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Dielectric constants and pair interactions in polar molecules

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Dielectric Constants and Pair Interactions in Polar Molecules

by

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ABSTRACT

Intermolecular interactions effect the physical properties of polar substances to varying degrees. One property for which there exists the possibility of separating out the various components of this interaction (pairs, triplets, etc.) is the total molar polarization of a substance. These effects are quite dependent upon temperature and pressure, so if one is going to make measurements over a large range of these variables, one must develope a system that is capable of handling the conditions. Along with this there must be the necessary instrumentation and other apparatus for measuring dielectric constants which define total molar polarization. In this thesis, the theory behind these measurements will be studied along with the necessary equipment. Also, since one molecule which shows very interesting intermolecular effects is hydrogen fluoride, there will be some investigation into the problems in handling such a corrosive material and the preparation of its isotope, deuterium fluoride, for measurements of the effect of isotopic sustitution.

I would like to dedicate this thesis to my grandfather, Nicoala Pozza, who passed away on November 12, 1974.

ACKNOWLEDGMENTS

The author would like to acknowledge the assistance of a number of persons who contributed to this project. In particular, the author would like to thank Prof. Herbert Sutter for the suggestion of this topic and his guidance throughout this project.

The author would also like to thank the Union College Machine Shop which did the machining of the bulk of the parts used in the test system and the gas handling system itself. Thanks are also extended to Prof. Galantowicz for the design of the amplifier used in the measuring system, Prof. Schaefer for many helpful suggestions on the handling of HF, and in particular my co-worker Kurt Hillig for the work he did with the system in general and his help with understanding the electronic circuitry.

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1. INTRODUCTION

In the course of the experimental work presented here, what will be studied is not individual molecules, but a system of many molecules and how they interact. To be examined is how this interaction varies with such conditions as temperature, density, and isotopic substitution. In the long run the objective will be to find how these experimental observations agree with the theoretical predictions from classical and quantum theories of intermolecular forces.

Of course, if extensive molecular interactions are to be studied, then polar molecules will be of the most interest. The simplest (as far as the theoreticians are concerned) of dipolar molecules to show large intermolecular interaction (such as hydrogen bonding) is hydrogen fluoride. Experimenters find that HF presents a challenge. Due to its corrosive nature, there are many practical problems with materials and procedures. Much of the experimental work included in this thesis was centered on these problems. Upon completion of this phase of the work, another problem faced was the production of relatively pure DF since it was not commercially available. Although the ultimate goal was the making of measurements and comparison of them with theoretical predictions, complications with the previous two problems prevented such work.

2. THEORY

The Clausius-Mossotti function which represents total molar polarizability (${}_{T}P$) is given by:

$$(1) \quad {}_{T}P = \frac{\epsilon - 1}{\epsilon + 2} V_m$$

ϵ = dielectric constant
V_m = molar volume

The quantity ${}_{T}P$ can be better understood if it is thought of as the vector sum of all the dipole moments of the molecules in one mole of the material at unit field. The quantity ${}_{T}P$ can be expanded in inverse powers of the molar volume.

$$(2) \quad {}_{T}P = A_{\epsilon} + \frac{B_{\epsilon}}{V_m} + \frac{C_{\epsilon}}{V_m^2} + \cdots$$

In this case, A_{ϵ} is the ideal gas contribution to ${}_{T}P$, that is, the value of ${}_{T}P$ without any interaction between molecules. The term B_{ϵ}/V_m represents the contribution of pairs of molecules to ${}_{T}P$, C_{ϵ}/V_m represents triplet contributions, and so on. To the student of physical chemistry, equation (2) may look familiar. It resembles the common form of the expansion of the compressibility factor PV_m/RT for gases:

$$(3) \quad \frac{PV_m}{RT} = 1 + \frac{B_P}{V_m} + \frac{C_P}{V_m^2} \quad \cdots$$

In this case, 1 is the ideal contribution, B_P/V_m accounts for pair interaction, etc. In this equation, B_P, C_P, ... vary with temperature. Later it will be seen how B_{ϵ} and its counterparts vary. However, before proceeding further, a look at the origin of equation (2) is in order.

For this, the classical approach of Debye can be employed.[1] The simplest case can be presented as a single particle in a dielectric medium between two evenly charged plates. The total field felt by the particle is made up from three contributions,

(4) $F = F_1 + F_2 + F_3$

The quantity F_1 is the field due to the charges on the plates. From classical electrostatics,

(5) $F_1 = 4\pi\sigma$

σ = surface density of charge on the plates

Consider next a sphere of arbitrary size surrounding the particle. The quantity F_2 is the additional field due to the dielectric outside the sphere. Thus F_2 has two parts. From classical electrostatics,

(6) $F_2 = -4\pi I + \frac{4}{3}\pi I$

$I = \frac{\text{electric moment}}{\text{unit volume}} = \text{polarization}$

The first term on the right hand side of equation (6) represents the field due to the layers of induced charge on the dielectric facing the plates and the second term represents the field due to the charges on the surface of the spherical cavity. The field F_3 is from the material within the sphere. In the case of a gas, however, the sphere can be chosen such that there are no other particles in the sphere, thus $F_3 = 0$. The result for the ideal gas is :

(7) $F = 4\pi\sigma - 4\pi I + \frac{4}{3}\pi I$

The second fundamental law connecting electric dipoles with charge shows that D, the electric displacement, is given by:

(8) $D=\epsilon E = 4\pi\sigma = E + 4\pi I$

ϵ = dielectric constant
E = the average field in the dielectric

By then combining equations (7) and (8) the result is:

(9) $F = E + \frac{4\pi}{3} I$

If a molecule is considered with no permanent dipole moment, the moment induced by the field is given by:

(10) $\overline{m} = a_0 F$

a_0 = polarizability
F = actual field intensity
$\overline{m}$ = average electric moment

Letting I equal the induced electric moment of one c.c.,

(11) $I = nm = na_0 F$
$= na_0(E + \frac{4\pi}{3} I)$

A combination of equations (7) through (9) and (11) yields:

(12) $\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3}\pi n a_0$

Multiplying both sides by M/ρ ($= \frac{\text{molecular weight}}{\text{density}} = V_m$ for gas)

(13) $_TP = \frac{\epsilon - 1}{\epsilon + 2} V_m = \frac{4}{3}\pi \frac{nM}{\rho} a_0 = \frac{4}{3}\pi N_A a_0$
$= 2.54 \times 10^{24} a_0$

N_A = Avagardro's number

It has already been noted that only the distortional part of the electric moment was being considered in deriving equation (13). The effects of the permanent dipole existing without the field have yet to be added in .

Consider a molecule which is "rigid", and cannot distort at all in a field. By analyzing the potential energy of a set of such molecules, the terms can be developed which describe their equilibrium distribution. The electric moments of a molecule can be described, and a dipolar molecule defined as one with a finite $\overline{m}$, the average dipole moment in the absence of a field. The solutions that can be formed for the electrostatic potential due to the molecule at any point can be explained in terms of the existence of dipoles and higher order multipole moments in the molecule. The simple dipole (a positive and a negative charge separated by a distance r) can be placed parallel to itself to form a quadrupole. Formation of a quadrupole parallel to itself is referred to as an octapole. This system can be extended indefinitely. Better values for the potential energy of the system can be obtained by introducing these higher multipoles, but, of course, the calculations involved become much more complicated. In this work, moments beyond the quadrupole will be ignored.

The next consideration is the orientation of the polar molecule in an applied field. The potential energy of a polar molecule (which cannot be distorted) in a field is:

$$u = -\overline{m}(F) \tag{14}$$

$u =$ potential energy
$\overline{m} =$ average moment
$F =$ actual field intensity

In the case of no forces acting on the molecules, the moments of the molecules will be randomly oriented in space. However, in a field, polar molecules have been shown to align themselves according to the direction of the applied field. Using statistical mechanics, Debye determined that m for a single molecule would be $\mu_0^2/3KT$ in the case of small fields. Thus, if the total moment of a molecule is desired, equation (10) must have this term added:

$$(15) \quad \bar{m} = a_0 F + \frac{\mu_0^2}{3KT} F = (a_0 + \frac{\mu_0^2}{3KT}) F = a F$$

Therefore, the equation derived earlier for ${}_TP$ is correct, only the value of a_0 must be converted to a. Note, all this work has included no mention of intermolecular interaction; it is all based on a single molecule. Thus, the result for ${}_TP$ is actually the A_ϵ of equation (2).

To consider the effects of intermolecular interaction between pairs (B_ϵ in equation (2)), it becomes necessary to make further use of statistical mechanics.[2] Though the numerical methods are too involved to present in this thesis, the result for B_ϵ is:

$$(16) \quad \frac{N4\pi}{3\Omega} \int \left[(\tfrac{1}{2}a_{12} - a_0 \partial \quad \frac{1}{3KT}(\tfrac{1}{2}\mu_{12}^2 - \mu_0^2) \right] \text{ x } \exp(\frac{-U_{12}}{KT}) \, d\tau$$

a_{12} = polarizability of the pair
$\mu_{12} = \mu_1 + \mu_2$ = dipole moment of the pair
Ω = integral over all angular components
$\Omega V_m = \int_\tau d\tau$

In equation (15), the further separation of the quantities a_0 and μ_0 is seen. Again, a_0 is the polarizability of the molecule, the average tendency of the molecule to distort in the presence of a field, while a_{12} is the total polarizability of the pair. By subtracting a_0 from $\frac{1}{2}a_{12}$, one obtains the change in polarizability per molecule due to pair interactions. Both a_0 and a_{12} are tensors. In the presence of a uniform field, a_0 is symmetric and can be reduced to three component vectors, a_{xx}, a_{yy}, a_{zz}, which are all non-zero and independent. If the molecule is symmetric, then all of the components are equal and indistinguishable. However, if the molecule is linear, then $a_{0xx} = a_{0yy} = a_{0\perp}$ and $a_{0zz} = a_{0\parallel}$ where z is chosen as the direction along the molecular axis. When two molecules must be considered (a_{12}), the solution for the components that make up the polarizability becomes much more complex. Note that the quantity a_0 is defined in terms of the molecular axis, it has no dependence upon the orientation of the molecule in the field. The quantity μ_0 is a vector, so μ_{12} is a vector as well and depends upon how the molecules orient with respect to one another in the field. For example, if the moments are arranged so that they are parallel (pointing in the same direction), the result is:

$$\bullet\!\xrightarrow[\mu_1]{\hspace{3em}} \quad \bullet\!\xrightarrow[\mu_2]{\hspace{3em}} \qquad \mu_1 = \mu_2 = \mu_0$$

$$(17)\quad \mu_{12} = \mu_1 + \mu_2 = 2\mu_0$$

However, if the moments are arranged so that they are antiparallel (pointing head to head),

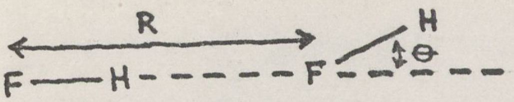
$$\bullet\!\xrightarrow{\hspace{3em}} \quad \xleftarrow{\hspace{3em}}\!\bullet \qquad \mu_1 = \mu_2 = \mu_0$$

$$(18)\quad \mu_{12} = 0$$

Thus B_ϵ is heavily dependent upon the way in which the molecules prefer to orient as they interact. This is very unlike the quantity B_P in equation (3) which is relatively insensitive to angular dependence of interaction.

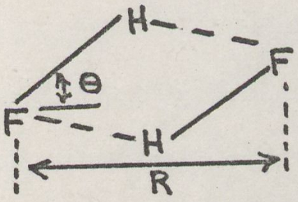
One point overlooked thus far is evidence of the actual existence of dimers in polar molecules, particularly the ones being considered, hydrogen fluoride and water. Most studies of the existence of such molecules have been theoretical in nature. One method has involved <u>ab</u> <u>initio</u> calculations for the energies of dimer formation. The accuracy of such calculations depends upon the size of the basis set of atomic orbitals used to find the energies. Using the rather large double zeta set of Gaussian atomic orbitals, fairly good agreement with the experimental results can be reached. Kollman and Allen found that using such a basis set they obtained a minimum energy of -99.996a.u. at a bond distance of .946Å for the HF monomer.[3] Experimentally, Herzberg found a bond distance of .917Å for HF.[4] By adding more energy determined linear coefficients to the basis set of orbitals used, the result is a bond distance of .916Å (energy of -100.013a.u.). For the water monomer, the second basis set was used by Kollman and Allen to obtain an (O--H) bond distance of .957Å in both bonds, compared to Kuchitsu's and Bartell's experimental answer of .957Å.[5] These methods of calculating potentials were also used by Kollman and Allen for dimers. The HF linear dimer showed a minimum energy of 4.6 kcal/mole at a θ of 20°, $R = 2.87$Å (Fig.1).

Fig.1



The cyclic HF dimer showed a minimum energy of 3.1 kcal/mole at $\Theta = 60^{\circ}$, $R = 2.80$Å(Fig.2).

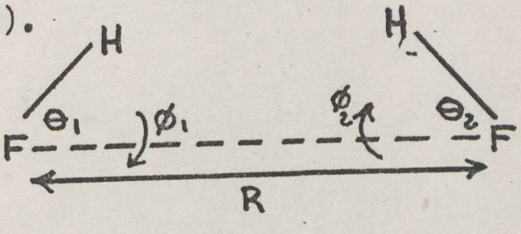
Fig.2



It can be seen that both dimers are relatively stable, and (depending on temperature) it could be expected that each could be found in appreciable concentration.

If a smaller basis set of atomic orbitals is chosen for the *ab initio* calculations, the results are not as good. Pople and Del Bene used a minimal basis set of Slater type atomic orbitals to obtain a bond length of .938Å for the HF monomer.[6] Their application of this method to the HF dimer showed an equilibrium form where $R = 2.55$Å, $\Theta_1 = 4^{\circ}$, $\Theta_2 = 111^{\circ}$, and $\phi = 180^{\circ}$ (see Fig.3).

Fig.3



This dimer would have a binding energy of 5.2 kcal/mole. Experimental estimates by Smith[7] and by Frank and Meyer[8] range from 5 to 7 kcal/mole. The importance of this method is that since the basis set is smaller, the calculations are not so involved and it can be used to make predictions for the higher polymers of HF ($(HF)_n$ where $n = 3$ to 6). It is found that these higher polymers are even more stable in terms of energy, and that the cyclic forms are more stable than the chain ones. Similar results are found for water.[9]

The little experimental work that has been done on HF molecular interaction has taken the form of molecular beam-electronic resonance spectroscopy. Mass spectrometers hooked into such systems have shown m/e values of 21, which would indicate a parent $(HF)_2$, but there is the possibility of interference from heavier polar species. The esr has shown the correct radiofrequency and microwave transitions for $(HF)_2$ without any appearence of impurities. By using frequency and plate voltage data under least squares analysis, one can obtain Stark coefficients which provide the dipole moment of the species and its vibrational-rotational energy scheme. Other factors can be brought in, but the results as calculated by Dyke and his co-workers are roughly:[10]

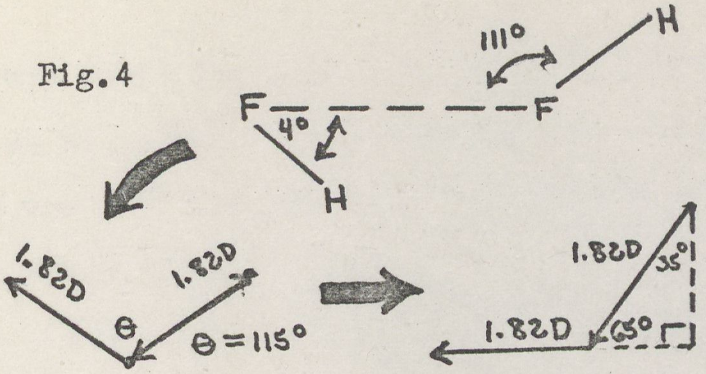
$(DF)_2$= 2.993D to 2.997D

(HFDF)= 3.03D

$(HF)_2$= 2.989D to 2.987D

A comparison can be made between these and what was found from the *ab initio* calculations. Dipole moments from the earlier calculations for the HF monomer are found to be way off (Pople and Del Bene[6] calculate μ=1.39D while Weiss[11] found μ=1.82 experimentally). Thus if the experimental μ is used along with the equilibrium orientation found by Pople and Del Bene , the calculated dipole moment of the dimer is:

Fig.4



Adding these two dipoles as vectors, the result is:

$$(19)\quad \mu_{total} = 1.82\ D + 1.82(\sin 35°) = 2.85\ D$$

This less than what is seen by experiment. The trouble with the method used is that it ignores intermolecular polarization which would in effect "strengthen" the dipoles and lead to a greater overall moment.

Another observation of the experimental results is that isotopes are not causing a very large difference (≈1%) in the dipole moment of the dimer, and this probably is not within the realm of experimental error. However, if a closer look is taken at the second virial coefficient, it is found that a greater deviation can be seen. In fact, B_ϵ can be broken down into three quantities: B_{Cl}, a classical part; B_Q^{Tr}, a translational quantum correction; and B_Q^{Rot}, a rotational quantum correction. Calculations for water have shown that these corrections effect B_{Cl} by 20%, and that B_Q^{Rot} provides 90% of this effect.[12] A look at the formal equation shows that B_Q^{Rot} is inversely proportional to I, the moment of inertia. Since H_2O is a three body problem (and that is what the available data is for), consider a simpler two body molecule which is similar in pair interaction characteristics, such as HF. One way of changing the moment of inertia of HF is to use its isotope, DF. The moments of inertia in these cases would be:

$$(20)\quad \underline{\mathrm{DF}}\qquad I = \frac{(m_1)(m_2)}{m_1 + m_2} r^2 = \frac{(2)(19)}{2+19} r^2 = \frac{38}{21} r^2$$

$$\underline{\mathrm{HF}}\qquad I = \frac{(m_1)(m_2)}{m_1 + m_2} r^2 = \frac{(1)(19)}{1+19} r^2 = \frac{19}{20} r^2$$

Independent measurements of r for these dipoles have shown that they are equal out to three places, so r^2 should be the same for both inertial moments. The reduced mass is the determinant, and the reduced mass of DF is twice that of HF ($1.81r^2$ vs. $.95r^2$). Thus (recalling that B_Q^{Rot} is inversely proportional to I), B_Q^{Rot} for DF should be smaller. Assuming that water is similar to HF, and using MacRury's and Steele's[12] value of 20% for the effect of B_Q^{Rot} on B_{Cl} for water, the B_Q^{Rot} for HF should show a 20% effect and DF one in the area of 10%. When comparing the overall B for HF and DF, a difference of as much as 10% could be expected. This difference is easily within the realm of the instrumentation methods to be discussed, and perhaps at this time it would be useful to have a look at them.

3. EXPERIMENTAL APPLICATIONS OF THEORY

As stated before, the main interest of this project is studying the effects of molecular interaction on the pair interaction of molecules of a gas. Thus, looking back to equation (2):

$$(2)\quad {}_{T}P = A_{\epsilon} + \frac{B_{\epsilon}}{V_m} + \frac{C_{\epsilon}}{V_m} + \cdots$$

the quantity that is important here is B_{ϵ}. Since it has been shown:

$$(3)\quad {}_{T}P = \frac{\epsilon - 1}{\epsilon + 2}\, V_m$$

it is necessary to measure V_m and ϵ. V_m is a difficult quantity to measure. In order to get B_{ϵ} within 10%, V_m would have to be measured to within 1 part in 10,000. V_m is usually measured by taking the pressure and converting to V_m through an equation of state (equation(3)), but this is seldom as accurate as the above necessitates, particularly at high pressure. For ϵ, accuracy of about 1 ppm is in order, and this is readily attainable through direct measurement.

The quantity V_m is avoidable through a process known as the Burnett expansion technique.[13] In Figure(5) the apparatus for such a method is pictured. It consists of a measuring cell (V_A) and an expansion cell (V_B). Both cells are filled with gas, allowed to equilibrate, and closed off. A measurement of ϵ is made, then V_B is opened and evacuated, V_B is closed back up, and the gas from V_A is allowed to expand into V_B and equilibrate between the two cells. This

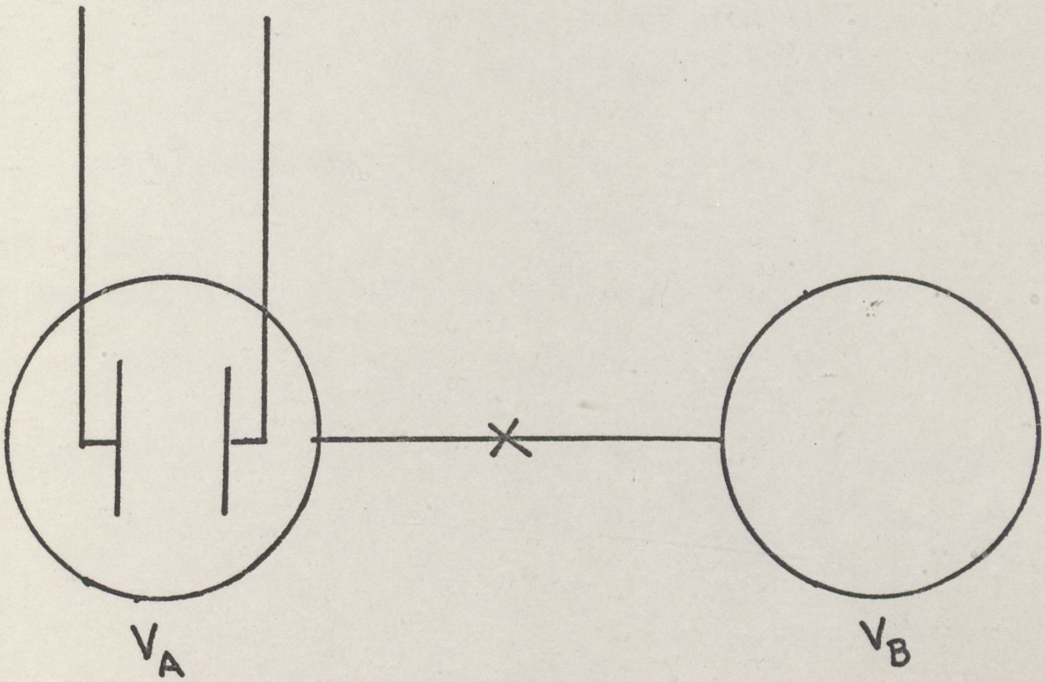


Figure (5). Cell system for the simple Burnett expansion technique process can be repeated a number of times to get a series of values for $\epsilon-1/\epsilon+2$. If the i^{th} measurement of $\epsilon-1/\epsilon+2$ is referred to as f_i, then the ratio f_i/f_{i+1} is:

$$(21)\quad \frac{f_i}{f_{i+1}} = \frac{A_\epsilon d_i + B_\epsilon d_i^2 + C_\epsilon d_i^3 + \ldots}{A_\epsilon d_{i+1} + B_\epsilon d_{i+1}^2 + C_\epsilon d_{i+1}^3 + \ldots}$$

$$\text{where } d_i = \frac{1}{Vm\ (i)}$$

If the values of V_A and V_B are fixed,

$$(22)\quad d_{i+1} = \frac{V_A}{V_B + V_A}\ d_i = N d_i$$

Substituting the result of equation (22) into equation (21),

$$(23)\quad \frac{f_i}{f_{i+1}} = N^{-1} + \frac{B_\epsilon}{A_\epsilon}(N^{-1} + 1)d_i + \left\{\frac{C_\epsilon}{A_\epsilon}(N^{-1} - N) + \left(\frac{B_\epsilon}{A_\epsilon}\right)^2 (N-1)\right\} d_i^2 + \ldots$$

If d_i is expressed in terms of f_i,

$$(24)\quad d_i = \frac{1}{A_\epsilon} f_i - \frac{B_\epsilon}{A_\epsilon^3} f_i^2 + \frac{2B_\epsilon^2 - A_\epsilon C_\epsilon}{A_\epsilon^5} f_i^3 + \ldots$$

Combining equations (23) and (24),

$$(25)\quad \frac{f_i}{f_{i+1}} = N^{-1} + \frac{B_\epsilon}{A_\epsilon^2}(N^{-1} - 1) f_i + \left(\frac{C_\epsilon}{A_\epsilon^3} - \frac{B_\epsilon^2}{A_\epsilon^4}\right)(N^{-1} - N) f_i^2 + \ldots$$

As can be seen, the variable V_m has now been eliminated. By plotting f_i/f_{i+1} vs. f_i, a straight line is obtained whose slope is $(B_\epsilon/A_\epsilon^2)(N^{-1}-1)$ and an intercept of N^{-1}. All that remains is the separation of B_ϵ and A_ϵ.

A modified version of the Burnett technique will be used in this work and offers certain advantages.[13] A simple diagram of the apparatus for such a method is shown in Figure (6). There are now three cells, all connected and all capable of measuring ϵ. The cells are placed in a temperature controlled bath, filled with gas, and closed off. Measurements of ϵ are then made in all three cells. Cell V_C is then evacuated, and the gas in V_A and V_B is allowed to expand into empty V_C. The measurements of ϵ are again made, then V_B is evacuated, and the gas from V_A and V_C is allowed to expand into V_B. This process can be repeated a number of times in rotation (next V_A is evacuated, then V_C, V_B, and so on) to obtain a series of measurements. Now the i^{th} and $i+1^{th}$ densities are related by,

$$(26) \quad d_{i+1} = \frac{2}{3} d_i$$

$$d_{i+3} = \frac{8}{27} d_i$$

If the same steps are used as in developing the equations for the simple Burnett technique it is found that:

$$(27) \quad f_i - \frac{27}{8} f_{i+3} = \frac{B_\epsilon}{A_\epsilon^2} \left(\frac{19}{27}\right) f_i^2 + \left\{ \frac{C_\epsilon}{A_\epsilon^2} \left[1 - \left(\frac{8}{27}\right)^2\right] - \frac{2B_\epsilon}{A_\epsilon^4} \left(\frac{19}{27}\right) \right\} f_i^3 + \ldots$$

The left hand side of the equation (27) can be plotted vs. f_i^2, giving a slope of $B_\epsilon / A_\epsilon^2 \left(\frac{19}{27}\right)$ and an intercept of zero.

It is virtually impossible to match the cell volumes V_A, V_B, and V_C exactly. If instead,

$$(28) \quad V_A = V \qquad V_B = V + \delta_B \qquad V_C = V + \delta_C$$

it can be shown that $d_{i+3} = R d_i$ where R is given by:

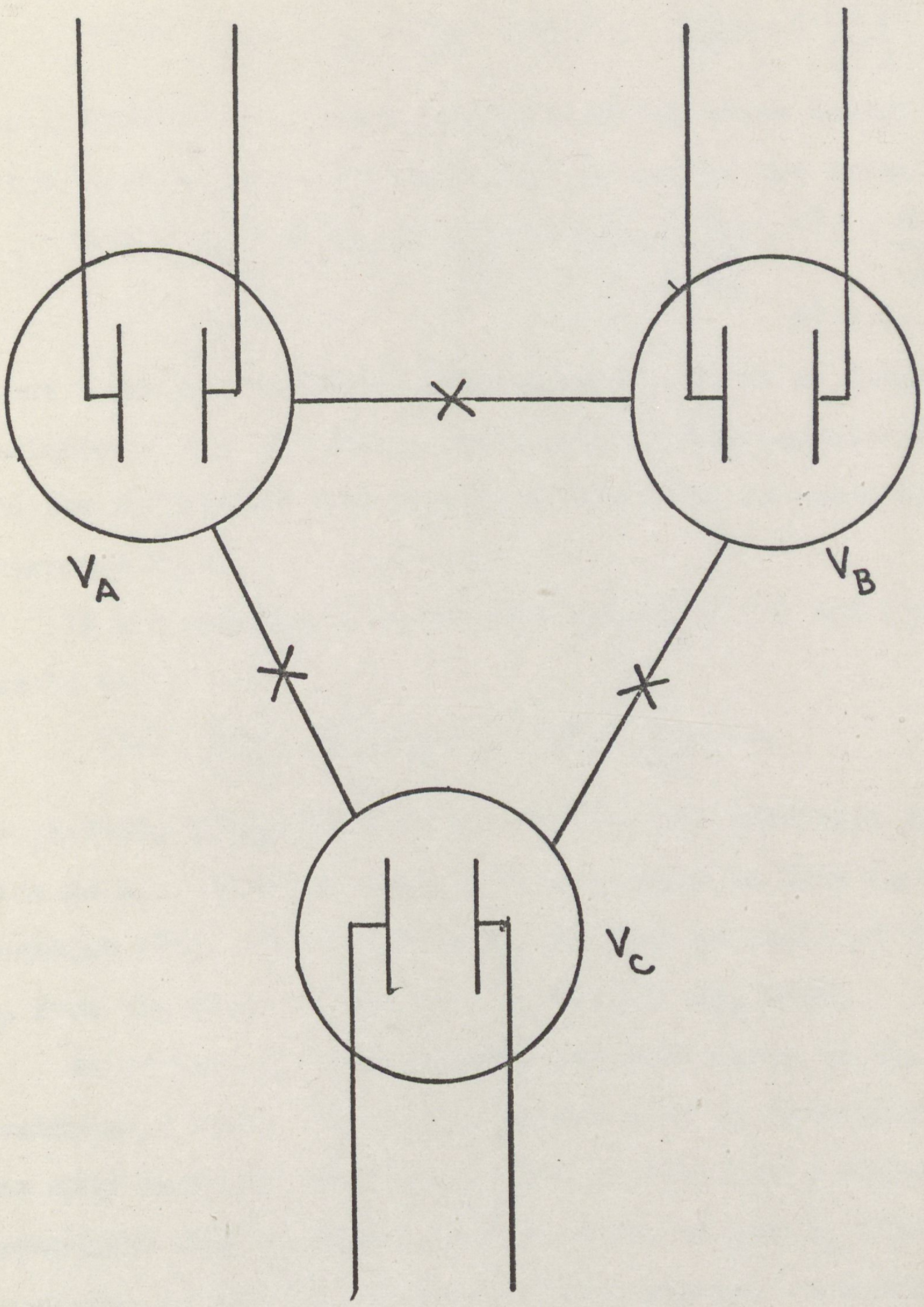


Figure (6). Cell system for the modified Burnett expansion technique

$$(29)\quad R = \frac{8}{27} - \frac{2}{81}\left\{\left(\frac{\delta_B}{V}\right)^2 \left(\frac{\delta_C}{V}\right)^2 = \frac{\delta_B \delta_C}{V^2}\right\} + 0\left\{\frac{\delta}{V}\right\}^3$$

The differences in volume can be measured close enough to get R to a few ppm. Equation (27) is now of the form:

$$(30)\quad f_i - R^{-1} f_{i+3} = \frac{B_\epsilon}{A_\epsilon^2}(1 \pm R) f_i^2 + \left[\frac{C_\epsilon}{A_\epsilon^3}(1-R^2) - \frac{2B_\epsilon}{A_\epsilon^4}(1-R)\right] f_i^3 + \ldots$$

Since R can be determined independently, it is no longer variable in the expansion experiment. Using equation (30) and the instrumentation presented later, it is possible to determine B_ϵ to 2 to 5 percent.

If one eliminates V_m between equations (2) and (3), the result is:

$$(31)\quad \frac{\epsilon - 1}{\epsilon + 2}\,\frac{RT}{P} = A_\epsilon + (B_\epsilon - A_\epsilon B_P)\frac{P}{RT} + \ldots$$

By plotting $(\epsilon-1/\epsilon+2)$(RT/P) vs. (P/RT), the intercept of the line is A_ϵ. This can then in turn be used to find B_ϵ in equation (30). The quantity B_ϵ can then be utilized to find B_P from the slope of the plot of $f_i RT/P$ vs. P/RT.

As of yet, no consideration has been given to the measurement of ϵ. The actual bridge will be described in the next section. For now, a view of the theory behind the instrument will be presented.[13] In order to get B_ϵ with any accuracy, f_i must be measured to five places. A modified Wheatstone bridge is employed in this experiment, and is pictured in Figure (7). L_1 and L_2 are inductive arms across which voltages E_1 and E_2 are developed. C_1 and C_2 are capacitances, and G is a current or voltmeter. At balance,

[illegible]

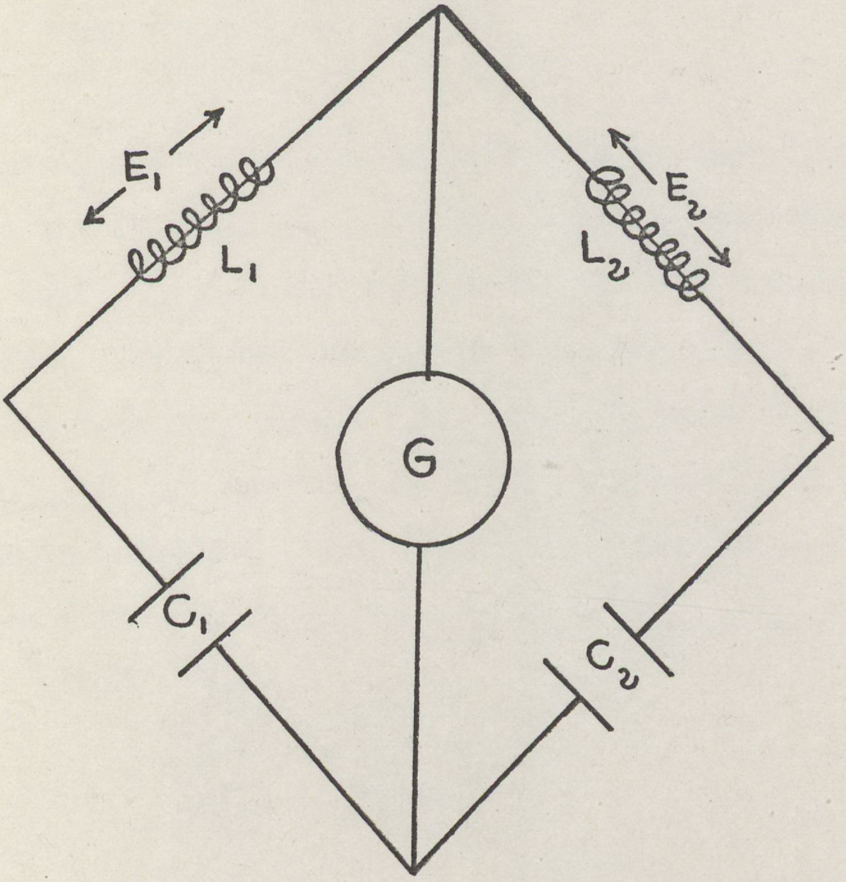


Figure (7). Basic Wheatstone bridge.

the meter reads null and there is no current flow (or voltage difference) across the meter. In that case,

$$(32)\quad C_1 = \frac{E_1}{E_2} C_2$$

C_1 and C_2 may be single capacitances or more than one capacitor in parallel. In this work, C_2 was simply a reference cell (C_{ref}). The voltage E_1 is held constant and E_2 is varied. First, the circuit is balanced with C_1 at vacuum. In this case, C_1 equals C^v_{meas} and the ratio E_2/E_1 is equal to C^v_{meas}/C_{ref}. Then C_1 is filled with gas, and the circuit is again balanced. Now, C_1 is the capacitance of the cell filled with gas, C^g_{meas}, and E_2/E_1 is C^g_{meas}/C_{ref}. Thus,

$$(33)\quad \frac{\dfrac{C^g_{meas}}{C_{ref}}}{\dfrac{C^v_{meas}}{C_{ref}}} = \frac{C^g_{meas}}{C^v_{meas}} = \epsilon$$

Since ϵ has been found here, f_i must be measured to five places, so E_2/E_1 must be measured to seven. This can be done by using a decade transformer as the voltage supply. The transformer itself is calibrated to 1 part in 10^6 which is sufficient.

4. EXPERIMENTAL APPARATUS

Electrical system: First to be described is the bridge which was just described in theory. A rough diagram of the experimental bridge system is pictured in Figure (8). The transformer used to supply the voltages was a Model DT72A decade transformer from Electro Scientific Instruments. This transformer utilized two different voltage taps. One was set at -0.1 of the input voltage, while the other was variable from -0.1 to 1.1 of the input voltage, the value showing up on the dials out to seven places. In this case the standard -0.1 was applied to the reference cell capacitor, and the variable output was applied to the measuring cell. The capacitances were related by:

$$(34)\quad \frac{C_{ref}}{C_{meas}} = \frac{S\ (\text{input})}{0.1\ (\text{input})} \qquad \text{where } S = \text{dial reading}$$

$$C_{ref} = 10\ (S)\ C_{meas}$$

The oscillator used to supply the initial signal to the transformer was part of the detector used to determine when the system was at balance. This detector was a Model 120 lock in amplifier by Princeton Applied Research. The signal from the oscillator (1000Hz) was then passed through an amplifier designed by Prof. Galantowicz of the Union College E.E. department and built by Kurt Hillig. The amplifier can be found described in greater detail in Mr. Hillig's thesis.

Capacitor cells: A cut away view of one of the cells

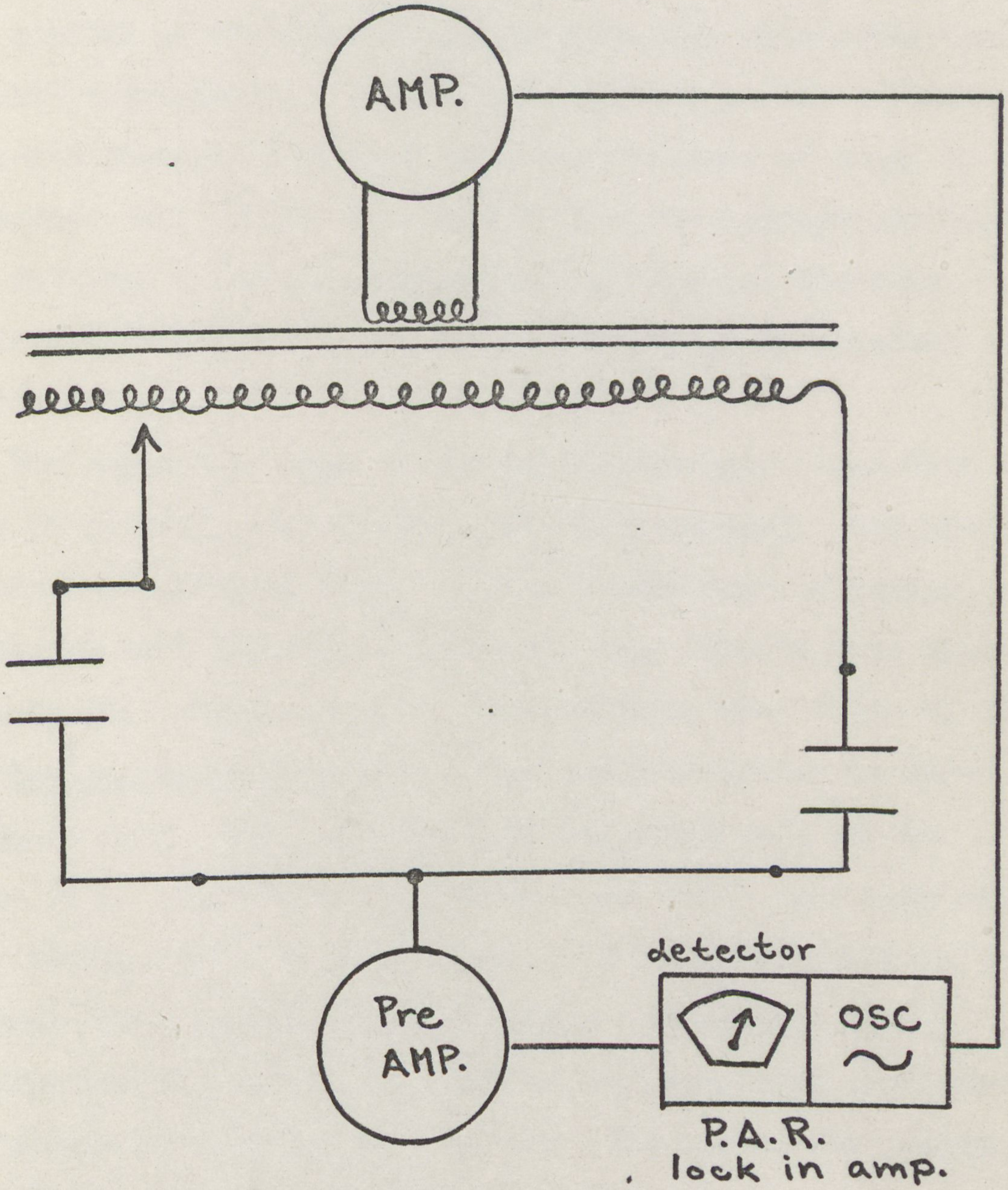


Figure (8). Diagram of bridge used for experimental measurements.

with the capacitor in place is shown in Figure (9). The cell body itself was constructed of nickel for two reasons: its high thermal conductivity and its corrosion resistance to HF. All fittings and screws were of monel or inconel which have similar properties but are more readily obtainable (and cheaper) than nickel. Voltage was supplied to the capacitors by single passage Ceramaseal Mini Feedthroughs of monel by Ceramaseal Inc. These were sealed into the appropriate push type fittings by vacuum welding done at General Electric. The feedthroughs were connected to the bridge by shielded coaxial cables.

The capacitors were of the multiplate type (each with about 20 plates), each plate alternately charged. The plates, spacers, and stacking rods were all constructed of nickel. The plates were insulated by ceramic type 502-600 from Aremco Products Inc. Complete plans are available from Prof. H. Sutter.

<u>The gas handling system</u>: The complete system is shown in Figure (10). The fittings into the cells were of the Aminco type. The connections between the cells were made with monel tubing (3/32" I.D., ¼" O.D.), utilizing Sno-Trik valves of monel with crushed aluminum packing. In regions which HF would not wet, the valves were either stainless steel Sno-Trik valves or brass Whitney valves. The piston for pressurizing samples was by High Pressure Equipment.

Once completed, the whole system was immersed in a bath G.E. Silicone Fluid (SF-1093 (500)) which had been donated by

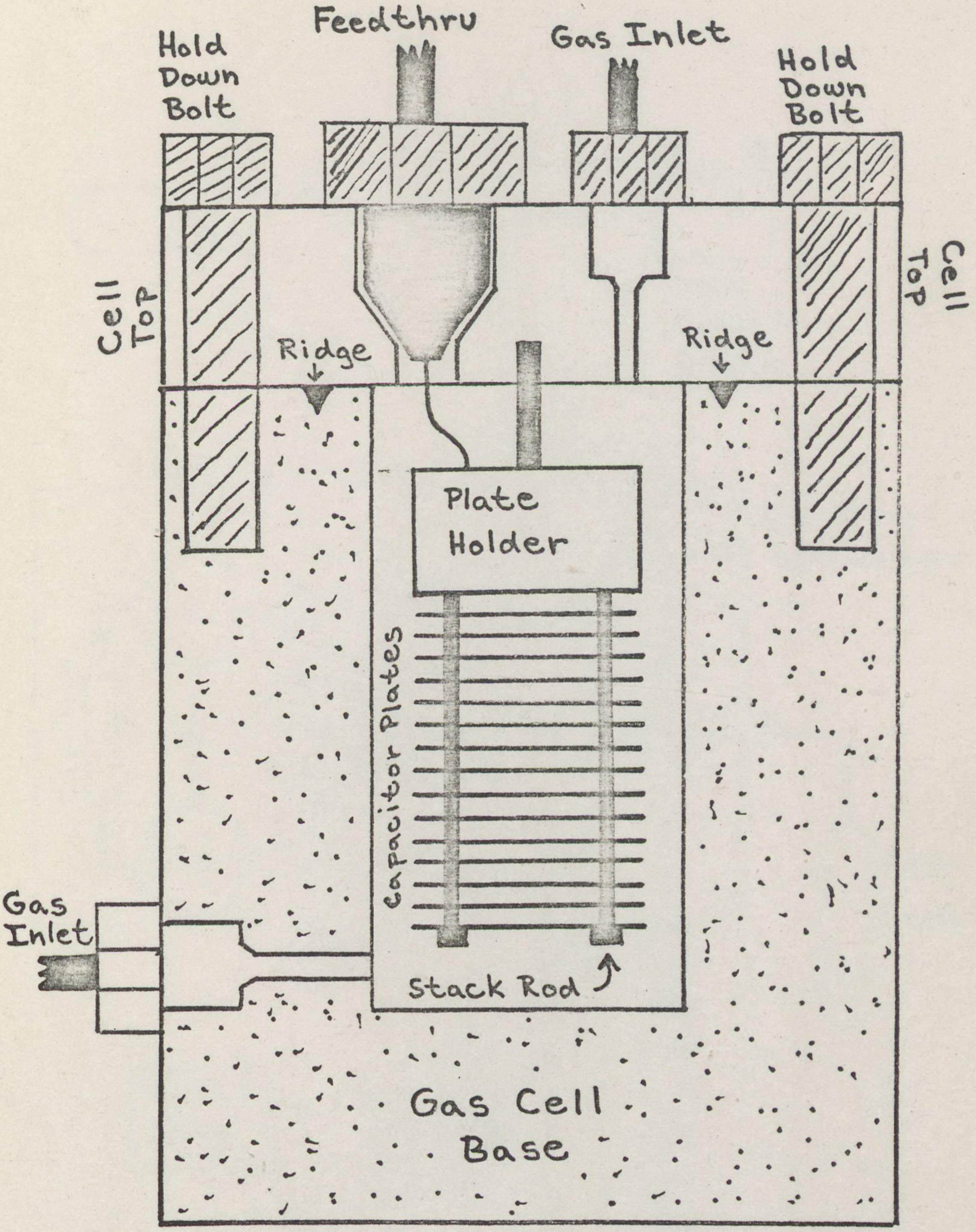


Figure (9). Cut away view of capacitance cell with the capacitor in position. Actual dimensions are available from Prof. H. Sutter, Union College, Schenectady, N.Y.

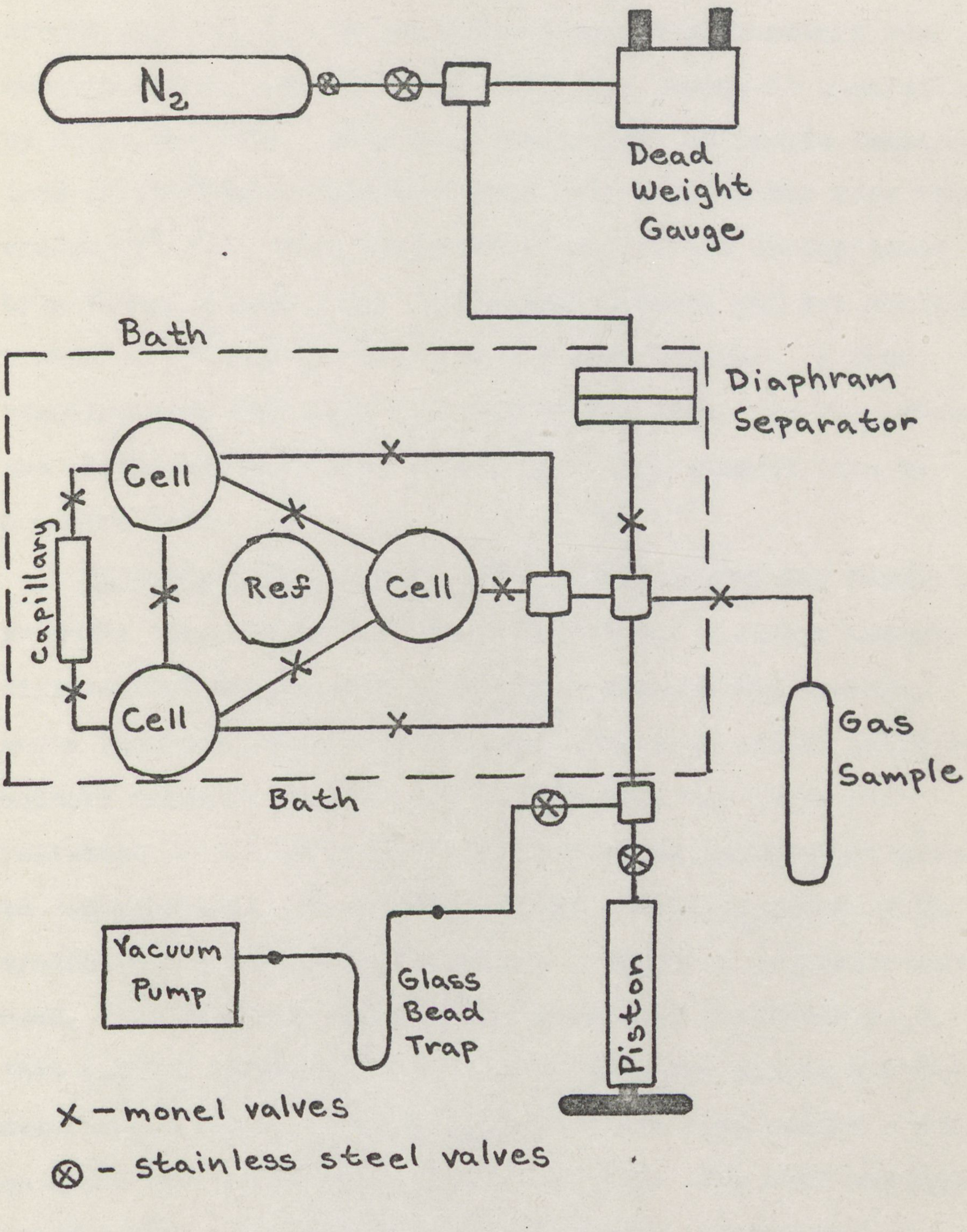


Figure (10). Schematic of the gas handling system.

General Electric. To the bottom of this steel bath were attached ten 500 watt heating coils for a primary heat source. Around this inner bath, an outer insulating framework was constructed of plywood and 2" thick J-M Thermo-12 insulation by Johns-Manville. With this insulation, an inside temperature of 300°C was attainable while only raising the room temperature 2°-3°C. Fine temperature control was accomplished by a Fisher Proportional Temperature Control and two heating probes of 250 and 500 watts by the same company. A free standing hood was built over the entire bath, two feet above the surface of the bath, with a four inch exhaust pipe to a nearby hood.

Pressure measurements: The overall system for measuring pressure consists of a diaphram separator, a linear variable differential transformer (LVDT) by Schaevitz Engineering, and a Budenburg dead weight gauge. The dead weight gauge can measure pressure to five parts in 10,000, but it is not resistant to corrosion by HF and cannot be operated at elevated temperatures. To isolate the hot corrosive gases in the system from the dead weight gauge, a diaphram separator was used. The diaphram separator (Figure(11)) consisted of a thin (.002") nickel plate placed between the system and the dead weight gauge. To this separator was spot welded a rod on which was placed the core of the LVDT. The LVDT was made up of a core within transformer windings. As the core moves in the windings, a signal is produced which can be

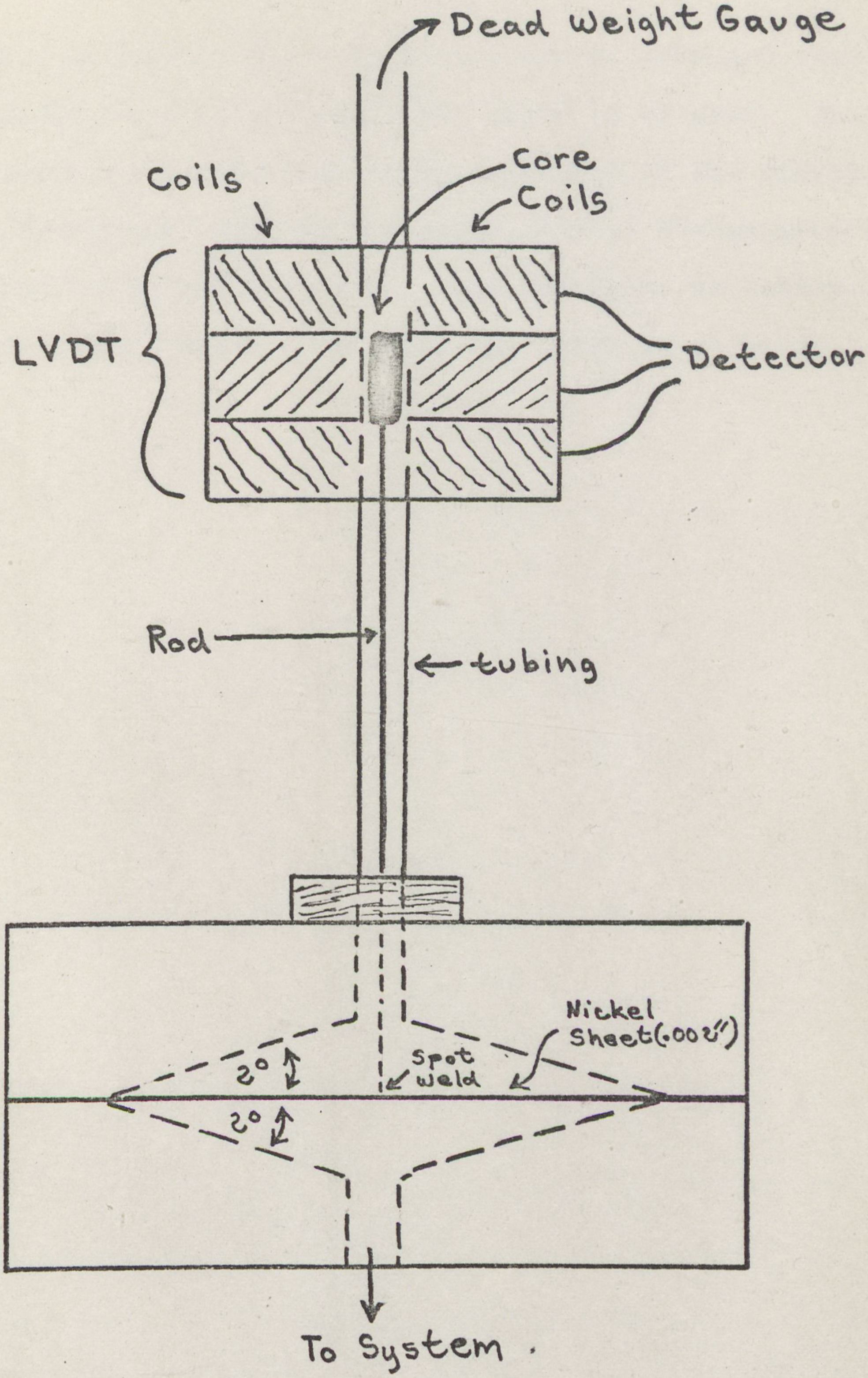


Figure (11). Diaphram separator for pressure measurements.

detected by a meter. The electronics can be arranged such that when the core is centered, the meter is at zero. This core is moved back and forth by the movement of the nickel sheet. Nitrogen is used on the gauge side of the separator to balance the system pressure. When the plate is centered (pressure on both sides is equal), the meter is at zero.

5. EPERIMENTAL PROCEDURE

Nearly a full term of this work was spent building the system shown in Figure (10). This included the construction of the bath and hood assembly, assembling and cleaning capacitors, arranging for bath stirring, and so on. While this work was necessary, it is not of any importance to note the specifics here.

The first problem of any experimental significance was whether or not the system that had been built would stand up to a material as corrosive as HF. Thus a test system was made using the same components as the measuring system. The test system is pictured in Figure (12). The procedure for using this system was the following:

(a) The piece to be tested was placed in the test cylinder.
(b) Valves 1 and 2 were opened and HF was allowed to equilibrate in the system.
(c) Valve 1 was closed and time for reaction was allowed.
(d) Valve 3 was opened and HF was frozen off into the monel trap using liquid N_2.
(e) Valve 3 was closed, valve 4 was opened, and any remaining HF was pumped off through a glass trap packed with glass beads and in a bath of liquid N_2.
(f) The test piece was removed and checked for attack by weighing and visual inspection.

This system was used in a hood, and rubber gloves and goggles were worn at all times. Further safety information was obtained from a bulletin by the Harshaw Chemical Company.[14] The system was tested for leaks using low pressure SO_2 and high pressure (130 atm) helium. The glass trap packed with glass beads wa was suggested by Prof. R. Schaefer of the Union

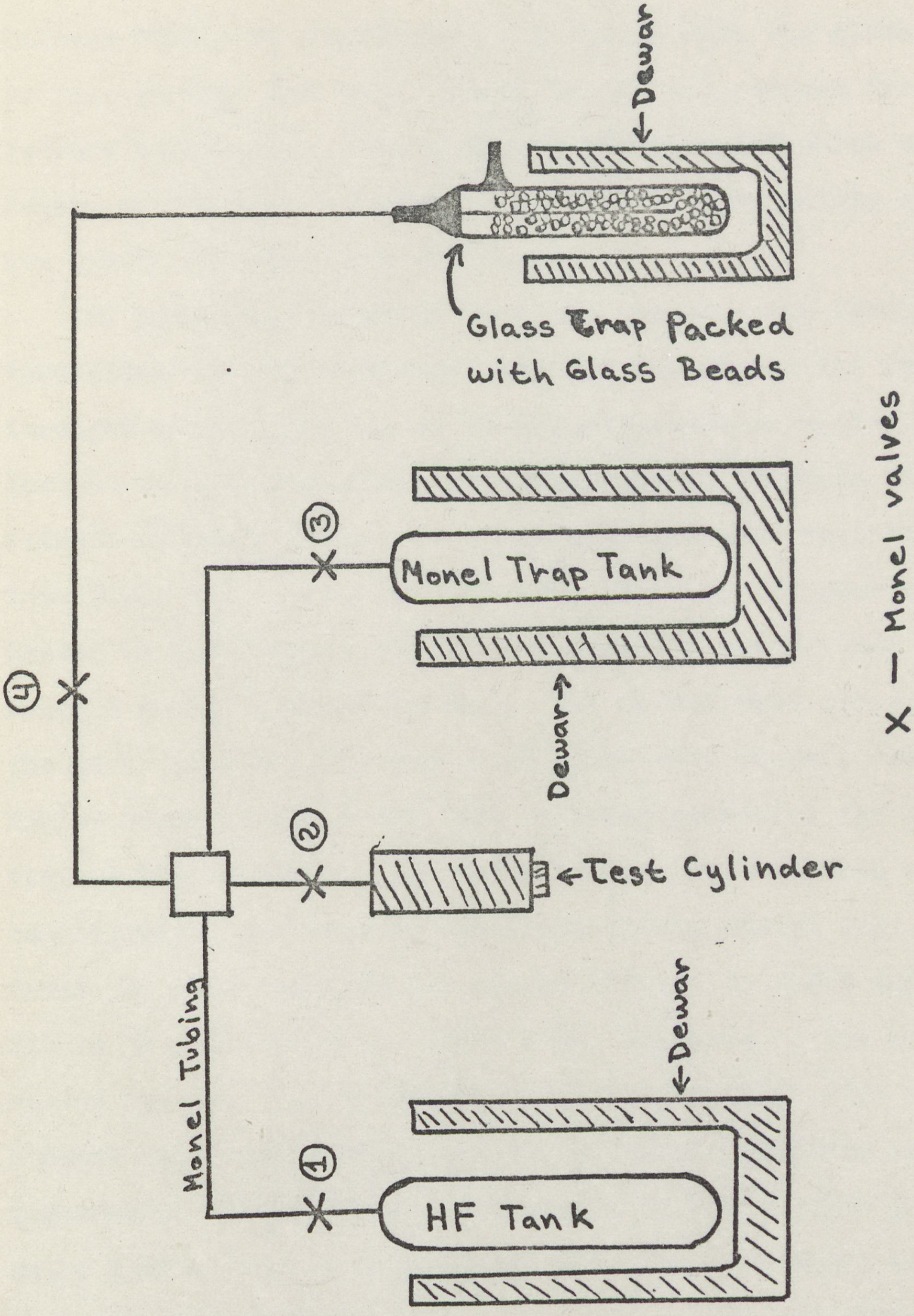


Figure (12). System for testing pieces under HF.

College Chemistry department. HF reacts with the glass beads to form several siliates. First the HF was removed from its lecture bottle into a monel tank containing NaF which would remove any water. The monel tank allowed for heating which was usedto attain higher pressures.

Of particular interest were the tests on the ceramic insulators for the capacitors and the ceramic in the feedthroughs since there was no HF corrosion data on either. Instead of having a number of paragraphs to describe the results of these tests, the conditions and data were reduced into Table (1). For high pressure, the test cylinder was heated to 300°C using one heating tape and the HF tank brought to 150°C using another. The HF was then allowed into the test cylinder, and then both tanks were closed. The higher temperature of the test cylinder prevented the formation of any HF liquid. As noted in Run (4), at these higher temperatures, the unequal expansion of the nickel test cylinder vs. monel pushing nut caused the nut to sieze and it had to be machined out. After this, all nuts in the main system and the test system that would come under high temperature were coated with Fel-Pro anti-sieze compound, before tightening. Overall, the test system failed to show any major leaks, thus it was assumed that the components in the measuring system would hold. The test pieces did show some weight loss indicating a reaction, but this was negligible and the parts would be acceptable in the main system.

Run	Test Piece	Conditions	Time	Results	Notes
1	ceramic washer(.645g)	~ 23°C	40 hrs.	No visible attack, no weight change	
2	ceramic washer(.645g) galvanized steel(2.875g)	~ 23°C	43 hrs.	Steel showed some flaking, weight 2.890g Washer showed no attack, weight .642g	
3	feedthrough (40.409g)	~ 23°C	42 hrs.	No visual attack, weight 40.386g	
4	ceramic washer(.646g)	test cylinder ~ 300°C	43 hrs.	*	* Plug could not be removed from test cylinder, had to be machined, washer coated with oil, but still appeared intact.
5	feedthrough (41.094g) ceramic (.511g)	test cylinder ~300°C	37 hrs.	Neither showed any visual signs of attack. feedthrough 41.053g ceramic .511g	
6	feedthrough (41.053g) ceramic (.511g)	test cylinder ~270°C	168 hrs.	Neither showed any visual attack. feedthrough 41.039g ceramic .510g	

Table (1). Data from HF testing

The next difficulty occured when it was found that the DF for isotope studies was not commercially available. A search through the literature showed that the simplest method for producing HF was a reaction often pictured in elementary chemistry texts:

$$(35)\quad CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\ HF$$

This is easily adaptable to the production of DF since all that must be done is replace H_2SO_4 by D_2SO_4 which is available commercially. The system that had been used for testing with HF was used for the reaction. The monel tanks and the remainder of the system were cleaned and dried. A check was made of the vacuum in the system and it was found to be very poor. The packing was leaking on two of the valves, and it was necessary to apply excessive force to get them to seal. These valves also proved troublesome when tubing was fitted into the measuring system. If the tubing was not at exactly the proper angle going into the swage type fitting, the softness of the monel tubing allowed it to slip back through the collar and form a poor seal. A valve with Aminco type fittings would definitely be an asset in further work.

With the system repaired, 500gm of D_2SO_4 were frozen down (to prevent reaction) in one of the monel tanks in a bath of liquid N_2, and then 200gm of CaF_2 were added on top of the D_2SO_4. The tank was closed up, allowed to come to room temperature, shaken, and placed back in the system. Table (2) is a breakdown of the attempts to remove DF from the reaction

Run	Conditions	Time	DF obtained	Comments
1	Reaction tank 25°C Trap tank -196°C	1 hr.	None (±4g)	Possible trouble with solution of CaF_2. Placed $\frac{1}{2}$" sections of monel tubing in reaction tank for better mixing.
2	Reaction tank 65°C Trap tank -196°C	1 hr.	None (±4g)	Found patents that indicate 230°C necessary for reaction
3	Reaction tank 230°C Trap tank 0°C	1 hr.	None (±4g)	Trap tank valve plugged; cleaned and replaced
4	Reaction tank 230°C Trap tank 0°C	½ hr.	None (±4g)	Reaction tank valve plugged so cleaned and replaced. Spot welded nickel disk to bottom of tank plug to prevent any solid from entering.
5	Reaction tank 230°C Trap tank 0°C	$\frac{3}{4}$ hr.	.07 lb (30g)	
6	Reaction tank 230°C Trap tank 0°C	$\frac{3}{4}$ hr.	No increase	Found nickel disk destroyed by D_2SO_4. The system must be revised.
7	Reaction tank 25°C Trap tank -196°C Connect directly by 3/16" I.D. polyethylene tubing.	1 hr.	Increased to total of .11 lb. (49g)	Polyethylene will resist HF (or DF) attack up to 100°C. Reaction temperature can be increased.
8	Reaction tank 40°C Trap tank -196°C Still connected by polyethylene.	1 hr.	Increased to total of .18 lb (81g)	
9	Reaction tank 75°C Trap tank -196°C Still connected by polyethylene.	1 hr.	Increased to total of 112g	Only should get 100g of DF. Probably some solid passed through large bore polyethylene tubing.

Table (2). Data on the production of DF

tank. After Run (2), the lack of production of DF led to another literature search which turned up patents by Haywood and his co-workers[15] and Asio and his co-workers.[16] These patents call for an initial reaction temperature of 230°C. However, it was also found that solid from the reaction was clogging both the monel tubing and the valves. Since the reaction had been heated enough to go to completion, in Run (7) the tanks were connected directly by a piece of polyethylene tubing of 3/16" I.D. This netted a substantial amount of DF, in fact, apparently too much. The amounts of D_2SO_4 and CaF_2 used should have produced only 100gm of DF. The polyethylene tubing was large enough to allow some solids to pass through. These were easily removed by first cleaning the reaction tank, transferring the DF to it, and then cleaning the trap tank. However, since the polyethylene tubing was not equipped with valves, it was removed or replaced by freezing down both tanks in liquid N_2. Such a process allowed air and water vapor into the tanks which must be removed before any measurements.

The method for purifying DF was obtained from work done by Osgood, Sackett, and Javan.[17] There were five basic steps:

(a) Pump on DF while frozen at 77°K (liq. N_2).
(b) Allow DF to melt, freeze again at 77°K.
These two steps remove all H_2, N_2, and O_2.
(c) Distill HF from trap at 240°K to a trap at 77°K.
(d) Repeat step(c). These steps remove H_2O
(e) Check impurity content by specific conductivity measurement.

While the equipment for step (e) was not available, the first four steps were carried out. Attaching the DF tank and the empty tank back into the test system, step (a) was attempted, but it was found that at 77°K, large quantities of some gas were being given off. This could not be DF, so the tank was brought up to 0°C (where DF would still be frozen) and opened to the air. A large volume of gas was exhausted, apparently air which had been trapped in the DF. The tank was frozen back down, and steps (a) and (b) were completed without further complications.

Steps (c) and (d) proved more difficult. Table (3) shows a breakdown of the conditions used in two attempts at step (c). In place of dry ice for thr 240°K bath, slushes were made from mixtures of chlorobenzene and benzene were made by adding liquid N_2 to solutions of the proper concentrations. The correct percentages of chlorobenzene and benzene were found in The Physico-Chemical Constants of Binary Systems in Concentrated Solutions by Jean Timmermans.[18] As can be seen in Table (2), both attempts at step (c) failed to produce measurable amounts of DF. The problem again may be the small bore tubing. At the low temperatures used for this distillation, the vapor pressure of DF may be so small that the small tubing passage effectively inhibits the flow of DF. A system with a larger passageway, but which does not have to be opened to the atmosphere (like the polyethylene tubing used earlier) was in order. However, it was at this point that time ran out for any further experimentation.

Run	Bath (% by weight)	Temp.	Time	DF obtained	Comments
1	40% chlorobenzene 60% benzene	-32°C	1 hr.	None ($\pm 4_g$)	At such a low temperature, the vapor pressure of DF so small that may see effects of small bore monel tubing. Also, isotope effects may cause DF to have a higher melting point. Try increasing temperature.
2	30% chlorobenzene 70% benzene	-22°C	1 hr.	None ($\pm 4_g$)	This temperature should be great enough to overcome any isotope effects. The small bore tubing is probably the limiting factor. A system must be designed with a larger diameter passage

Table (3). Data from attempts at drying DF.

6. CONCLUSION

In no other branch of chemistry do theory and practicality split so far apart as they do for the physical chemist. But if the knowledge is desired, it is up to him to bring the two together and resolve the problem. The work presented here is a perfect example. Perhaps no ingenious conclusions were reached or fascinating discoveries made, but a system has been developed and fairly well perfected for the measurement of intermolecular interactions under harsh conditions. Also, although not purified, much of the groundwork has been done for producing sample DF, along with gaining some insight into the production of corrosive gases in general. In sum, this was an excellent introduction to research in physical chemistry.

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