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A PROCEDURE FOR PRODUCTION OF PHYSICAL PROPERTY DATA TO DEVELOP NEW REFRIGERANTS

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ABSTRACT

In our search for new refrigerant formulations our approach has been to produce data sets as quickly as possible by making full use of estimation techniques. Initially with only the measured normal boiling point and structural information available we would estimate the critical properties using the Ambrose group contribution method and the ideal gas heat capacity (C_p) from the Benson group contribution method. We could then estimate the thermodynamic properties using a three constant equation of state such as the Redlich Kwong Soave equation. This approach provided a screening method to produce a short list of fluids considered worthwhile for experimental investigation. Firstly saturated vapour pressure and critical points were measured and the thermodynamic data refined. Finally P-V-T measurements were carried out on the most promising fluids. The effect of improving data accuracy on refrigerant performance calculations is shown for CFC-12. Improvements for group contributions to estimate critical points are suggested.

We report measurements for critical properties, saturated vapour pressure by an automated static apparatus and P-V-T data. The latter are correlated by the Martin Hou Equation of State. Compounds studied include:

HFC 134a (1,1,1,2 tetrafluoroethane)
HFC 125 (pentafluoroethane)
HCFC 123 (1,1 dichloro,2,2,2 trifluoroethane)

NOMENCLATURE

n Bpt - normal boiling point at 1 atmosphere pressure
T_c - Critical Temperature
P_c - Critical Pressure
omega - Acentric factor
H_v - Latent heat vapourisation
P° - Saturated liquid vapour pressure equations 1,2
T - Temperature equations 1,2
C_p - Ideal gas heat capacity

INTRODUCTION

There is currently an urgent need to produce thermodynamic data to develop new refrigerants. This study shows how both estimation techniques and careful experimental measurements have a role to play where time to produce the data is an important consideration as well as data accuracy.

DEMANDS ON A DATA PRODUCING TEAM TO DEVELOP NEW REFRIGERANTS

The team needs to be technically and economically effective in using its resources to meet customer requirements. The resources available are:

- (i) people
- (ii) computerised estimation methods
- (iii) measurement equipment
- (iv) various computerised data fitting routines

The possible approaches to production of a pressure enthalpy diagram, thermodynamic tables or computer package are shown in Table 1.

TABLE 1
APPROACHES TO PRODUCTION OF THERMODYNAMIC DATA FOR REFRIGERANT

Approach	Property				
	n Bpt	ideal gas specific heat (Cp)	critical props	vapour pressure temperature curve	equation of state
A	M	E Benson	E	E	E for coeffs of cubic equation eg RKS
B	M	"	M	M	"
C	M	"	M	M	measure P-V-T fit to Martin Hou Eqn
D	M	Obtain vibn frequencies	M	M	"

M = measurement E = estimation

As the approach moves in the direction A to D the data produced is of increasing accuracy but the time required and cost of production increase considerably.

Customer requirements differ. Research Management (RM) want to know what compounds there are to meet a particular technical need and an indication of the production cost. Marketing (MK) want preliminary data sets of a new product to be given to customers for them to be able to check whether it might meet their needs. The Refrigeration Engineer (RE) needs accurate data to calculate the refrigeration duties.

The approach C or D for customer (RM) could involve considerable waste of resources in particular experimental measurement on a compound which proved to be unsuitable as a refrigerant. Approach A or B would not give data of sufficient accuracy for customer (RE).

EFFECT OF DATA ACCURACY ON REFRIGERATION PARAMETERS

Table 2 shows the effect of increasing data accuracy (direction R1 to R5) upon the CFC-12 refrigeration parameters for the evaporator and condenser temperatures shown. For R1 it is assumed that only an accurately measured n boiling point is available. Moving from R1 to R2 shows the effect of perturbing the critical temperature by 3K and the critical pressure by -4 bar an extent that might well represent errors as a result of inaccurate data. The R5 cycle has been calculated from interpolation of the Watson tables (Ref 1) and are taken as a very accurate data set. The results for R1 to R4 were obtained from a refrigeration cycle computer program with ideal gas specific heat obtained from Benson Group contributions and enthalpy departures calculated using Redlich Kwong Soave equation of state.

TABLE 2
REFRIGERATION CYCLE CALCULATIONS FOR CFC-12
EFFECT OF INCREASING DATA ACCURACY

	Evaporator Temp = 263.15K Condenser Temp = 313.15K				
	R1	R2	R3	R4	R5
	n Bpt + estimation	perturbation of R1	n Bpt + measured Tc&Pc	R3+measured vap press-assume accurate Hv	Watson Tables
Tc	385.0	388.0	384.2	384.2	384.2
Pc	45.1	41.1	41.2	41.2	41.2
omega	0.206	0.154	0.179	0.179	0.179
upper temp	322.7	320.5	321.5	321.5	320.4
super ht	750	575	650	650	655
Hv (313K)	15860	15320	15420	15650	15650
COP	3.92	3.93	3.91	3.98	4.14
Press evap	2.2	2.2	2.2	2.2	2.2
Press cond	10.2	9.3	9.6	9.6	9.6
Molar Vol Evap	9.2	9.4	9.3	9.3	9.3
Notes	Temp in K	Press in Bar	Heat in kJ/(kg mole)	Vol in litres/g mole	

It is seen that the coefficient of performance (COP) is rather insensitive to data accuracy. Even in run R1 it is only 5.3% low and this value is reduced to 3.8% when the accuracy of the heat of vapourisation is improved (R4). The progression from R3 to R4 represents the change from estimating the heat of vapourisation from the Pitzer estimation method to calculation by Clausius Clapeyron Equation with supporting vapour density data from an equation of state.

The error in vapour volume at the evaporator and cycle pressures as revealed at runs R1 & R2 have been effectively removed by the time R3 is reached. The condenser temperature used in Table 2 has been chosen as typical of many refrigeration cycles. For cycles in which the condenser temperature is much higher and even approaching the critical temperature; R1 and R2 will become increasingly unsatisfactory, indeed only R5 will be adequate.

The ability of estimation methods to measure critical temperatures and pressures is shown in Table 3. The list of fluorine containing hydrocarbons includes both perhalogenated and hydrogen containing molecules. Several of our own measured values are given. It is seen that the methods of Lydersen (Ref 2), Ambrose (Ref 3) and Joback (Ref 2) can all estimate critical temperature to well within 10K. By extending the fluorine containing group contributions to allow for different molecular environments (see Table 4) the critical temperatures of the compounds listed in Table 3 can be reproduced to within 4K.

TABLE 3
COMPARISON OF CRITICAL PROPERTY ESTIMATION METHODS AGAINST OUR SELECTED VALUES

	Mol Wt	n Bpt(°C)	Tc(K)	Tc(K) (Estimated - Selected)			
				selected	Ambrose	Joback	Lydersen
CF ₂ Cl ₂	121.0	-29.8	385.0	-0.7	1.4	0.0	0.0
CF ₃ Cl	104.5	-81.4	302.0	0.8	2.2	0.9	0.9
CF ₃ .CF ₂ Cl	154.5	-38.7	353.2	-0.1	4.4	0.0	0.7
CF ₂ Cl.CFCI ₂	187.4	47.6	487.3	-4.1	3.5	-2.1	-2.0
CH ₃ .CHF ₂	66.1	-24.7	386.7	3.5	6.4	7.4	2.7
CHCl ₃ .CF ₃	153.1	28.1	457.5	0.8	4.0	1.0	1.1
CH ₂ F.CF ₃	102.0	-26.2	374.2	5.2	7.6	5.3	1.2
CHF ₂ .CHF ₂	102.0	-19.7	391.8	-2.2	-3.2	-4.0	-3.1
CHF ₂ .CF ₃	120.0	-48.7	339.4	1.7	3.6	1.1	1.9
CH ₂ .CFCI ₂	116.9	32.0	478.0	Decomposing			
CHFCl.CF ₃	136.5	-12.0	396.0	1.3	3.8	1.0	1.1
	Pc		Pc (Estimated-Selected)				
	(bar)		(bar)				
	Selected	Lydersen	This Work	Sources of Selected Data			
CF ₂ Cl ₂	41.2	4.5	4.5	Watson (Ref 1)			
CF ₃ Cl	36.7	5.8	0.4	ESDU (Ref 4)			
CF ₃ .CF ₂ Cl	32.3	0.1	0.1	Ambrose(Ref 5)			
CF ₂ Cl.CFCI ₂	34.1	-0.9	-0.9	Ambrose(Ref 5)			
CH ₃ .CHF ₂	45.0	-0.4	-4.1	Ambrose(Ref 5)			
CHCl ₃ .CF ₃	33.7	2.4	2.4	ICI measured			
CH ₂ F.CF ₃	40.6	-3.6	-0.7	"			
CH ₂ .CHF ₂	43.7	-6.0	-2.3	"			
CHF ₂ .CF ₃	35.9	-1.5	-0.1	"			
CH ₂ .CFCI ₂	35.0	Decomposing		"			
CHFCl.CF ₃	35.9	-0.5	-0.5	"			

TABLE 4
MODIFIED CRITICAL PROPERTY GROUP CONTRIBUTIONS

Group	AT		AP	
	This work	Lydersen	This work	Lydersen
-CH ₃	0.030	0.020	0.320	0.227
=CH ₂	0.020	0.020	0.227	0.227
≡CH	0.012	0.012	0.210	0.210
-C-	0	0	0.210	0.210
-CF ₃	0.054	0.054	0.882	0.882
-CHF ₂	0.047	0.048	0.620	0.658
-CH ₂ F	0.047	0.038	0.390	0.451
=CF ₂	0.036	0.036	0.658	0.658
=CHF	0.030	0.030	0.434	0.434
≡CF	0.018	0.018	0.434	0.434
-Cl	0.017	0.017	0.360	0.320

These groups to be used with Lydersen equations

PVT MEASUREMENT

Apparatus

The apparatus (Fig 1) is in two parts:

- (a) Filling manifold - This consists of a material reservoir, a detachable weighing vessel, 1 litre vapour expansion vessel, pressure transducer and vacuum pump. This manifold is connected to the measurement manifold via valve V1.
- (b) Measurement manifold - This consists of a small sample pot for condensing material during transfers, an expansion vessel and a KAMAN SCIENCE KP 1911 pressure transducer. It is isolated through valve V1 and completely enclosed in a circulating air oven, thermostatically controlled using Eurotherm type 815 controllers. The pressure transducer is housed in its own separate oven and the pipe between ovens is trace heated. The temperature is recorded using platinum resistance thermometers (PRT) at five different places on the manifold for reasons explained later. These are on the sample pot (T1), two places on the expansion volume (T2, T3), the connecting trace heated pipe (T4) and the pressure transducer (T5). The PRTs are read using a COMARK Model 6800 meter.

CALIBRATION PROCEDURE

Volume - The volume of both manifolds were calibrated by expanding a similar known volume of ambient air and observing the pressure drop. The accuracy of this method is estimated as ± 0.05 ml. The volume of the measurement manifold can be altered by replacing the expansion vessel.

Pressure - The Kaman Science pressure transducer has a range 0-70 bars and was calibrated at the measuring temperature using a BUDENBURG 100 bar pneumatic dead weight tester and is resolvable to ± 10 mbars and accurate to .05% full scale.

Temperature - The circulating air ovens control to .1 degree. The PRTs were calibrated using a Class A standard PRT calibrated at Harwell calibration laboratories and are accurate to ± 0.05 degree.

OPERATING PROCEDURE

Degassing - The pure material >99.9% by wt is thoroughly degassed on the filling manifold by cooling the reservoir in liquid nitrogen and pumping inerts to vacuum and then warming to room temperature before recooling to check residual pressure. This process is repeated until no residual pressure is observed at -196°C .

Charging - Liquid from the reservoir is allowed to vapourise into the 1 litre expansion vessel to the required pressure. This gives a crude weight of sample which is condensed into the detachable sample bomb for accurate weighing. This sample is then transferred by vacuum distillation into the measuring manifold by cooling the sample pot in liquid nitrogen. After the transfer is complete the detachable sample bomb is reweighed to give the weight transferred.

Measurement - The sample is isolated in the measurement manifold by closing valve V1. The bottom oven is then brought up to the temperature of the transducer and left to equilibrate, shown when all five temperatures and the pressure remain steady.

Mean temperature - The mean temperature is chosen by giving each PRT a volumetric weighting, ie multiplying each reading by the volume fraction of that particular part of the manifold over the total volume.

Volume correction for thermal expansion - A coefficient of thermal cubical expansion of the vessel was calculated on the assumption that the vessel was a cylinder manufactured in stainless steel.

RESULTS

Table 5 shows a comparison of compressibility constants derived from our results for dichlorodifluoromethane (CFC-12) against values calculated from Watson (Ref 1) It can be seen that the correction for volume expansion of the vessel gives closer agreement.

The same method and apparatus were used to produce PVT data for 1,1,1,2 tetrafluoroethane (HFC 134a). This was fitted to the Martin-Hou Equation of State to give the coefficients shown in Table 6.

CRITICAL PROPERTY MEASUREMENT

Critical Temperature

Apparatus - The apparatus (Fig 2) consists of a thermally controlled cylindrical block. A sealed glass capillary tube containing the thoroughly degassed sample is placed in the centre of the block through which there is an observation window. The block is heated and the temperature is monitored using a calibrated PRT $\pm 0.05^\circ$.

Procedure - A preliminary run is carried out by heating the block quickly and recording the temperature at which the liquid meniscus disappears. Once this approximate temperature is obtained the block is controlled by slowly increasing the temperature (2 to 5deg/hr) in the region of the critical point and monitoring the disappearance and reappearance temperatures of the liquid meniscus.

With careful calibration the mean temperature between disappearance and reappearance gives the critical temperature to ± 0.2 deg.

TABLE 5
PVT MEASUREMENTS FOR ARCTON 12

RUN No	Weight (gms)	Temp ($^\circ\text{C}$)	Press (bar)	COMPRESSIBILITY FACTOR				
				WATSON	EXPTL	DIFF	EXPTL VOL COR	DIFF
1	5.793	39.52	5.95	.896	.890	-.006	.891	-.005
3	2.738	40.50	3.01	.950	.950	.000	.951	.001
4	2.615	60.12	3.09	.959	.961	.002	.963	.004
5	5.902	60.17	6.57	.908	.906	-.002	.908	.000
6	8.712	59.93	9.24	.864	.863	-.001	.865	.001
7	12.077	60.05	12.02	.815	.809	-.006	.811	-.004
9	16.271	60.32	14.98	.754	.748	-.006	.749	-.005
10	14.826	79.68	15.38	.802	.796	-.006	.799	-.003
11	18.610	79.63	18.21	.754	.751	-.003	.754	.000
12	8.789	60.15	14.77	.758	.756	-.002	.757	-.001
13	8.389	79.92	15.71	.798	.796	-.002	.798	.000
14	7.816	80.13	14.88	.811	.809	-.002	.811	.000
15	10.024	80.22	17.92	.761	.759	-.002	.761	.000
16	12.624	80.21	20.91	.703	.703	.000	.705	.002
17	10.707	100.17	20.66	.776	.775	-.001	.778	.002
18	8.706	99.91	17.57	.815	.811	-.004	.815	.000
19	6.998	99.79	14.72	.850	.846	-.004	.850	.000
20	13.135	99.67	23.80	.729	.729	.000	.732	.003
21	15.997	99.79	26.86	.677	.675	-.002	.678	.001
22	19.627	99.90	29.98	.615	.614	-.001	.617	.002
23	25.072	99.86	32.92	.534	.528	-.006	.530	-.004
24	24.277	99.86	32.60	.544	.540	-.004	.542	-.002
25	1.290	80.00	2.94	.967	.968	.001	.970	.003
26	1.268	80.14	2.89	.968	.968	.000	.971	.003
27	5.781	80.31	11.67	.859	.857	-.002	.859	.000

VOLUME OF MEASURING MANIFOLD

RUNS 1-11 186.14 mls
RUNS 12-27 103.08 mls

TABLE 6
EQUATION OF STATE (MARTIN-HOU) FOR HFC 134a

$$P = \frac{RT}{V - B} + \frac{(A_i + B_i T + C_i \exp(-KT))}{(V-B)^{i+1}}$$

where $T = T/T_c$, $P = P/P_c$, $V = V/V_c$

$$B = 0.27320512503$$

$$K = 10.017112768$$

$$R = 8.31434 \times T_c$$

($P_c V_c$ mol.wt)

$$T_c, P_c, V_c = 374.15, 40.55, 2.0347823153$$

$$A_1, B_1, C_1 = -9.8781473793, 4.5038162268, -5444.0183833$$

$$A_2, B_2, C_2 = 8.4889276646, -4.1940175591, 1810.7383319$$

$$A_3, B_3, C_3 = -1.7381548519, 0.0, 0.0$$

$$A_4, B_4, C_4 = -1.0275969978, 1.2276987529, 1794.9218452$$

CRITICAL PRESSURE

Apparatus - This is the same as described for PVT (Fig 1) except the expansion vessel on the measurement manifold is removed to give an overall volume of approximately 30 ml.

Procedure

Calibration and accuracy - The PRTs and Kaman Sciences pressure transducer are calibrated as described above and are accurate to $\pm 0.05^\circ$ and $\pm 0.05\%$ full range pressure respectively.

Operation - The pressure transducer is controlled at a temperature 25 degrees above the highest temperature at which the sample pressure is to be measured, to avoid condensation. Sufficient material to saturate the vapour space of the apparatus up to the critical point is vacuum distilled into the measurement manifold. The saturated vapour pressure at temperatures up to and above the observed critical temperature is then measured. By changing the weight of material transferred to the measurement manifold, and hence the vapour density in the supercritical region, it was observed that lines of constant vapour density on a pressure temperature plot converged at the critical point. Therefore if sufficient material to saturate the vapour up to the critical point, without liquid filling the apparatus, has been added, the observed pressure at the observed critical temperature should be the same for various weights of material transferred. The critical pressure using this method has an estimated accuracy of ± 5 bars.

SATURATED LIQUID VAPOUR PRESSURE

Apparatus - Fig 3 shows a typical apparatus. It consists of a filling manifold as described above and a measurement manifold. In this case the measurement manifold is trace heated up to and including the MKS baratron transducer except for the sample vessel which is controlled in a water glycol bath. The bath operates over a temperature range -40°C to $+90^\circ\text{C}$. This is controlled to better than $\pm 0.05^\circ$ using a combination of a Cryocool heater/fridge with an Exatrol controller. The temperature of the sample is monitored with a PRT strapped to the sample vessel accurate to $\pm 0.05^\circ$. The MKS baratron pressure transducer is controlled at a temperature 25° above the highest run temperature to avoid condensation. Its accuracy is $\pm 0.1\%$ of reading over its full range.

This apparatus is semi-automated using an Apple 2e computer. The computer updates the bath temperature through a prescribed range, logs the temperature and pressure, assesses that an equilibrium condition is achieved and incorporates various failsafe procedures.

Procedure - Sample preparation and calibration of temperature and pressure transducers are the same as above. The sample is transferred to the measurement manifold and the computer starts the temperature program. At the end of the run the temperature pressure data is fitted into the Antoine equation (equ 1) and the normal boiling point is calculated.

$$\ln P^* = A + B/(C+T) \quad (1)$$

The vapour pressure data and critical properties data are then combined in the Extended Antoine equation (equ 2)

$$\ln P^* = A + B/(C+T) + DT + E \ln T \quad (2)$$

Results for HFC 134a, HCFC 123 and HFC 125 are shown in Table 7.

TABLE 7
SUMMARY OF PHYSICAL PROPERTIES

HFA 134a	HCFC 123	HFA 125	ACCURACY	
Tc (K)	374.15	457.5	339.4	±0.2
Pc (bar)	40.55	33.7	35.9	±0.5
n Bpt (K)	246.93	301.22	224.42	±0.05

EXT. ANTOINE

A	137.1371	52.0597	74.8328
B	-6068.74	-4083.41	-3974.74
C	0.0	0.0	0.0
D	0.035196	0.005223	0.019813
E	-22.0058	-6.60028	-11.3707

CONCLUSION

Both Experimental and Estimation methods have a role to play in generating data for our customers.

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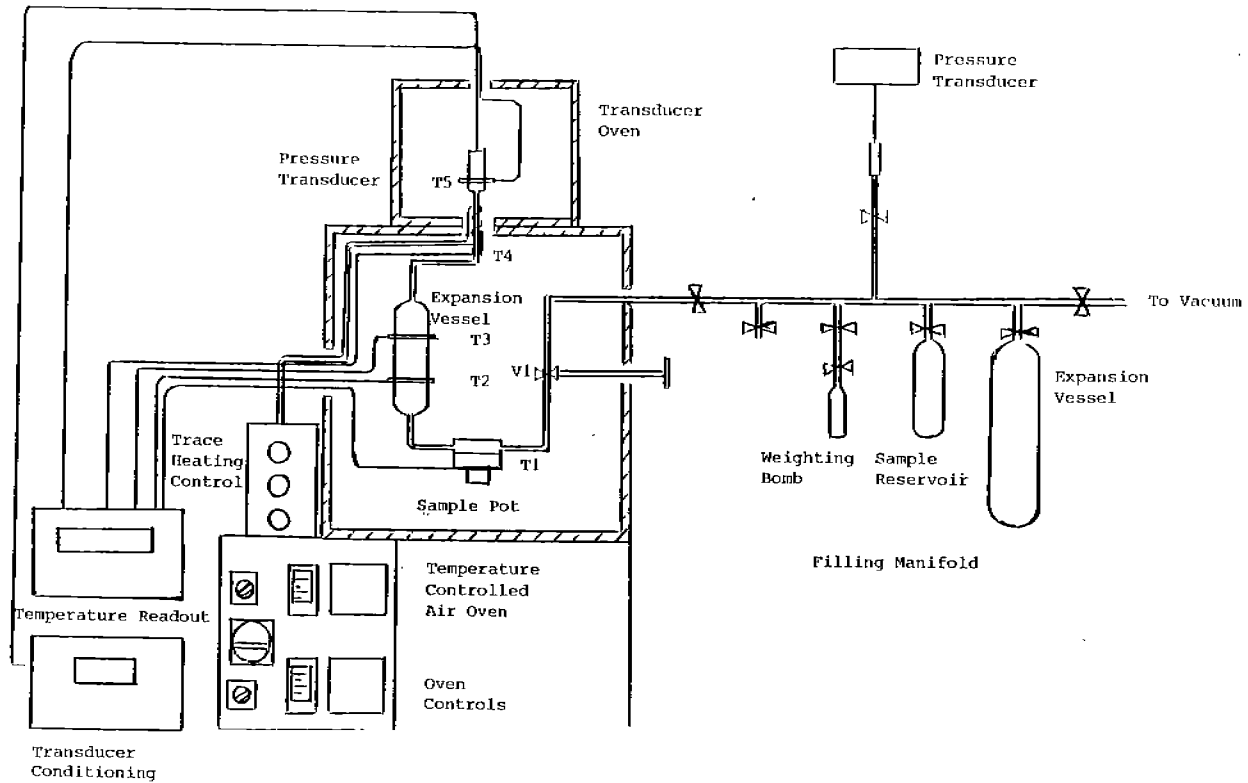
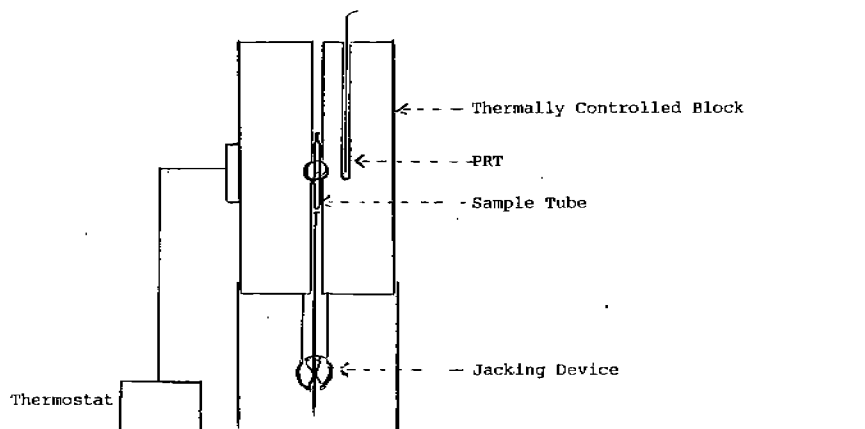


FIG 1 - PVT APPARATUS

FIG 2 - CRITICAL TEMPERATURE APPARATUS



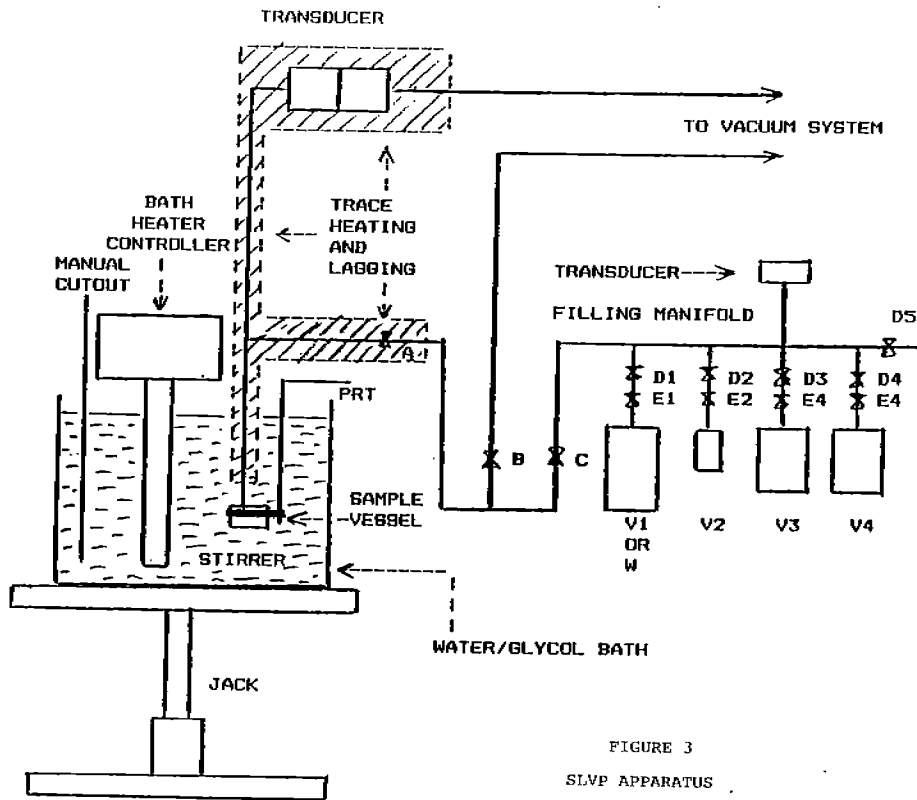


FIGURE 3
SLVP APPARATUS