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**Ultrasonic Relaxation and Attenuation
in Freons, in Relation to Their Use in
Supersonic Wind Tunnels**

By

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Ultrasonic Relaxation and Attenuation in Freons, in
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SUMMARY

From the point of view of their use in supersonic wind tunnels in which it is desired to obtain a high Mach number without great expenditure of power, the substitution of the air by vapours having a low velocity of sound is of interest. The freons (halogen-substituted methanes) suggest themselves for this. It is shown that these vapours have ultrasonic relaxation times in the neighbourhood of 10^{-7} sec coupled with high-absorption coefficients in the ultrasonic range. Though this may limit their usefulness when comparison with the forces on bodies in the atmosphere near sea-level is desired, the relaxation effects may be useful to simulate conditions at high altitudes.

It is shown that admixture of air, up to 10 per cent does not change the relaxation time nor the absorption coefficient in freon.

To obtain a ratio of specific heats to correspond to that of air at sea-level, a rare gas may be added to the freon, but the velocity of sound in the mixture is thereby raised and some of the advantage in Mach number lost.

1. Introduction

The substitution of the air in a supersonic wind-tunnel by a vapour which has a low velocity of sound, in order therein to attain a given Mach number at a smaller expenditure of power, has been considered on several occasions in the past fifteen years.^{1,2,3,4,5}

The freons (or arctons as they are called in Britain), suggest themselves for this purpose since they are inert non-poisonous and fairly readily obtainable on account of their use in the refrigeration industry. We were asked to make measurements of velocity of sound in some of these (notably freon 12, CCl_2F_2) and to observe whether these values remained constant as the conditions of excitation changed, i.e., if either the frequency of the sound or the pressure or temperature was varied. Such a dispersion of the velocity would indicate a relaxation in the attainment of thermal equilibrium, as between the different possible internal energies (translation, vibration, rotation) of the molecules. (The theory of relaxation, in relation to sound waves is given in an Appendix).

We have in addition measured the attenuation of the sound waves in the vapours.

The experimental method (which is described in more detail in §.2) involves the measurement of the wave-length and amplitude absorption coefficient for ultrasonic compressional waves of frequency (f) 1 Mc/sec approx. in a gas at fixed temperature (T), but variable pressure (p); since it is well known (since early work on carbon dioxide⁶) that relaxation times are proportional to pressures in most gases. The velocities and absorptions can then be plotted against the parameter f/p to give a single curve. A rise in velocity from its low-frequency (V_0) to its high-frequency (V_∞) at a certain value of this parameter, together with high attenuation at the same location is a certain indication of thermal relaxation in the gas, which may limit the usefulness of this vapour as a substitute for air as a medium in which aerodynamic models are tested.

For example, if a relaxation time 1.5×10^{-7} sec in this freon is confirmed it means that a shock taking place at a local $M = 2$ ($v = 300$ m/s) at a distance of 0.05 mm from the surface of the model would be unrelaxed, as to its high-frequency components, in this distance, whereas a shock wave in air at N.T.P. would be unaffected in the corresponding trajectory (cf. Kantrowitz²).

Subsidiary problems in relation to these substitute vapours concern the nearness of their critical points to the operating conditions. While the velocity of sound is at its lowest at the critical point the vapour is then, of course, far from a perfect gas and this in itself may cause it to behave differently in the tunnel from atmospheric air.

With regard to the variation of flow field with γ , von Doenhoff, Braslow and Schwartzberg⁷ have shown that, at a particular speed, variation of γ can be compensated by a change in the relative thickness of the model although a change in γ from 1.4 in air to 1.13 in freon involves an almost negligibly small change in the thickness/chord ratio. The speed range over which neat freon is an adequate substitute for air is, however, limited and is in fact from low speeds up to about 1.2 times the speed of sound.

Chapman⁸ who has recently examined the presumed behaviour of models in substitute vapour tunnels in relation to full-scale flight at high altitudes points out that the important parameter in this connexion is not the relaxation time itself but the product of it and the thermal capacity of the molecules in vibration. He shows that thermal capacity lag should be important in boundary layers at combined low Reynolds number and high Mach number, a condition which would be realised in very high altitude flight. Relaxation effects may be considerable under these conditions and in certain conditions it may be possible to represent this in a tunnel using substitute gases whereas they could not be represented using air. Chapman gives figures to support this conclusion.

2. Apparatus and Mode of Operation

The standard apparatus for ultrasonic work in gases remains the Pierce⁹ variable-path interferometer, in which the load on a quartz or other transducer due to the stationary wave pattern in a gas column is made to influence the anode current in the electronic valve coupled to the transducer.

The reaction on the driving circuit causes a proportionate change in grid voltage as the path is varied. This gain results in a cyclic change in mean anode current every half wave-length (λ).

There/

There is a simple way of deriving the absorption coefficient α from a series of resonant and antiresonant peaks (δI) in the anode current as the reflector is moved.

We determine α from a straight line plot of $\log \delta I$ against λ but the method should not be adopted without consideration of the conditions of operation of the interferometer.

A number of interferometers were constructed for this research. The ultimate form is shown in Fig. 1. The gland of the moving shaft carrying the reflector is sealed by rubber packing and the screw moves the reflector by pressing up against it a small steel ball, thus ensuring the linear motion of the reflector.

The accuracy of reading of the setting of the reflector is about 0.008 mm which corresponds to 0.2 m/sec in velocity. The quartz crystal used is 2 inches diameter, about 1.016 Mc/s in its fundamental frequency. The crystal is supported by three pins at nodal points. Temperature is measured by an iron-constantan thermocouple calibrated against ordinary mercury and alcohol thermometers. The reflector is made of photographic plate glass, and the variation of anode current is measured by the sensitive galvanometer using a counter-balance circuit. The sensitivity of the galvanometer is about 10^{-8} amp/div.

The circuit diagram is shown in Fig. 2, the power supplies being accumulators. At each velocity measurement, frequency is measured by a heterodyne frequency meter. The frequency meter and oscillator are coupled by a resistance-buffer amplifier. To get the maximum sensitivity, the coupling of the main tank coil and that of the grid turn is adjusted. When the coupling is reduced gradually, the oscillation stops at some point. The maximum sensitivity is obtained just before that point.

In Fig. 3 the gas-handling system is shown. Ordinary vacuum grease is used as the lubricant of the taps but must be frequently renewed. The gas is caught by the solid carbon dioxide trap, traces of dissolved gases being removed by evacuation, then introduced into the reservoir or the measuring vessel. Usually all systems are kept at high vacuum, and it is desirable to avoid keeping the gas standing for a long time. The pressure is read by an open type mercury manometer in conjunction with a barometer. The automatic temperature control system is sufficient to maintain the temperature within the range of 1°C .

3. Calculation of Results

In order to standardise the apparatus, measurements were first made on dry air.

The specific heat at constant volume is calculated by the Planck-Einstein equation at various temperatures using spectroscopic data:-

$$C_{V0} = \sum R(h\nu/kT)^2 \cdot e^{h\nu/kT} / (e^{h\nu/kT} - 1)^2 \quad \dots(1)$$

where ν = (optical) frequency, c/s, h Planck's constant, k Boltzman's constant, R gas constant, and T absolute temperature¹⁰. For freon 12, the wave-numbers corresponding to ν values were taken from the Raman spectroscopic determinations of Classen¹¹ as 261.5, 322, 435, 446, 457.5, 667.2, 922, 1099, 1162.

Actual flow-calorimetric measurements of the specific heat of freon 12 have been made by Buffington and Gilkey¹².

These/

These values and those derived from equation (1) were then reduced for the second virial coefficient B in

$$pv = RT + B(T).p \quad \dots(2)$$

by the terms $2p \frac{dB}{dT}$. Also

$$C_p - C_v = R + 2p \frac{dB}{dT} \quad \dots(3)$$

$$\text{So } \gamma(\text{actual}) = \gamma(\text{ideal}) \left(1 + 2 \frac{p}{C_v} \frac{dB}{dT} \right) \quad \dots(4)$$

$$\begin{aligned} \text{and } V(\text{actual}) &= V(\text{ideal}) \left(1 + 2 \frac{pB}{RT} \right) \\ &= V(\text{ideal}) \left(1 + \frac{pB}{RT} \right) + p/C_v \cdot \frac{dB}{dT}. \end{aligned} \quad \dots(5)$$

Here γ is the ratio of specific heats and V the velocity of sound.

TABLE I

Specific Heat of Freon 12

T.	From Spectroscopic Data		From Calorimetric Data	
	$C_{v0}(\text{ideal})$	$C_{v0}(\text{actual})$	$C_{v0}(\text{ideal})$	$C_{v0}(\text{actual})$
293.8°K	15.22 cal/mole	15.02	15.62	15.42
290.6	15.12	14.92	15.52	15.32
265.5	14.35	14.15	14.80	14.60
253.3	13.97	13.77	14.45	14.25

TABLE II/

TABLE II

Second Virial Coefficient of Freon 12

$$pv = RT + B(T)p.$$

T	B(T)
238.71°K	-637 cc/mole
244.27°	-604
249.82°	-586
255.38°	-560
283.16°	-454
310.94°	-347

The calculated values of S/RT are as follows:-

T	S/RT
298.2°K	0.0096 ATM ⁻¹
293.8°	0.0106
290.6°	0.0112
265.5°	0.0171
253.3°	0.0206

Approximately, S/RT changes linearly with temperature.

Relaxation Time

The relaxation time of energy transfer between translational and vibrational states is obtained from above data, using the equation (see Appendix).

$$\tau = \frac{1}{2\pi f_m} \cdot \frac{V_\infty^2}{4V_0^2 - 3V_\infty^2} \left(\frac{V^2 - V_0^2}{V_\infty^2 - V_0^2} \right)^{\frac{1}{2}} \quad \dots(6)$$

Here f_m is the relaxation frequency read-off from the centre of the 'upcast' of the velocity against f/p curve and V_0 and V_∞ are limiting velocity at low and high frequencies respectively given by:-

$$V_0^2 = \frac{RT}{M} \left(1 + \frac{R}{C_{vo}} \right)$$

$$V_\infty^2 = \frac{4RT}{3M} \quad \dots(7)$$

M being the molecular weight.

4. Results in Freon 12

The measured and ideal values of velocity over the attainable range of f/p are shown (at three temperatures) in Tables III, IV and V, and on the graphs Figs. 4, 5, 6 while Table VI gives the values of relaxation times at the same temperatures, deduced from the graphs.

TABLE III/

TABLE III

Ultrasonic Velocity of Freon 12 at 290.6°K

log	MC/ATM	V(actual)	V(ideal)
0.01	log MC/ATM	151.0 m/sec	152.6 m/sec
0.15		152.5	153.7
0.28		154.5	155.4
0.55		158.4	158.9
0.01		150.9	152.5
0.13		152.6	153.8
0.67		160.3	160.6
0.02		150.6	152.3
0.30		155.2	156.1

TABLE IV

Ultrasonic Velocity of Freon 12 at 265.5°K

log f/p	V(actual)	V(ideal)
0.16	143.9	145.6
0.35	145.9	147.0
0.13	143.9	145.8
0.24	144.6	146.0
0.82	142.2	152.5
0.02	142.9	145.3
0.19	144.2	145.8
0.03	142.8	145.1
0.19	144.2	145.7
0.02	142.8	145.2
0.18	144.3	145.9

TABLE V/

TABLE V

Ultrasonic Velocity of Freon 12 at 253.3°K

log f/p	V(actual)	V(ideal)
0.01	138.8	141.6
0.10	139.6	141.8
0.24	141.3	143.0
0.38	142.2	143.5
0.70	146.3	146.9
0.16	138.6	140.7
0.49	139.5	143.6
0.12	138.3	140.8
0.08	139.7	142.1
0.22	140.8	142.6
0.35	142.1	143.4
0.04	138.4	141.2
0.02	138.4	141.2
0.36	142.5	143.8
0.64	145.9	146.6
0.05	138.5	141.1
0.35	141.3	142.6
0.17	139.9	141.9
0.02	138.4	141.1
0.13	139.1	141.3
0.41	142.5	143.6
0.02	137.5	140.2
0.14	138.2	140.3
0.45	143.7	144.7
0.45	143.0	144.0

TABLE VI

Relaxation Time of Freon 12

T	τ
290.6°K	1.70×10^{-7}
265.5	1.00
253.3	0.84

TABLE VII/

TABLE VII

Absorption Coefficient of Freon 12 at 290°K

log f/p	α
0.01	0.19
0.28	0.31
0.13	0.21
0.02	0.23
0.30	0.38

Theoretical Values
(if $\tau = 1.70 \times 10^{-7}$)

log f/p	α
0.00	0.20
0.20	0.25
0.40	0.26
0.60	0.22
0.80	0.16

TABLE VIII

Absorption Coefficient of Freon 12 at 265.5°K

log f/p	α
0.16	0.27
0.35	0.31
0.24	0.29
0.02	0.24
0.19	0.20
0.03	0.13
0.19	0.13
0.18	0.19

Theoretical Values
(if $\tau = 1.00 \times 10^{-7}$)

log f/p	α
0.00	0.13
0.20	0.19
0.40	0.23
0.60	0.25
0.80	0.21
1.00	0.16

TABLE IX/

TABLE IX

Absorption Coefficient of Freon 12 at 253.3°K

log f/p	α
0.01	0.25
0.10	0.13
0.24	0.29
0.03	0.15
0.07	0.17
0.16	0.18
0.28	0.21
0.49	0.24
0.57	0.21
0.12	0.18
0.08	0.13
0.22	0.15
0.35	0.18
0.56	0.20
0.04	0.20

Theoretical Values
(if $\tau = 0.84 \times 10^{-7}$)

log f/p	α
0.00	0.11
0.20	0.17
0.40	0.22
0.60	0.24
0.80	0.22
1.00	0.17

Now Tables VII, VIII, IX give the absorption coefficients at the same three temperatures, together with the values which one would expect using the relaxation times of Table VI and equation (6).

These results are plotted on Fig. 7.

5. Relaxation in Freon 12 - Air Mixtures

In the operation of supersonic freon tunnels, it is the practice to isolate the working section when it is necessary to change the model. In this way some freon is lost but the majority remains. In this operation it is reported (from Langley Field) that the freon may become adulterated with a few per cent of air. Accordingly we thought it advisable to make measurements in freon 12 with additional dry air (up to 10 per cent by volume) expressed as mole fraction (x).

(1) Velocity

The actual velocity of ultrasonics in freon 12 - Air mixtures are shown in Table X, where the values were reduced to those of 20.6°C by using ideal gas law. See also Fig. 8.

TABLE X/

TABLE X

Velocity of Ultrasonics in Air - Freon 12 mixtures at 20.6°C

No.	log f/p	(V)actual	(V)ideal	x
3	1.887	155.9 m/sec	157.5 m/sec	0.092
4	0.022	156.8	157.9	0.092
5	0.140	157.7	158.5	0.092
6	1.955	157.3	158.6	0.106
7	0.010	158.0	159.1	0.106
8	0.168	159.0	159.8	0.106
9	1.940	158.5	159.8	0.123
10	0.004	159.0	160.1	0.123

The idealized velocity of the ideal gas is obtained by the same method as before, using the second virial coefficient. Here, the second virial coefficient of air is assumed to be zero, and that of the mixture as proportional to the mole fraction. The actual second virial coefficient of the mixture is unknown, and may not be linear in respect to the concentration, but in the present case the correction factor amounts to less than one per cent. The equation used is as follows:-

$$V_{obs} = V_{ideal} (1 - 0.106 P (1 - x)) \quad \dots(7)$$

where P is pressure in atmospheres, x concentration of air in mole fraction, and the numerical term 0.106 is the second virial term for freon 12 reported in Tables I, II. The values so obtained are tabulated also in Table XI.

TABLE XI

Limiting Velocity of Freon 12 Air Mixtures at 20.6°C

x	V ₀	V _∞
0.092	157.3 m/sec	170.4 m/sec
0.106	158.4	171.6
0.123	159.6	172.9

The limiting velocities of the mixture are calculated by the following equations

$$V_0^2 = \frac{RT}{M_{air} x + M_{fre} (1 - x)} \left\{ 1 + \frac{R}{C_{oair} x + C_{ofre} (1 - x)} \right\} \dots(8a)$$

$$V_{\infty}^2 = \frac{RT}{M_{air} x + M_{fre} (1 - x)} \left\{ 1 + \frac{R}{C_{oair} x + C_{ofre} (1 - x)} \right\} \dots(8b)$$

where/

where M_{air} is the molecular weight of air, 28.97, M_{fre} the molecular weights of freon 12, C_{oair} is the constant volume molar specific heat of air without vibration and equal to 4.9499 at 0°C. The temperature coefficient of the specific heat is less than 0.00017 per degree, and temperature correction of the specific heat of the air from 0°C to 20.6°C is not necessary. The values so obtained of the limiting velocity are shown in Table XI.

(2) Absorption

Amplitude absorption coefficients per wave length μ of air-freon 12 mixtures at various concentrations are shown in Table XII and Fig. 9. As is seen in this Fig., the absorption coefficient is not sensitive to the variation of concentration.

TABLE XII

Absorption Coefficient of Freon 12
Air Mixtures at 20.6°C

No.	$\log f/p$	x	Ampl. absorption coeff. per wave length μ
3	1.887	0.092	----
4	0.022	0.092	0.16
5	0.140	0.092	0.20
6	1.955	0.106	0.15
7	0.010	0.106	0.15
8	0.168	0.106	0.25
9	1.940	0.123	0.16
10	0.004	0.123	0.16

The relaxation times are also obtained from the absorption data. The solid line in Fig. 9 shows the theoretical curve using the value of relaxation time 1.20×10^{-7} . This is a little larger than the value indicated by Fig. 8.

From the velocity data, it could be expected that the velocity of sound of mixture at very high and low frequency is expressed by the equation (8) in which molecular weight and heat capacity at constant volume are both proportional to the mole fraction.

As for the relaxation times, it appears that the addition of air up to ten per cent does not give any remarkable change in the numerical values for pure freon 12.

6. Relaxations in Mixtures of Freon 12 and Rare Gases

It is well-known that expressions for the forces on models in supersonic wind-tunnels involve the ratio of specific heats in the gas used (γ). Now the value of γ for air at N.T.P. is 1.41 whereas that for freon 12 is, as we have seen, 1.13 at low and 1.34 at high frequencies.

In order to get equivalence between an air and a freon tunnel, it has been suggested that the freon should be mixed with argon or helium ($\gamma = 1.6$) to bring it up to atmospheric air conditions at N.T.P., although as Dean Chapman points out, this would not make the mixture simulate flight conditions in the stratosphere for which γ is lower.

We have therefore measured ultrasonic relaxation in freon 12 + argon and freon 12 + helium mixtures.

It is assumed (a) that in equation (5) the 'correction term' is to be multiplied by x the mole fraction of freon in the mixture, (b) the specific heats at low frequency and high are respectively

$$C_0 = C_{ofre} + C_H (1 - x); \quad C_\infty = 3Rx + C_H (1 - x) \quad \dots(9)$$

C_H being the specific heat of the rare gas (2.98 cal/deg/mol). (c) the limiting values of the velocity of sound in the mixture.

$$v^2 = \frac{RT}{M} \left(1 + \frac{R}{C_1} \right) \quad \dots(10)$$

$$[M = M_{fre} \cdot x + M_H \cdot (1 - x)]$$

The relaxation times for the mixture are plotted together with the specific heats against concentration on Fig. 10, using equation (6), and the velocities on Fig. 11.

The values plotted are also shown in Tables XIII, XIV, XV, XVI, XVII.

TABLE XIII

Argon-Freon 12, x = 0.248, T = 291.5°K

log f/p	V(actual)	V(idea ¹)
0.09	238.9 m/sec	239.4 m/sec
0.19	240.5	241.0
0.15	237.9	238.4
0.26	241.3	241.9
0.26	239.2	239.8
0.39	244.8	245.0
0.53	243.3	243.3

Argon-Freon 12, x = 0.488, T = 291.3°K

log f/p	V(actual)	V(ideal)
0.08	196.0 m/sec	196.8 m/sec
0.16	196.6	197.4
0.25	197.2	197.8
0.15	197.2	198.0
0.26	197.8	198.4

Argon-Freon 12, x = 0.722, T = 288.6°K

log f/p	V(actual)	V(ideal)
0.08	170.6 m/sec	171.8 m/sec
0.15	169.9	170.9
0.21	172.6	173.5
0.27	171.6	172.5

TABLE XIV

Helium-Freon 12, $x = 0.246$, $T = 291.7$

log f/p	V(actual)	V(ideal)
0.06	319.5 m/sec	320.4 m/sec
0.24	319.5	320.1
0.55	323.0	323.3
0.13	322.0	322.7
0.38	322.8	323.1
0.71	325.8	326.1

Helium-Freon 12, $x = 0.496$, $T = 292.7$

log f/p	V(actual)	V(ideal)
0.08	218.8 m/sec	219.7 m/sec
0.22	219.5	220.2
0.40	220.8	221.2
0.15	219.7	220.6
0.32	221.1	221.8
0.50	222.5	222.9

Helium-Freon 12, $x = 0.745$, $T = 292.7$

log f/p	V(actual)	V(ideal)
0.08	176.0 m/sec	177.2 m/sec
0.19	176.0	177.1
0.32	179.4	180.1
0.32	179.4	180.1
0.13	176.1	177.2
0.23	178.9	179.8

TABLE XV

Relaxation Time of the Mixtures

Argon-Freon 12

x	T	τ
1.000	290.6°K	1.70×10^{-7} sec
0.722	288.6°	1.23
0.488	291.3°	1.26
0.248	291.5°	1.51

Helium-Freon 12

x	T	τ
1.000	290.6°K	1.70×10^{-7} sec
0.745	292.7°	0.88
0.496	292.7°	0.55
0.246	291.7°	0.78

TABLE XVI/

TABLE XVI

Calculated Values of Specific Heat and Ratio of Specific Heat of the Mixture of Freon 12 and Inert Gas at 290.6°K

x	C _{v0} (actual)	γ ₀
1	14.92	1.133
0.75	11.94	1.166
0.50	8.95	1.222
0.25	5.97	1.333
0.00	2.98	1.667

TABLE XVII

Calculated Values of Velocity of Sound at Low Frequency of the Mixtures

Argon-Freon 12

x	V ₀ (actual)
1	148.6 m/sec
0.75	165.7
0.50	193.4
0.25	230.4
0.00	317.7

Helium-Freon 12

x	V ₀ (actual)
1	148.6 m/sec
0.75	173.6
0.50	216.2
0.25	310.2
0.00	100.3
0.18	362.4

7. Freon 11 (CCl₃F)

Velocity and absorption have been measured in this vapour.

TABLE XVIII

Ultrasonic Velocity in Freon 11 at 292.7°K

log f/p	V(actual)	V(ideal)
0.21	145.1 m/sec	147.3 m/sec
0.20	145.0	147.0
0.34	146.5	148.1
0.21	145.8	147.3
0.22	145.2	147.3
0.14	143.2	146.5

Relaxation Time of Freon 11: $\tau = 1.5 \times 10^{-7}$ sec at 292.7°K

TABLE XIX

TABLE XIX

log f/p	α
0.21	0.17
0.20	0.18
0.34	0.12
0.34	0.22
0.21	0.15
0.21	0.16

Theoretical Values

log f/p	α
0.00	0.13
0.30	0.18
0.51	0.22
0.70	0.22
0.90	0.18

Using the fundamental frequencies for this molecule given by Classen¹¹, i.e., in wave-numbers - 241, 349.5, 398, 535.2, 847, 1085 cm^{-1} , we derive for the heat capacity at this temperature $C_{VO} = 6.407$, $R = 12.73$ cal/mole/deg.

Then using the values of second virial coefficient quoted by Hirschfelder, McClure and Weeks,¹³ we obtain a correction for gas imperfection.

$$V(\text{actual}) = V(\text{ideal}) (1 - 0.024p) \text{ at } 292.7^\circ\text{K}$$

Limiting Values of Ideal Velocity

$$V_0 = 143.1 \text{ m/sec}$$

$$V_\infty = 153.7 \text{ m/sec}$$

The experimental results are plotted on Figs. 12, 13.

8. Freon 22. (CHCl_2F_2)

Only velocity has been measured in this vapour.

TABLE XX

Ultrasonic Velocity in Freon 22 at 290.0°K

log f/p	V(actual)
0.01	179.0 m/sec
0.02	178.4
0.11	179.7
0.32	183.3
0.04	178.3
0.21	180.3
0.39	182.9
0.01	178.7
0.01	178.7
0.32	181.0
0.01	179.7
0.11	179.6
0.31	183.1
0.52	188.0

Relaxation Time 1.3×10^{-7} sec at 290.0°K

Calculated/

Calculated Values of Ideal Velocity

$$\begin{aligned}V_0 &= 181.2 \text{ m/sec} \\V_\infty &= 192.8 \text{ m/sec}\end{aligned}$$

Those values are calculated using the value of C_{v0} found in the literature¹⁴. It is strange that the low-frequency calculated velocity is far higher than the experimental one.

9. Freon 13. (CF₃Cl)

Only velocity has been measured in this vapour at 291.2°K and at values of $\log f/p$ in the neighbourhood of 0.02, when the velocity was 164.5 m/sec.

The second virial coefficient was calculated from critical data and specific heat from spectroscopic data, the wave-numbers being 350, 475, 8, 560, 781.7, 1105, 1212 cm⁻¹.

Calculated Values of Ideal Velocity

$$\begin{aligned}V_0 &= 165.5 \text{ m/sec} \\V_\infty &= 175.8 \text{ m/sec}\end{aligned}$$

Again, the experimental value is smaller than the theoretical low-frequency value.

APPENDIX/

APPENDIX

Relaxation

This change in the velocity of sound with frequency has been explained by Herzfeld and Rice in terms of a delay in the change of translational energy into vibrational energy of the molecules as the wave is propagated. When the time period of vibration becomes comparable with this "relaxation time" or "mean life of a sound quantum" the molecules become stiffer to the vibration (to use the expressive phrase of Hubbard) with a consequent absorption of energy and rise in γ , the ratio of specific heats.

Let E_x be the actual energy and E_T the energy which the molecules would have if at equilibrium at temp. T , and suppose that

$$\frac{dE_x}{dt} = \frac{1}{\beta} (E_T - E_x)$$

where β is the period of relaxation of the vibrational energy. If the gas is subject to adiabatic variations of temperature of frequency $\omega/2\pi$

$$T = T_0 + T_1 e^{i\omega t}$$

$$E_T = E_0 + C_\omega T_1 e^{i\omega t}$$

C_ω being the specific heat of vibrations. Substituting and solving, we find

$$E_x = E_0 + C_\omega T_1 (1 + i\omega\beta)^{-1} e^{i\omega t}.$$

If the total specific heat be regarded as made up of two parts, C_∞ due to vibration and C_1 due to translation (+ rotation).

$$C' = C_1 + C_\omega (1 + i\omega\beta)^{-1} \quad \dots(1)$$

wherein C_1 is the part associated with translation, C_ω that associated with vibrations (or rotations). The velocity of sound is given by

$$v^2 = \frac{p}{\rho} \left\{ 1 + (C_p - C_v) \frac{C_v + C_1 \omega^2 \tau^2}{C_v^2 + C_1^2 \omega^2 \tau^2} \right\} \quad \dots(2)$$

and the ratio of specific heats peculiar to sound propagation.

$$\gamma = 1 + R \frac{C_v + C_1 \omega^2 \tau^2}{C_v^2 + C_1^2 \omega^2 \tau^2} \quad \dots(3)$$

When V_0 is the low-frequency velocity, V_∞ the high-frequency velocity and the mid-frequency value $(V_0^2 + \frac{1}{2}(V_\infty^2 - V_0^2))$ occurs at a frequency f_m , the relation between V and f is

$$\frac{V^2 - V_0^2}{V_\infty^2 - V_0^2} = \frac{(f/f_m)^2}{1 + (f/f_m)^2} \quad \dots(4)$$

also/

also

$$f_m = \frac{1}{2\pi\tau} \cdot \frac{C_v}{C_1} \quad \dots(5)$$

and

$$\tau = \frac{1}{2\pi f_m} \cdot \frac{V_\infty^2}{4V_0^2 - 3V_\infty^2} \left(\frac{V^2 - V_0^2}{V_\infty - V_0} \right)^{\frac{1}{2}} \quad \dots(6)$$

If μ the (amplitude) absorption per wavelength is plotted against $\log f$, a symmetrical curve is obtained, of which the maximum μ_m is given approximately by

$$\mu_m = \frac{\pi R (C_v - C_1)}{2 C_1 (R + C_1)} \quad \dots(7)$$

If α/f^2 , α being the absorption per unit length, is plotted against $\log f$, the curve has the shape of the velocity dispersion reversed reaching the classical value (by interpolation of the viscosity coefficient) at high frequencies and lying $2\mu_v/f_m V_0$ higher at zero frequency.

—

References

<u>No.</u>	<u>Author(s)</u>	<u>Title, etc.</u>
1	R. Smelt	Power economy in high speed wind tunnels by choice of working fluid and temperature. R.A.E. Report Aero.2081. A.R.C. 9007. August, 1945.
2	A. Kantrowitz	J.Chem.Phys. <u>14</u> , 150 (1946).
3	Paul W. Huber	Use of Freon-12 as a fluid for aerodynamic testing. N.A.C.A. Technical Note No.1024. A.R.C. 10,389. April, 1946.
4	Paul W. Huber and A. Kantrowitz	J.Chem.Phys. <u>15</u> , 275 (1947).
5	Ernest F. Relf	Note on the use of rare gases in high speed wind tunnels. A.R.C. 14,732. 15th March, 1952.
6	W. Railston and E. G. Richardson	Proc.Phys.Soc. <u>47</u> , 533 (1953).
7	A. E. von Doenhoff, A. L. Braslow and M. A. Schwartz	Studies of the use of Freon-12 as a wind tunnel testing medium. N.A.C.A. TN 3000. August, 1953. 57 p. diagrs.
8	Dean R. Chapman	Some possibilities of using gas mixtures other than air in aerodynamic research. N.A.C.A. Technical Note 3226, August, 1954. A.R.C. 17,163. 5th November, 1954.
9	G. W. Pierce	Proc.Amer.Acad.Sci. <u>60</u> , 271 (1925).

References (contd.)

<u>No.</u>	<u>Author(s)</u>	<u>Title, etc.</u>
10	Z. Nernst	Electrochem. 17, 265 (1911).
11	H. H. Classen	J.Chem.Phys. 22, 50 (1954).
12	R. M. Buffington and W. K. Gilkey	Ind.Eng.Chem. 23, 1290 (1931).
13	Hirschfelder, McClure and Weeks	J.Chem.Phys. 10, 201 (1942).
14	A. F. Benning, R. C. McHarness, H. Markwood and W. Smith	Ind.Eng.Chem. 32, 976 (1940).

FIG 1

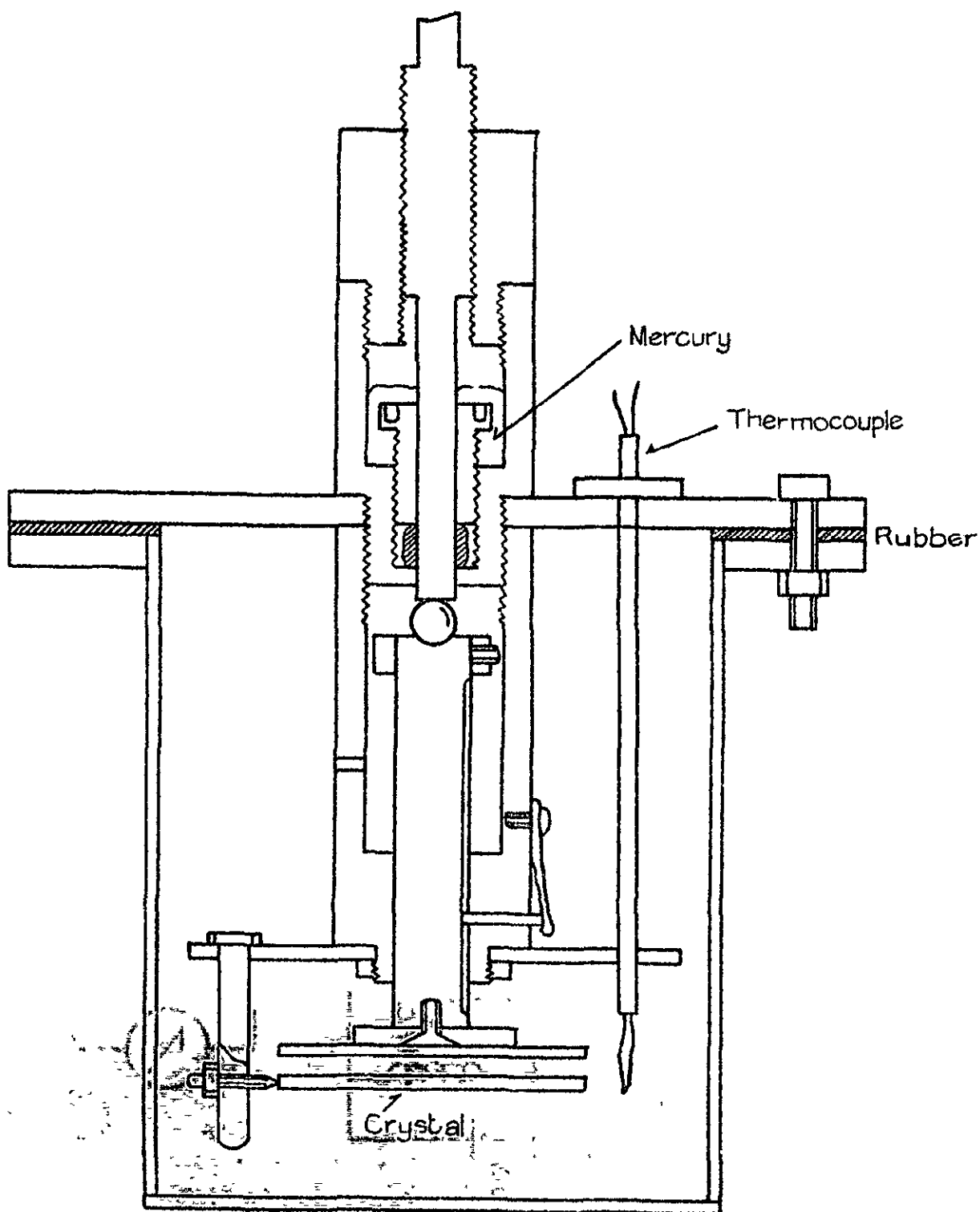
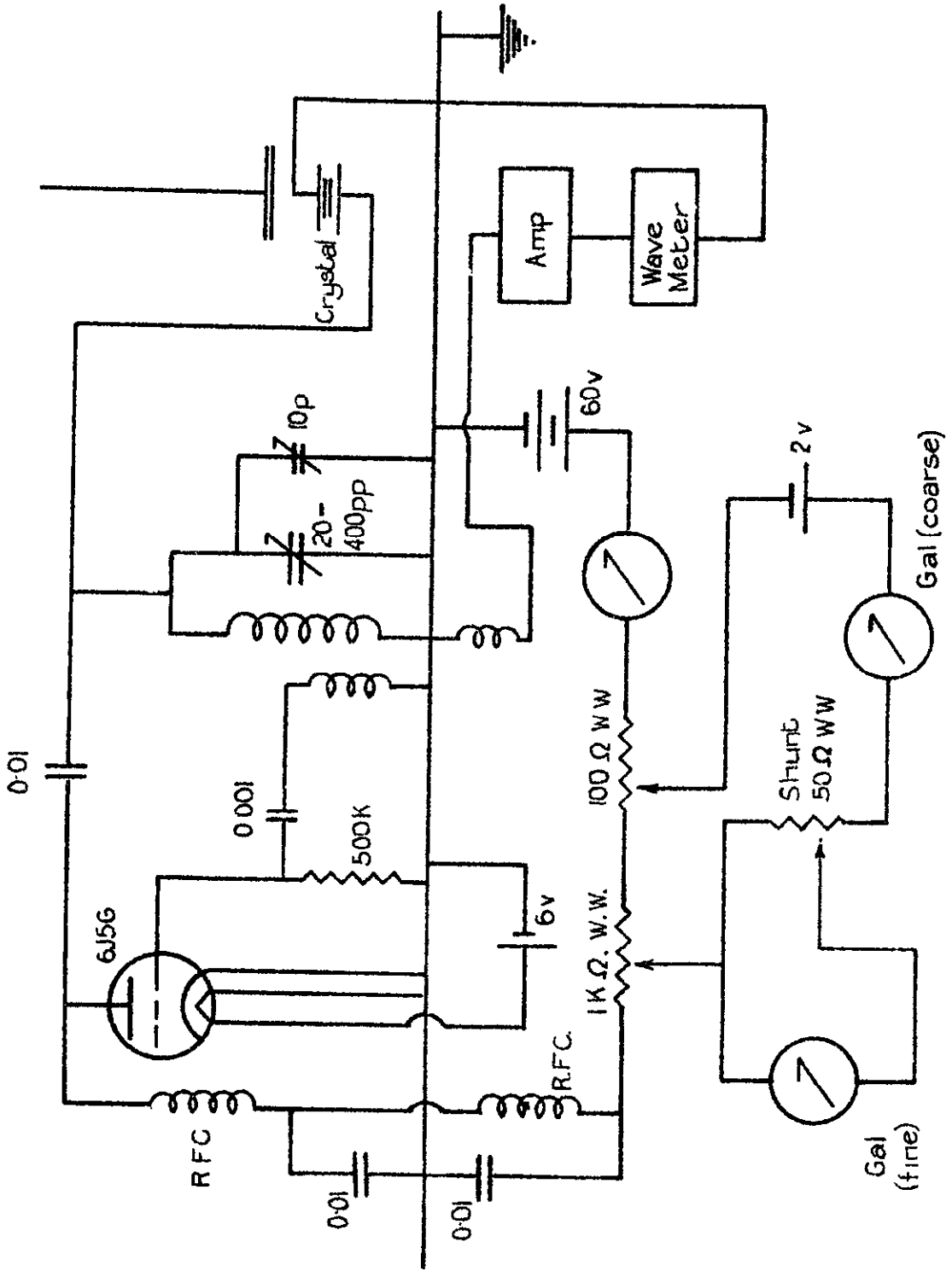
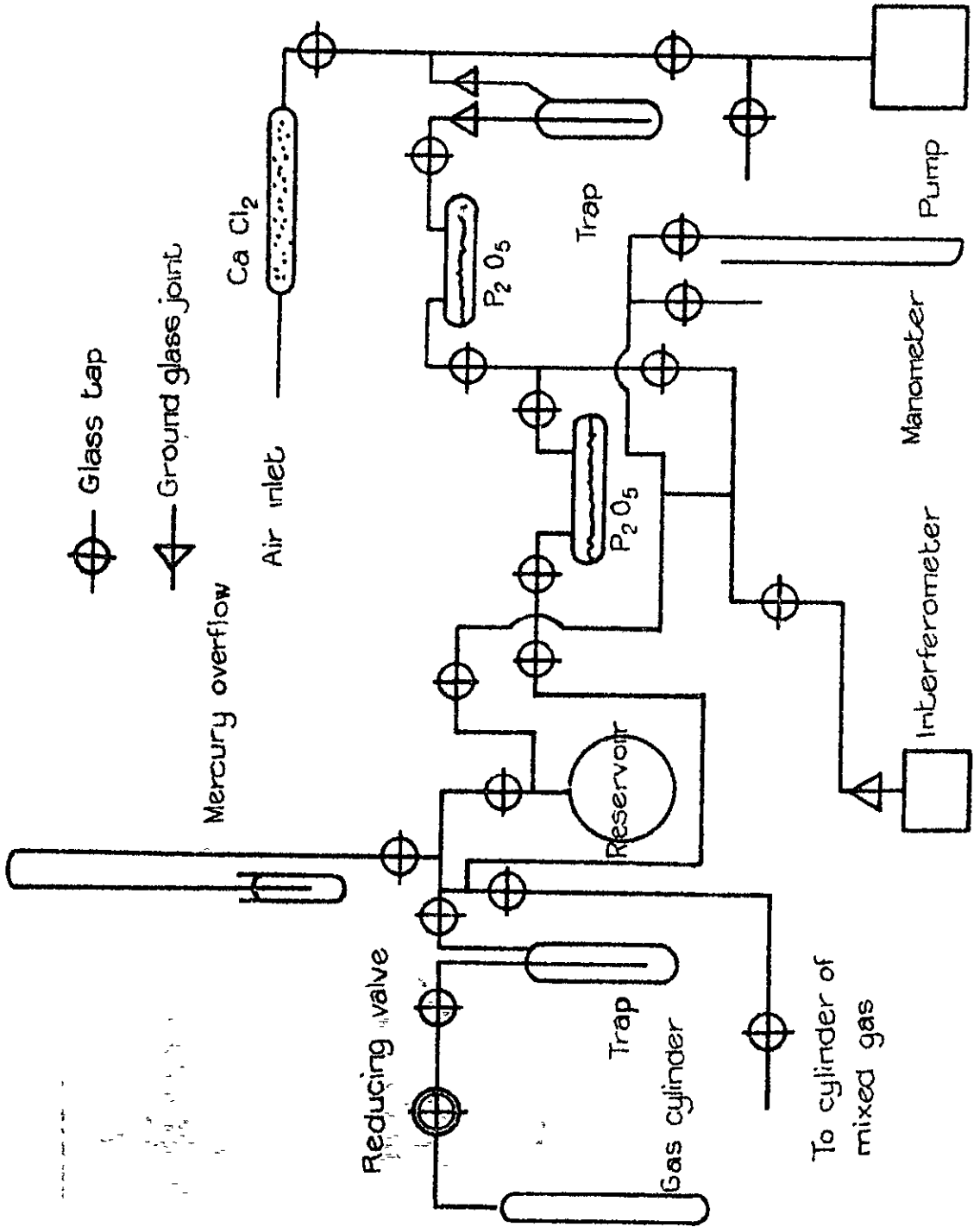


FIG 2



Electric circuit.

FIG 3

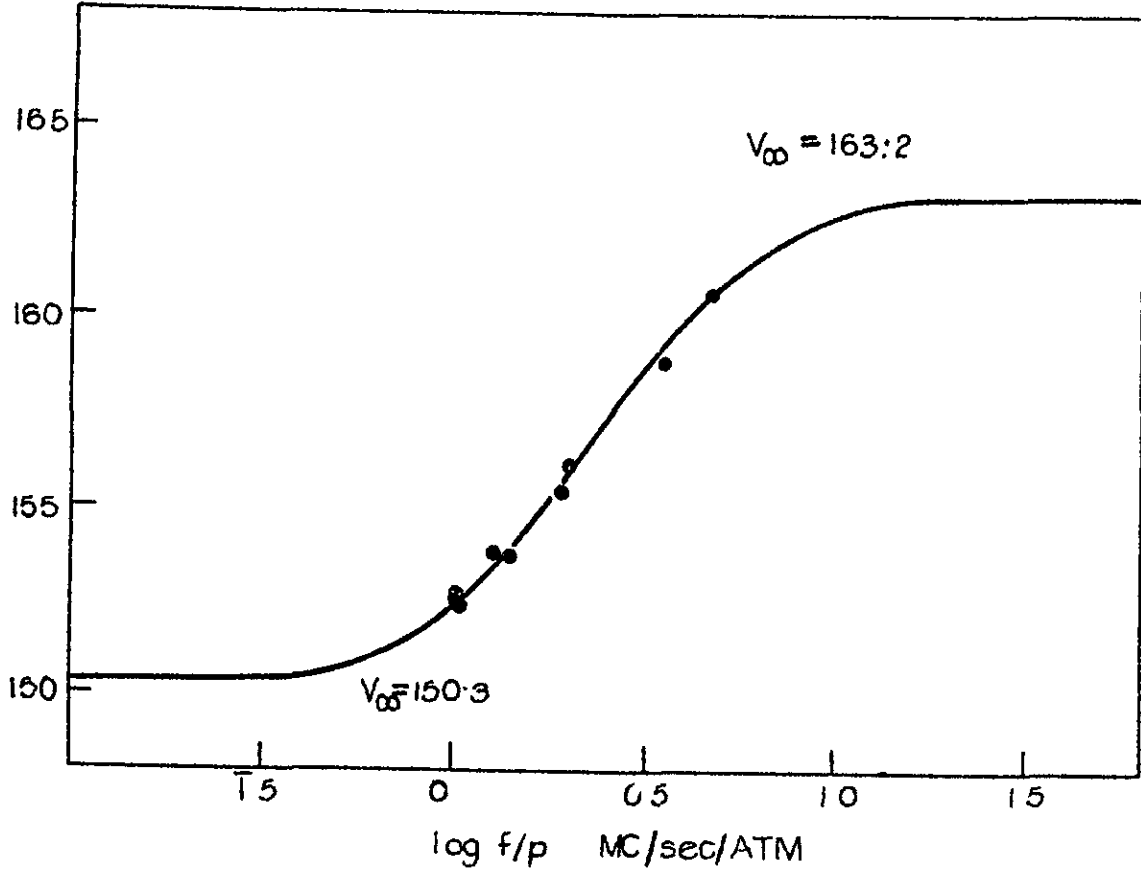


Gas handling system

FIG 4 & 5

V m/sec

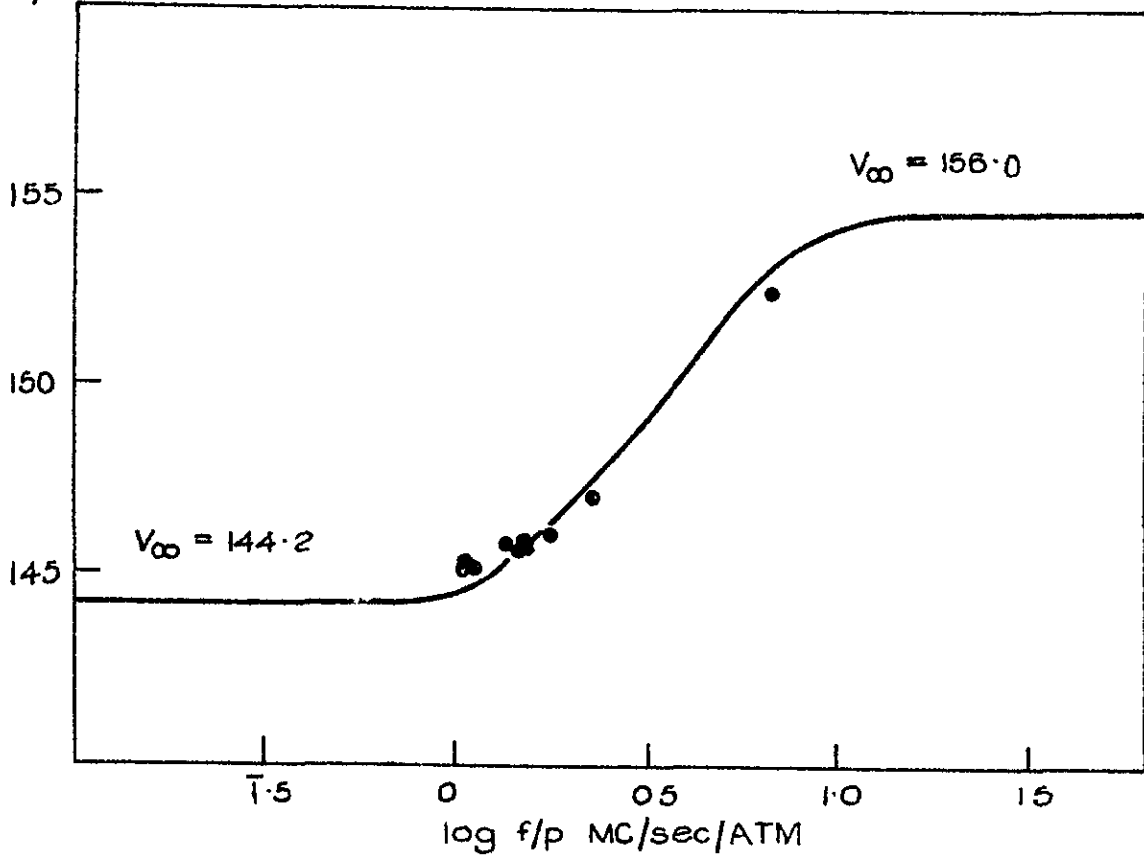
FIG 4



Idealized velocity of Freon-12 at 290.6°K

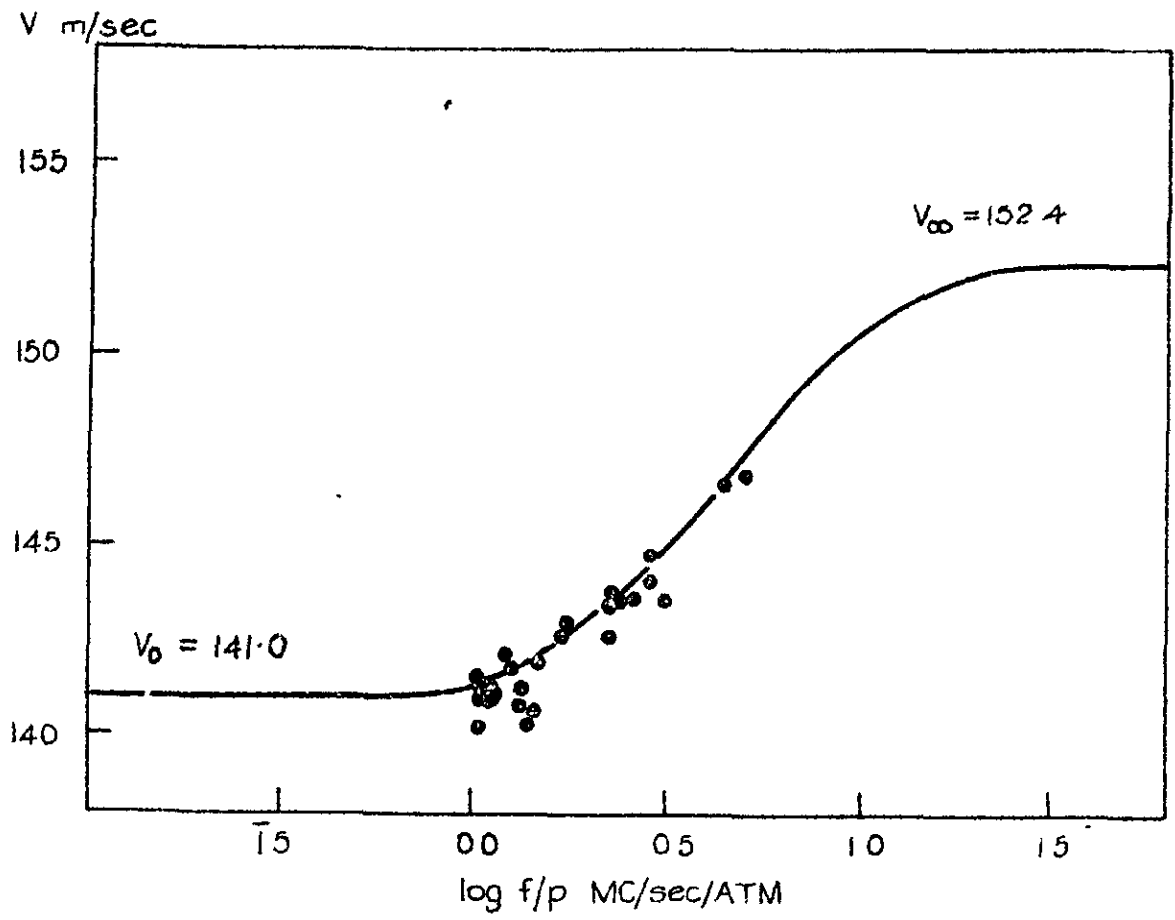
V m/sec

FIG 5



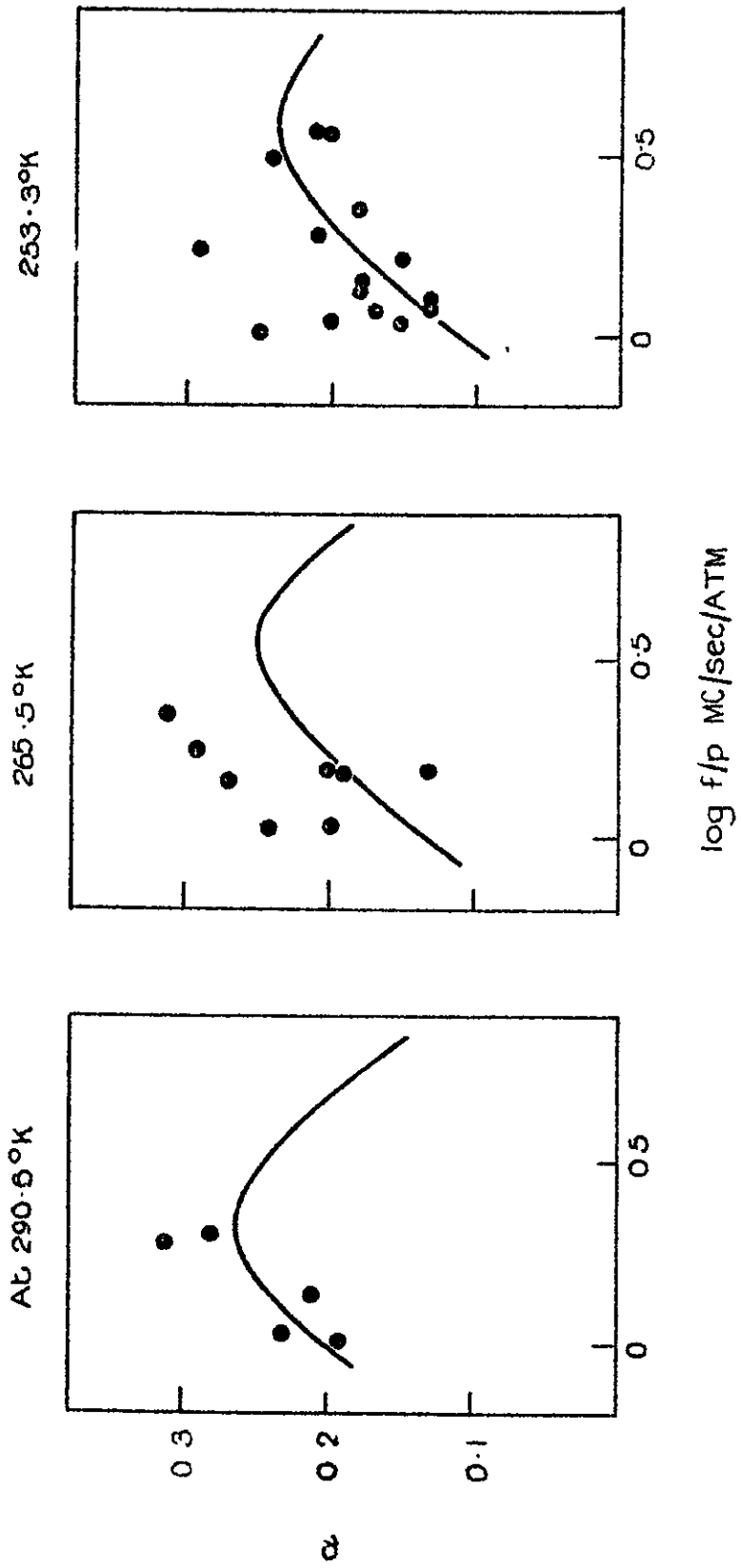
At 265.5°K

FIG. 6



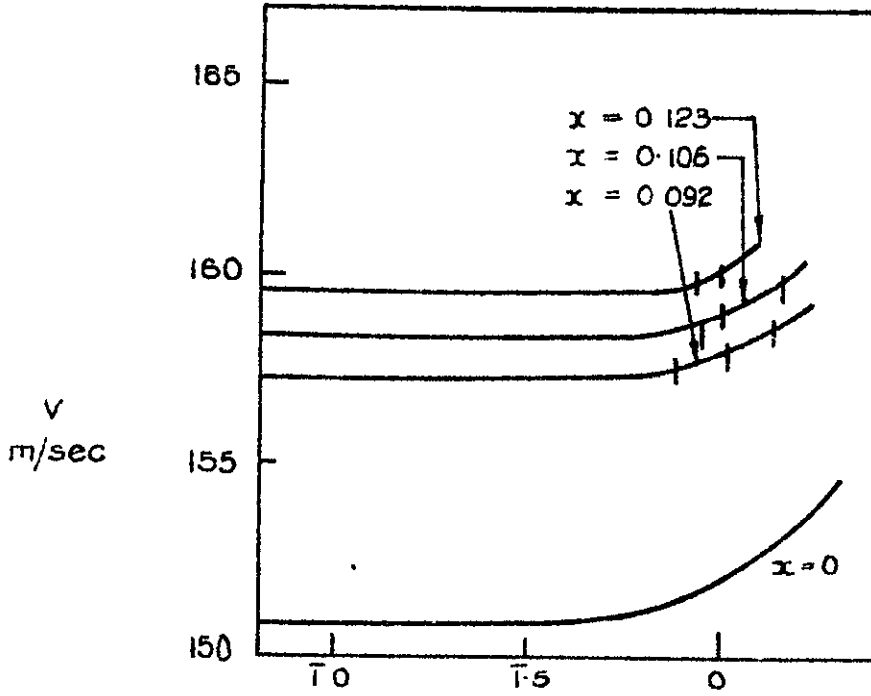
At 253.3°K

Fig 7



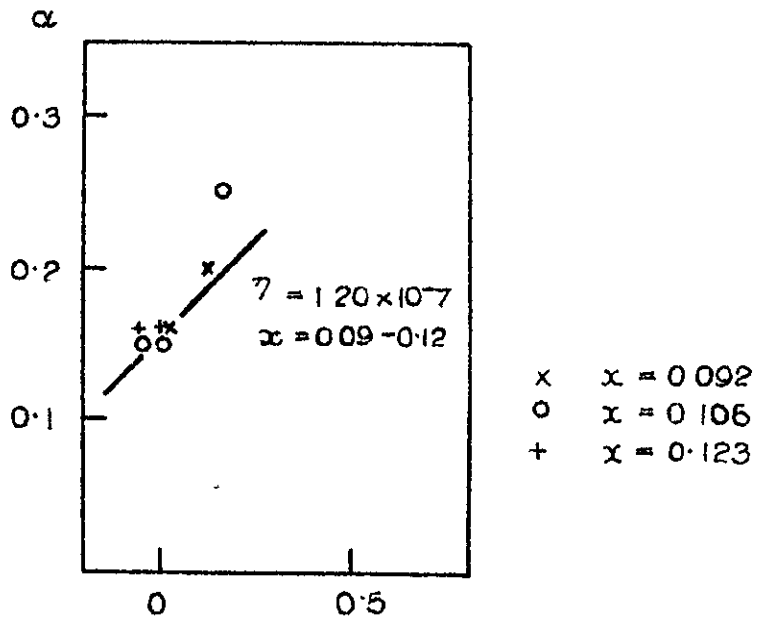
Absorption coefficients of Freon-12

FIG. 8 & 9



Idealized velocity of Freon-12 - air mixtures at 193.8°K

FIG. 9



Absorption coefficient of Freon-12 - air mixtures at 193.8°K

Fig. 10 & 11

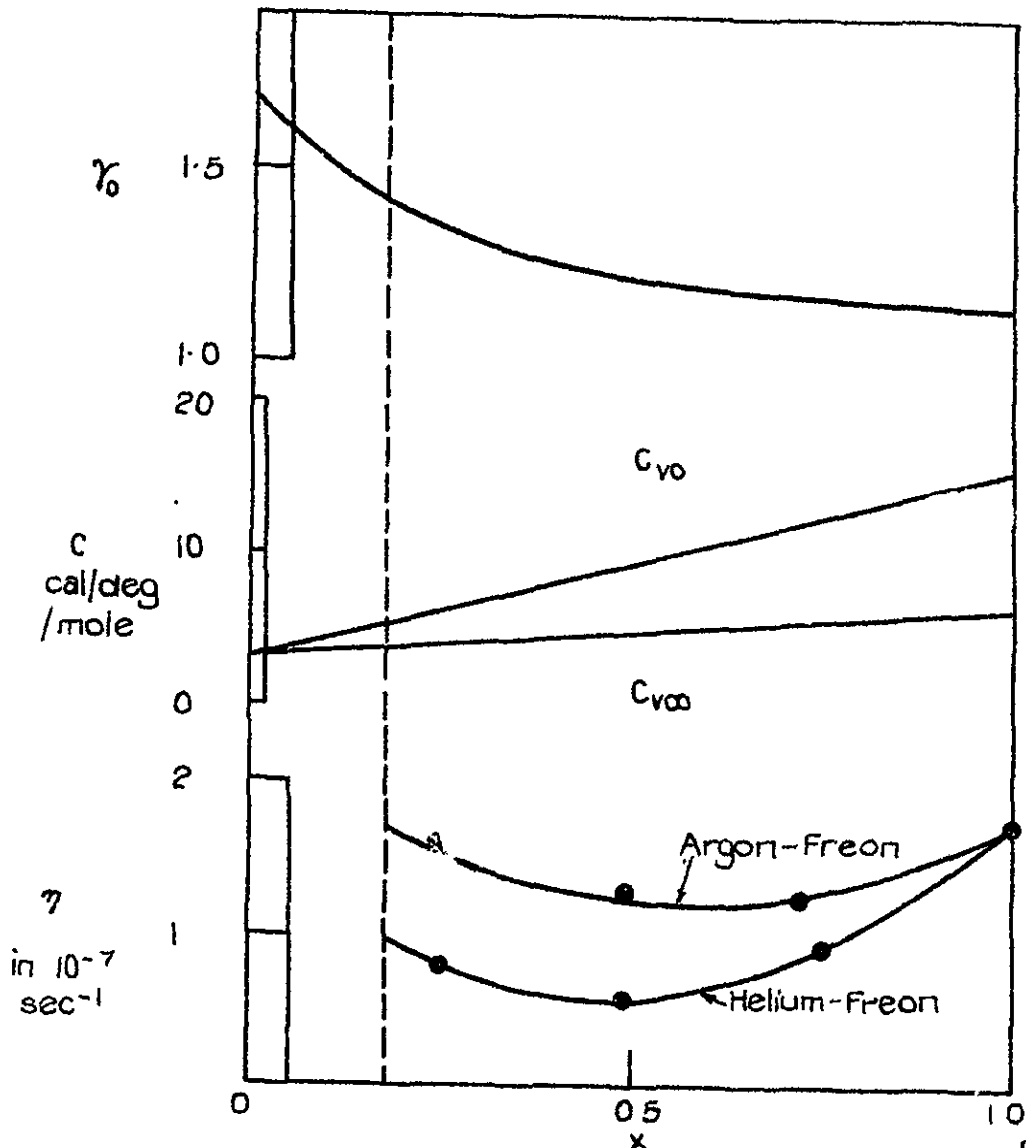


FIG. 10.

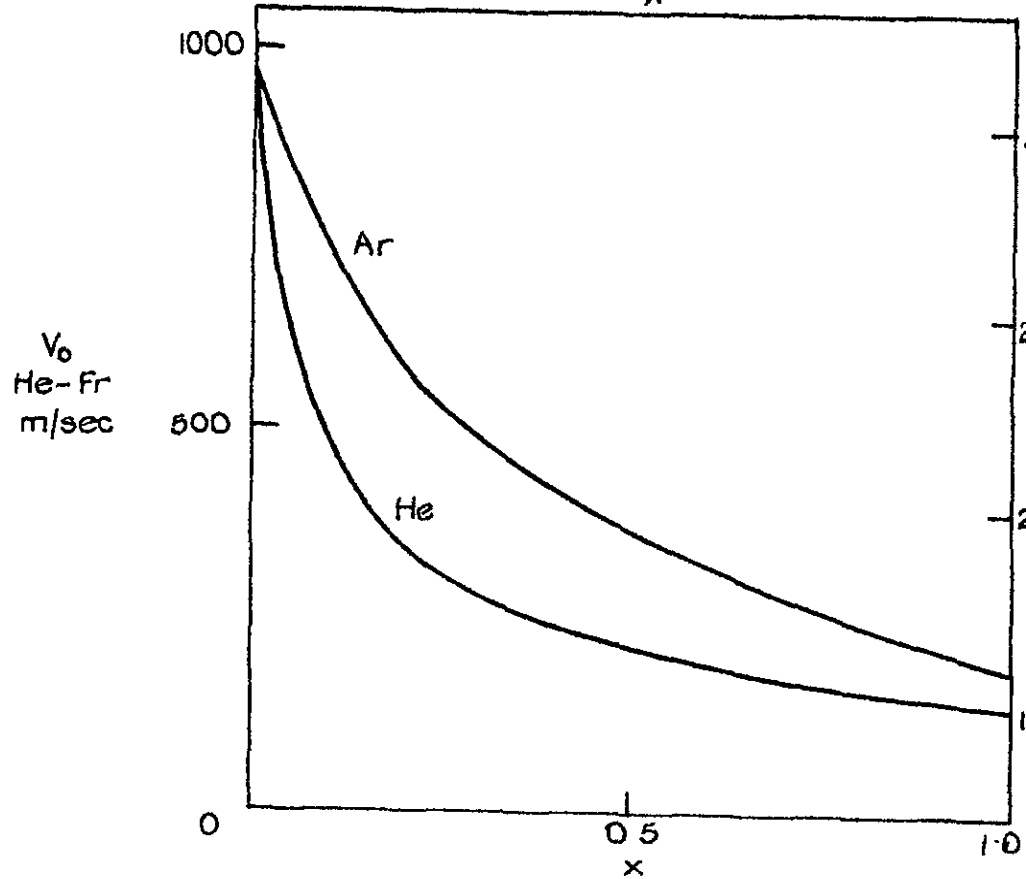


FIG. 11.

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