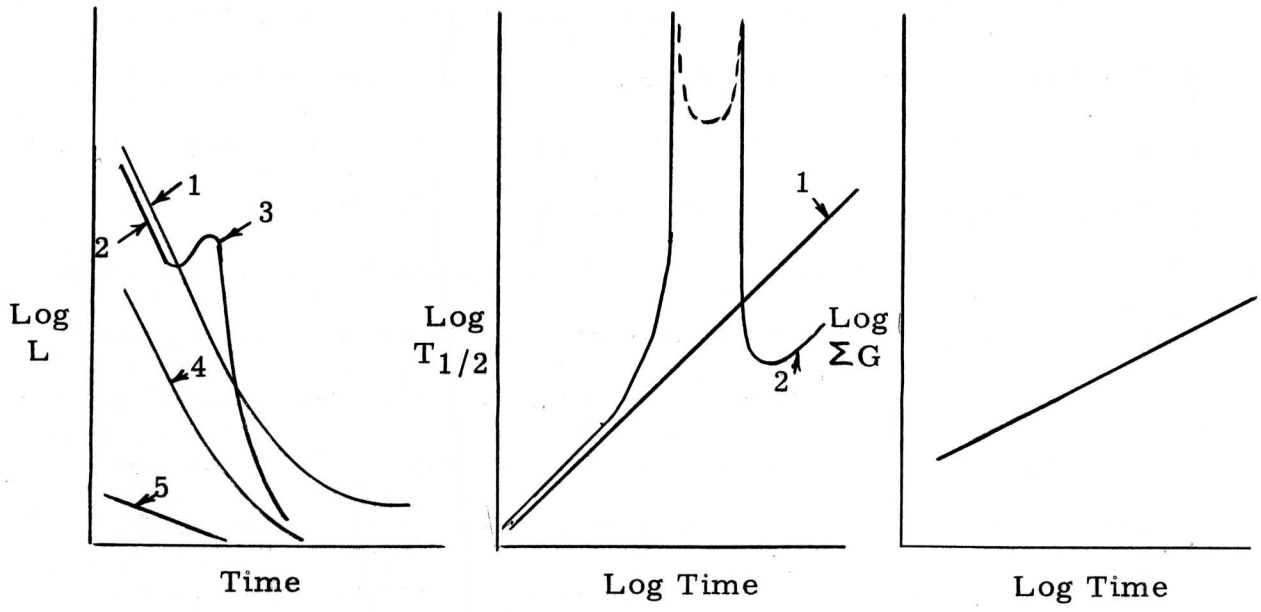


Figure 14 Material Outgassing Program

the time as shown on figure 13. In the early part of the process, the half life is sufficiently fast that generally some physical restriction is limiting the process. However, later in the cycle the half life of the free outgassing becomes so long that even the smallest restrictions have little effect on the process. Also, since there is such a considerable difference in the dimensions of the various restrictions (for example between the porosity of the paper and the exhaust port.), they will transist from viscous to molecular flow at different pressures. As a result, it is possible that several different parameters will take turns in acting as the limiting process. By understanding the interaction of these parameters, it is possible to design around the various limitations by either modifying the product or the process.

VII OTHER APPLICATIONS

As we became familiar with the technique many other applications occurred resulting in a variety of experiments. Most of these have only been preliminarily investigated and a great deal of work remains I would like to briefly discuss a few of these applications. Future reports will discuss these in more detail.

A.) Material Outgassing Studies

So many different types of insulating materials are used in various hermetically sealed devices that the question frequently arises as to what their relative outgassing quantities and rates are. To begin to answer this question, we set up a program to outgas various materials under different conditions as follows: (See fig. 14)

Figure 15

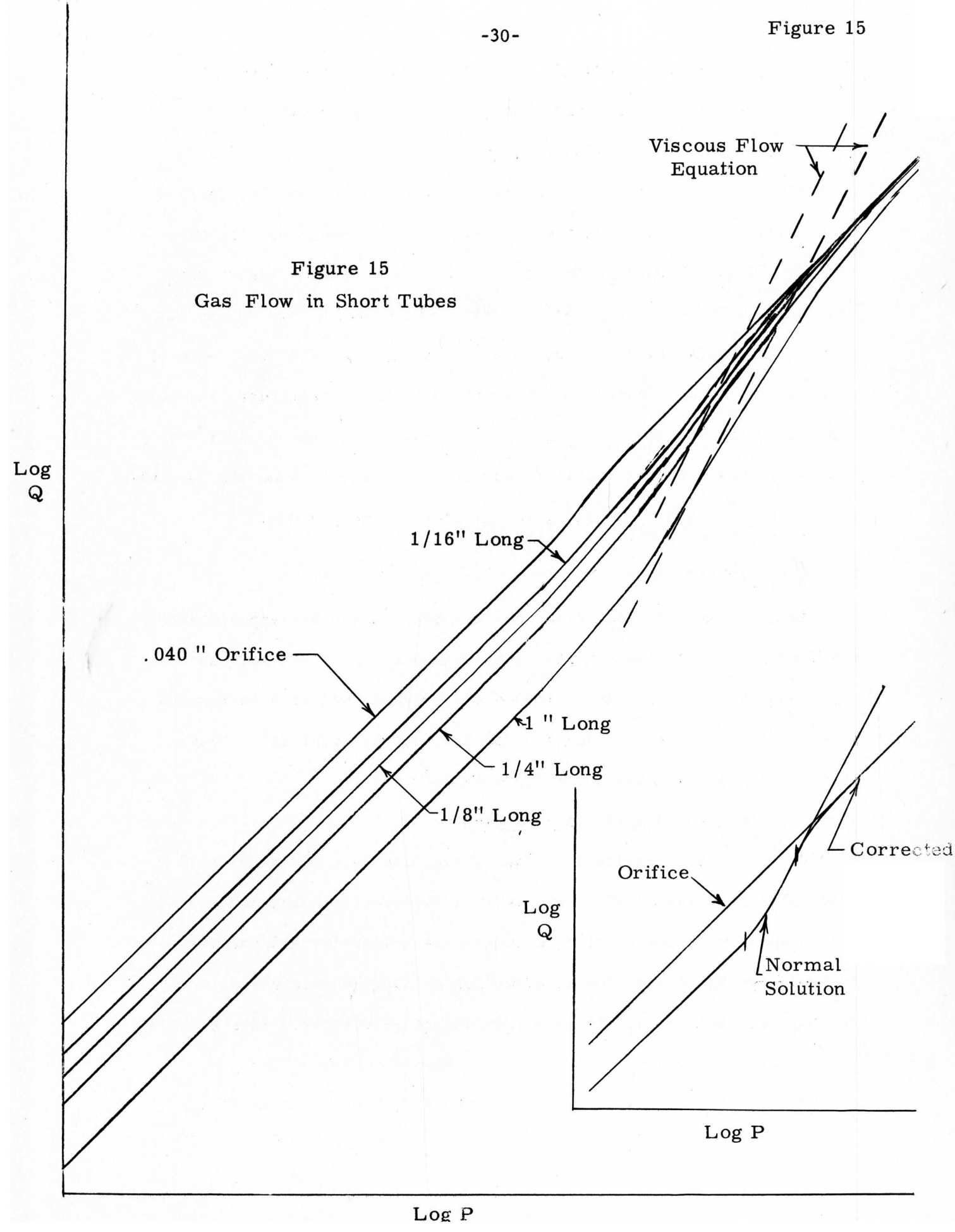


Figure 15

Gas Flow in Short Tubes

1) As received plus 24 hours in controlled humidity.

2) Outgassed plus 24 hours in controlled humidity.

3) Effect of increasing temperature.

4) Outgassed plus 10 minutes in controlled humidity.

5) Outgassed plus 24 hours in dry nitrogen.

To date, 28 different materials have been studied including various papers, nylon, teflon, mylar, silicone, etc. A considerable variation exists. Some materials while being quite gassey have a very low half life and will clean up quick. Others exhibit much larger half lives. The retake-up of moisture in 10 minutes also varied considerably, ranging from about 15% to 85% of saturation.

B.) Gas Flow Studies

In the process of calibrating various vacuum systems, it became apparent that very accurate measurements could be made on the conductance of orifices, valves and short tubes. A few preliminary experiments were then run to use the technique for the evaluation of both viscous and molecular entrance loss. The interesting family of curves in figure 15 resulted. The length to diameter ratio varied from 25 to zero (a sharp orifice). In molecular flow, the speed ratio for the orifice to the longest tube was 18 while for viscous flow it was only 1.4. Note also that the normal 2:1 slope for viscous flow shown by the dotted line, is missing. This is interesting from two points of view. First, if the curves continued appreciably above the 45^{o} line for the orifice, we would have the condition that there was more gas flowing through the tube than is incident on the end of the opening - an obviously impossible situation. The lower flow associated with turbulence does not give rise to this impossibility.

Calculated values of the Reynolds number at the point of transition generally range around 2000 depending upon the actual tube sizes. The second point of interest is that most vacuum system pipe lines are in actuality short tubes and as a result the vacuum engineer should be exceedingly cautious when applying the Poisuelle equation. In fact it is seldom that it can be used. It is possible to have the condition that a vacuum pipe line is limiting the mechanical pump when the Poisuelle equation suggests that it should not be. To correct for this situation on the Vacuum Engineering Nomograph, we have added the approximation shown on the right of the figure. The normal pipe P-Q curve is first drawn, then the molecular portion of an orifice the same size as the diameter of the pipe is added. This curve is then extended into the viscous region. Where it crosses the normal P-Q curve, it becomes the approximate curve relating pressure to mass flow.

C.) Vacuum Gage Calibration

Several times in our experiments, we observed that the calibration curve run on a clean system had obvious discontinuities or errors. These could only be attributed to the vacuum gage. This suggested a means of calibrating vacuum gages, but it posed the problem of which comes first. Do you use the gage to calibrate the orifice or the orifice to calibrate the gage. Once an orifice is obtained whose calibration can be believed, it can be used to calibrate any vacuum gage by evacuating a known volume through the orifice. By utilizing only the first portion of the Vacuum Process Evaluation program, that of $Q = -VdP/dt$ an apparent orifice calibration is obtained. By

comparing this to the known true orifice calibration, a complete calibration correction curve for the vacuum gage can be obtained.

D.) Getter Evaluation

Since getters are the reverse of outgassing, a simple modification may be made to convert the computer program to enable a study of this type of work. To test this, the barium getter studies reported by Dr. Della Porta [2,3] were chosen as the most accurate and up-to-date data available. The instantaneous values of the gas flow were extracted from the published curves, and the half life and total gas were computed as a function of time. Many of these plots showed the characteristic 1:1 half life slope and 2:1 total gas slope previously discussed for diffusion-type processes. In fact, these curves were still continuing up to the point where we could no longer read the original curves; however, the half life was becoming quite long at this point indicating a very slow diffusion process. Most of the data substantiated the conclusions reached by Dr. Della Porta in his report. We believe that this technique could be a valuable tool in studying getter reactions and hope to some day instigate a study of the reactions of various getter and gas combinations.

E.) Complex Material Outgassing

One of the most recent applications has to do with those situations where a complex surface or material is involved. One example of this can be obtained by reference to the work published by Dr. B. Todd[4,5] on the outgassing of glass surfaces. Dr. Todd states that the leveling effect of the outgassing at different

Figure 16

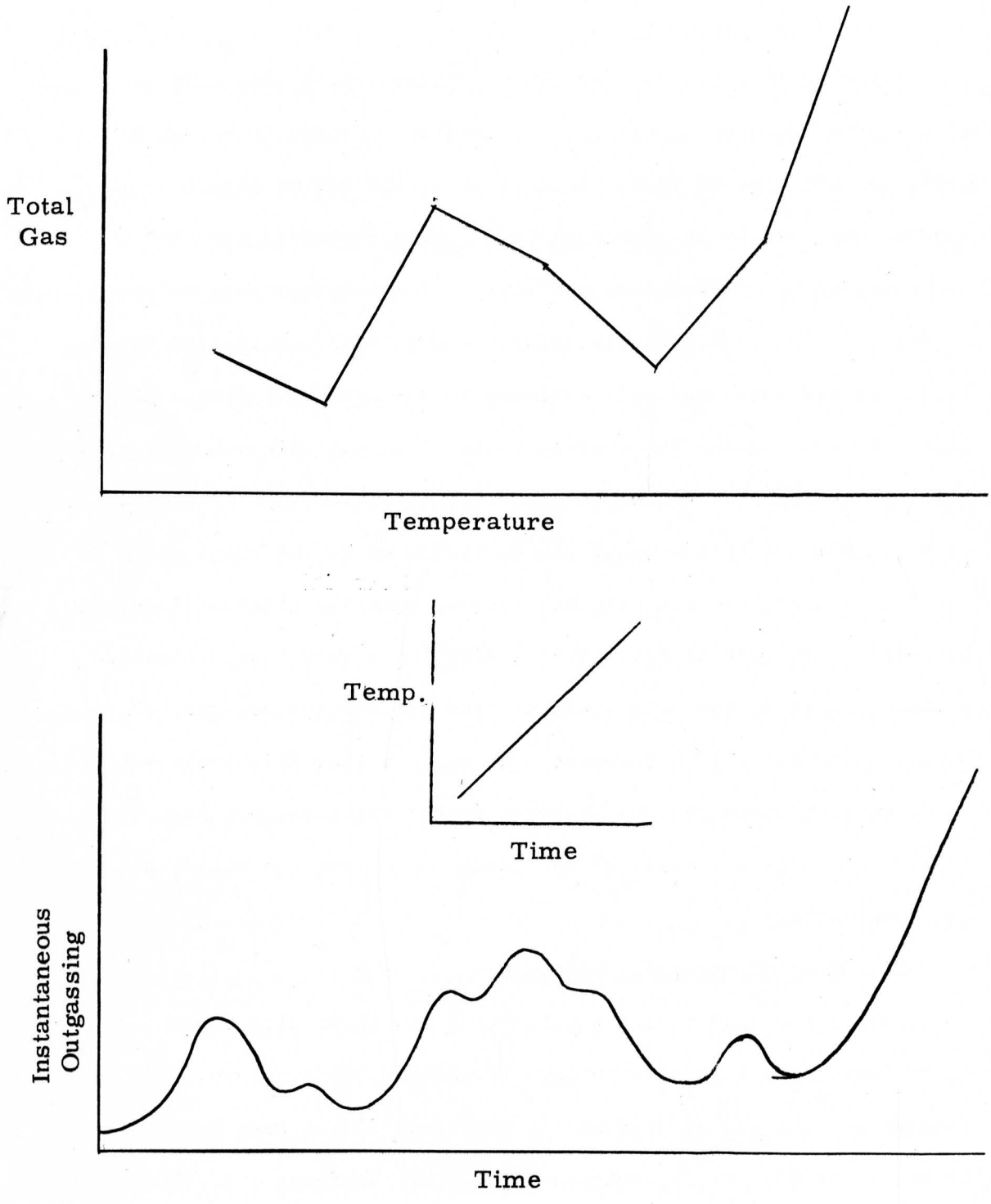


Figure 16 Glass Outgassing

temperatures suggests a complex hydrate structure on the surface. From his data, we can calculate the instantaneous outgassing and its half life. The 150° curve for example shows a constant half life of approximately two hours. Considering the 10% per decade temperature dependency referred to earlier, an increase of only approximately 40 degrees is required to reduce this half life by 10:1. Hence, at higher temperatures this particular component will outgas quite rapidly. We, therefore, propose the following test. Allow the temperature to increase at a slow but steady rate and measure the instantaneous outgassing as it is occurring. Figure 16 illustrates the anticipated results. On the top is a typical curve of the temp. dependent glass outgassing similar to those found in Dushman's "Vacuum Technique."[6] To obtain this type of curve, the total gas is collected over a long period of time at each temperature. Hence, each point represents an integration of all sources of outgassing over the full period of time. On the bottom is a curve illustrating the expected result for the instantaneous outgassing of a glass. As the temperature increases, the half life of all members of the complex surface decreases and one by one they reach a value where their particular outgassing is fast and their half life is of the order of magnitude of the measuring time. This is followed by depletion of the particular member and a resultant decay in the outgassing curve till the next member reaches a sufficiently low half life. Such a curve should result in a "fingerprint" of the particular glass being studied. By studying different glass compositions, it should be possible to identify the different sources of the hydrate breakdown. If a particular batch of glass

has been identified, the degree of hydration can be measured by comparing the outgassing curve of a test sample to that of a completely hydrated sample. This could also be used to study the rate of formation of the different hydrates. Many other possibilities exist in utilizing a controlled temperature change. For example, it may possibly be used to identify complex fuels or lubricants on the basis of their vapor pressures. Curves similar to the one shown for glass should result. It also may be possible to use this approach to aid in the study of complex decomposition reactions.

VIII. PROBLEMS

No new technique is without its associated problems. We have found many; some have been solved, others are in need of a solution. The following discussion of some of the more important problems is presented as an aid to those who might utilize this technique.

A.) Limitations During Initial Exhausts

During the first part of the pump down, the flow of permanent gases out of the volume is large as compared to the outgassing, and hence we are dealing with the small difference of relatively large numbers. This leads to considerable inaccuracy. As a result, the first part of the outgassing curve will always be missing or inaccurate. Since we generally use small calibrated orifices for the calibrated pumping system, this period of lost time can be minimized by inserting a high speed by-pass line. This, however, adds an additional valve and a resulting increase in the system outgassing.

B.) System Outgassing

One of the final limits on the study of outgassing near the end of the process is caused by outgassing of the system from sources other than that being studied. The computer program allows for the system outgassing to be measured and subtracted from the total outgassing. When the outgassing of the sample is small as compared to the system large errors are introduced. The only answer to this problem is cleaner vacuum systems. For very low level outgassing tests, this means that all organic materials must be eliminated and atmospheric contamination must be avoided. One generally unrecognized source of outgassing is that occurring from the thermal gradient between a liquid air trap and the main system. Along this gradient, we have a complete range of temperatures which will trap condensables and then allow for their reevaporation over a wide range of outgassing levels. If the liquid air level falls the situation is aggravated. Cascaded traps or baked out metal foil traps of the Alpert design can minimize this problem. Other system outgassing sources are from the fluxes used in brazing and soldering or the leakage in some metal "O" ring seals. These can be minimized by good system design. A highly desirable diffusion pump that would simplify some of these problems would be one which could be permanently welded into the system and the jet assembly removable through the bottom so that the one-flanged joint is on the rough vacuum side.

C.) Vacuum Gage Limitations

There are several problems in this category. One is the problem of gage calibration previously discussed. But even if an accurate

calibration is made using a particular gas, what is the true calibration for the gases being evolved during outgassing. A recording absolute vacuum gage is highly desirable. The limitation of the ranges of many of the gages frequently requires that at least two different types must be used. An additional problem of many gages, such as the ionization gage, is that they represent both a source and a sink for gases. A slight change in temperature will destroy the equilibrium and cause false readings. Outgassing of the grid is such a condition. Depending upon the circumstances, abnormally high or low readings will follow this outgassing. While it would be nice to make the generality that the grid should not be outgassed more than once during the exhaust, this is not always a good procedure. For example, if the gas composition changes, we may find ourselves with the condition that the grid is outgassing a particular type of gas not present in the gas phase and at a very high half life. Outgassing of the tube will then allow this particular gas to be rapidly eliminated even though we have destroyed the thermal equilibrium of the tube and hence must wait until everything readjusts. As long as the gage is acting as a pump, its reading cannot be believed. Elimination of gage tubulations will minimize this problem.

D.) Temperature

By far the most severe problem is that caused by temperature. This enters in several ways; temperature changes confuse the analysis and affect the calibration of vacuum gages, tubes, and pumps. We have found that in cases where a hot system is being evacuated through

a cold port, the contraction of the gas during cooling acts as an additional pump. As a result, the speed of the system is considerably higher than when calibrated cold. The easiest solution for this is to calibrate for the same temperatures as will be used in the outgassing study.

E.) Variable Pumping Speed

Vapor pumps are inherently variable in speed. The speed can be affected by many items such as oil level, power applied and degree of cooling. In addition, the pumping speed is different for many gases. These situations make vacuum process Evaluation difficult to apply. The easiest solution is to use a large pump in series with a small orifice of known calibration. If the speed ratio is made to be at least 10:1, variations of the pump speed will have a considerably reduced effect on the analysis. If liquid air traps or refrigerated baffles are used, these must be between the pump and the restriction to avoid the condition of having different pumping speeds for different gases.

VIII. FUTURE WORK

This technique is relatively new and a great deal of application work remains. Most of the experiments previously discussed need to be continued and better solutions found for some of the problems. In addition to this, there are two other major areas we would like to explore. The first of these has to do with gas analysis. In our studies, we frequently obtain simple half life curves which are easily analyzed. Just as frequently, we obtain very complex curves

which result from multiple outgassing sources and different gasses. For this reason, it is desirable to be able to study each gas separately. For example, an analytical mass spectrometer could be used to monitor several different gas sources and obtain pressure versus time curves for each. These could then be computed individually and the outgassing of each gas studied separately. To start this type of study, we have modified a General Electric type M mass spectrometer leak detector so that it might be used as a semi-quantitative mass spectrometer. While we still do not have as good a resolution as the more expensive analytical mass spectrometers, the success of the modification is indicated by the fact that we presently can use the modified instrument for leak testing with Argon at better sensitivity than we previously had with helium. Recently, we successfully found a small leak in a vessel charged with krypton. This allows for a considerable selection of gasses to be used for mass spectrometer leak detection. The actual application of the modified mass spectrometer to the study of outgassing problems has not yet started. We hope to get this program under way within the next year.

The second area of future work is concerned with conversion from digital computing to analog computing. In taking data, we obtain an analog signal. This must be converted to digital signals for calculating and then back to analog for plotting. An ideal solution would be to have an analog computer directly connected to the vacuum gage or mass spectrometer. This could then feed a bank of recorders and continuously plot the half life, total gas, etc., as functions of time while the data is being taken. For plotting the curves against the

logarithm of the time, an X-Y recorder could be used. For a little blue sky dreaming, we might envision a factory of the future where many outgassing processes are controlled by a single multichannel analog computer.

Our work in the area of outgassing is just a beginning; a great deal remains to be done. We have found that the technique of Vacuum Process Evaluation is a valuable tool in studying problems of outgassing, gettering, and gas flow. We sincerely hope that others will also use it in their work in vacuum engineering.

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