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A GENERAL CORRELATION BETWEEN INTERNAL PRESSURE OF LIQUIDS AND TEMPERATURE

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ABSTRACT

A simple linear relation, Pi = m (Tc-T) + C, is established between inter- nal pressure of various types of liquids and temperature in the entire range of liquid phase. The physical significance of paramenters appearing in the lin ear correlation has been discussed. The constant 'C' has been identified as a measure of stability of liquids. The 'C' values has been termed as residual internal pressure.

Keyword:- Internal Pressure, Viscosity, Temprature, Residual Internal Pressure etc.....

INTRODUCTION

Attempts have been made previously by re- searchers to correlate Internal Pressure (Pi) with viscosity (n) and temperature (T). Suryanarayana and Govindaswamy (1961) have correlated em pirically internal pressure (Pi) of liquids with vis- cosity (n) at different temperatures by the relation $\eta = A_e$ BPi where, A and B are constants and n is viscosity.

Doolittle (1065) has also tried to estimate the internal pressure over broad range of molecular mass and temperature of different liquids by processing specific volume data. However, these relations are of limited application considering various classes of liquids and wide range of tempretures of the liquid state. To the best of my knowledge, there is no general relationship be- tween internal pressure and temperature which governs the general behaviour of all classes of liq- uids in the entire range of liquid phase.

In the present investigation, a general correlation between internal pressure and tempera- ture is proposed, for the first time, which is appli- cable to various classes of liquids comprising metallic, inert gas, inorganic diatomic and organic liquids having different functional groups in the entire range of temperature of the liquid phase.

Estimation of Interest Pressure:

The internal pressure of liquids may be esti- mated by using the formula, Pi (dE/dV) T_1 = lv/Vi Iv x dl: where the terms have their usual significance. The Iv values of the substances have been calculated using modified Watson Giacalone equation

[Prasad, 1998]. the density data have been taken from Lange [1967] and Perry's [1973] Hand books and in some cases it has been estimated using Mathias equation [6]. The values of Pi and the correspoding temperatures of some representative liquids have been listed in table 1-8.

The Linear Relation between Pi and T:

From closer observation of the estimated values of internal pressure (Pi), it has been found that there is gradual decreasing trend of Pi with increasing temperature in the whole phase of liquid state. This trend attracted me to investigate a general and simple correlation, if any, between Pi and T. Among a number of functional relations for Pi vs (Tc-T), the following linear relatin was found to give a better fit to the estimated values. of Pi:

$$Pi=m (Tc-T) + C$$

Where, 'm' and 'C' are the parameters which vary from liquid to liquid. The representative graphs have been shown in figures 1-8. The values of 'm' and 'C' were obtained by the least square fit method of regression analysis. In case of each member of Various Classes of liquids studied. the correlation was found to be of high degree. The correlation coefficient (R) ranges from 0.83 to 0.99.

The values of m, C & R for 75 liquids studied have been mentioned in table 9.

DISCUSSION

The results clearly reveal that the linear cor- relation is indeed valid for all types of liquids for nearly entire range of liquid phase. However, points close to the critical temperature is found to deviate from linearity almost in all cases. The departure from linearity for Pi vs (Tc-
T) graphs seems realistic in view of the fact that almost all physical parameters of a liquid exhibit anomalous behaviour near c.t. (Critical temperature). The constant 'C' denotes the internal pressure at the c.t. and my be termed the residual internal pressure i.e. C = Pir at c.t. It has the dimension of internal pressure and the unit is cal/g/cc. The other least square fit parameter 'm' signifies the rate of variation of Pi with T and its unit is Cal/g/cc, K.

The close examination of the 'C' values of metallic liquids clearly reveals that there is marked relationship of atomic mass with the constant 'C'. The decreasing values of Pi in a group of P.T. reflects the greater degree of instability with increasing mass number. Thus constant 'C' of equation Pi = m (Tc-T) + C is a measure of stability of atoms of metallic liquids. Larger the value of 'C' greater will be the stability. This seems physically true because increase in atomic number will lead to decrease in Vanderwalls attraction among the atoms which in turn will require lesser amount of energy to evaporate the liquid. However, Au & W show exceptions to this general trend of stability probably because of their extral stability.

In organic liquids, however there is deviation of the above rule. Although Carboxylic acids conform to the decreasing trend of variation of 'C' with molecular mass, other classes of organic liquids initially show a decreasing trend then exhibit a rising trend in 'C'. Inert gas liquids also exhibit a decreasing trend in 'C' except Xe.

Table 1

Chromium

T	Tc-T	dl	Iv	Pi
2140	6762	6.382	1471.15	9388.68
2200	6702	6.357	1466.17	9321.06
2300	6602	6.317	1457.82	9208.58
2400	6502	6.276	1449.39	9096.28
2500	6402	6.235	1440.88	8984.16
2600	6302	6.194	1432.28	8872.19
2700	6202	6.154	1423.60	8760.82
2800	6102	6.113	1414.84	8648.86
2900	6002	6.072	1405.98	8537.42
2930	5972	6.060	1403.31	8504.06
3000	5902	6.031	1397.03	2426.17
3100	5802	5.991	1387.99	8315.08
3200	5702	5.949	1378.85	8204.15
3300	5602	5.909	1369.71	8093.37
3400	5502	5.869	1360.27	7982.76
3500	5402	5.828	1350.82	7872.27
400	4902	5.624	1301.87	7321.79
4500	4402	5.420	1249.72	6773.92
5000	3902	5.217	1193.76	6227.41
5500	3402	5.013	1133.15	5680.39
6000	2902	4.809	1066.72	5030.08
6500	2402	4.606	972.70	4572.16
7000	1902	4.402	908.50	3999.03
7500	1402	4.198	809.08	3396.58
8000	902	3.994	684.23	2733.07
8500	402	3.791	503.30	1907.84
8902	0	3.627		

Table 2

Aluminium

T	Tc-T	dl	Iv	Pi
933	7177	2.333	2520.98	5880.65
1000	7110	2.322	2512.01	5834.04
1100	7010	2.307	2498.53	5764.61

1200	6910	2.292	2484.93	5695.31
1300	6810	2.277	2471.20	5626.12
1400	6710	2.261	2457.30	5557.11
1500	6610	2.286	2443.36	5488.10
1600	6510	2.231	5419.42	2429.25
1700	6410	2.216	2415.01	5350.80
1800	6310	2.200	2400.62	5282.29
1900	6210	2.185	2386.09	5213.91
2000	6110	2.169	2371.41	5145.64
2100	6010	2.155	2356.59	5077.53
2200	5910	2.139	2341.61	5009.52
2300	5810	2.124	2326.48	4941.65
2400	5710	2.109	2311.18	4873.88
2500	5610	2.094	2295.71	4803.23
2600	5510	2.078	2280.08	4738.72
2700	5410	2.063	2264.26	4671.29
2720	5390	2.060	2261.08	4657.82
2800	5310	2.047	2248.27	4603.99
2900	5210	2.033	2232.08	4536.78
3000	5110	2.017	2215.71	4469.69
4000	4110	1.865	2039.72	3803.43
5000	3110	1.712	1834.68	3141.14
6000	2110	1.559	1583.22	2469.03
7000	1110	1.407	1240.32	1745.01
8000	110	1.254	1515.23	646.31
8110	0	1.238	0.00	0.00 Table 3

Helium

T	Tc-T	dl	Iv	Pi
1.07	4.00	0.1459	14.826	2.1631
1.46	3.61	0.1460	14.259	2.0818
1.79	3.28	0.1462	13.749	2.0101
1.97	3.10	0.1464	13.457	1.9701
0.08	2.99	0.1466	13.273	1.9458
0.17	2.90	0.1469	13.121	1.9274
2.24	2.83	0.1466	12.999	1.9056

2.43	2.64	0.1457	12.660	1.8446
3.17	1.90	0.1395	11.173	1.5586
3.30	1.77	0.1385	10.876	1.5063
3.77	1.30	0.1311	9.673	1.2681
4.09	0.98	0.1255	8.688	1.0931
4.10	0.97	0.1253	8.654	1.0843
4.46	0.61	0.1165	7.555	0.8452
4.58	0.49	0.1139	6.676	0.7604
5.07	0.00	0.0693	0.000	0.000 Table 4

Propene

T	Tc-T	dl	lv	Pi
88.0	276.2	0.756	138.124	104.427
90.0	274.2	0.754	137.744	103.815
100.0	264.2	0.742	135.813	100.756
110.0	254.2	0.730	133.836	97.710
120.0	244.2	0.718	131.811	94.675
130.0	234.2	0.706	129.732	91.649
140.0	224.2	0.695	127.600	88.687
150.0	214.2	0.683	125.406	88.637
160.0	204.2	0.671	123.1 18	85.333
170.0	194.2	0.659	120.820	82.637
180.0	184.2	0.647	118.420	79.648
190.0	174.2	0.636	115.932	76.668
200.0	164.2	0.624	113.357	73.689
210.0	154.2	0.612	110.898	70.714
220.0	144.2	0.600	107.898	67.739
225.0	139.2	0.594	106.460	64.761
230.0	134.2	0.588	104.991	63.269
250.0	114.2	0.565	98.786	61.776
270.0	94.2	0.559	91.779	51.304
290.0	74.2	0.553	83.822	46.353

310.0	54.2	0.494	74.392	43.383
330.0	34.2	0.470	62.450	36.746.
350.0	14.2	0.447	84.717	29.780
364.2	0.0	0.430	0.000	19.976 Table 5

Butyne

T	Tc-T	dl	lv	Pi
147.0	301.0	0.807	132.237	106.765
150.0	298.0	0.804	131.734	105.933
160.0	288.0	0.793	130.037	103.167
170.0	278.0	0.783	128.302	100.407
180.0	268.0	0.772	126.528	97.655
190.0	258.0	0.761	124.713	94.910
200.0	248.0	0.750	122.854	92.171
220.0	228.0	0.729	118.990	86.707
240.0	208.0	0.707	114.911	81.557
260.0	188.0	0.686	110.580	75.811
280.0	168.0	0.664	105.953	70.354
281.1	166.9	0.663	105.689	70.054
300.0	148.0	0.642	100.971	64.870
320.0	128.0	0.621	95.551	59.327
340.0	108.0	0.599	89.577	53.687
360.0	88.0	0.578	82.871	47.881
380.0	68.0	0.556	75.136	41.792
400.0	48.0	0.535	65.822	35.192
420.0	28.0	0.513	53.631	27.518
440.0	8.0	0.492	33.317	16.337
448.0	0.0	0.483	0.000	0.000 Table 6

Butyl alcohol

T	Tc-T	dl	Iv	Pi
182.8	380.2	0.917	180.53	165.575
190.0	373.0	0.911	179.2	163.119
200.0	363.0	0.900	177.38	159.719

210.0	353.0	0.891	175.51	156.329
220.0	343.0	0.881	173.60	152.939
230.0	333.0	0.871	171.66	149.561
240.0	323.0	0.862	179.69	146.495
250.0	313.0	0.852	167.67	142.824
270.0	293.0	0.832	163.52	136.108
290.0	273.0	0.813	159.18	129.401
300.0	263.0	0.803	156.94	126.054
320.0	243.0	0.784	152.29	119.357
340.0	223.0	0.764	147.40	112.657
360.0	203.0	0.745	142.23	105.940
380.0	183.0	0.425	136.74	99.192
390.7	172.3	0.715	133.64	95.553
400.0	163.0	0.706	130.85	92.774
420.0	143.0	0.687	124.50	85.470
470.0	93.0	0.638	105.72	67.438
520.0	43.0	0.590	78.86	46.470
540.0	23.0	0.570	62.17	35.426
550.0	13.0	0.560	50.05	28.033
560.0	3.0	0.550	28.67	15.779
563.0	0.0	0.547	0.00	0.000

Table 7

Formaldehyde

T	Tc-T	dl	lv	Pi
181.0	103.2	1.146	1000.474	1146.99
190.0	94.2	1.120	966.378	1082.16
200.0	84.2	1.090	926.032	1009.58
210.0	74.2	1.061	882.594	936.10
220.0	64.2	1.031	835.355	861.28
230.0	54.2	1.001	783.298	784.42
240.0	44.2	0.972	724.883	704.47
250.0	34.2	0.942	657.563	619.59
252.0	32.2	0.936	642.677	601.76
260.0	24.2	0.913	576.577	526.22
270.0	14.2	0.883	470.884	415.79
280.0	4.2	0.853	296.375	252.95
284.2	0.0	0841	0.000	0.000

Table 8

Propionic acid

T	Tc-T	dl	lv	Pi
251	359	1.037	172.48	171.852
260	350	1.027	170.82	175.486
270	340	1.017	168.95	171.757

280		330		1.006		167.05		168.038		
300		310		0.985		163.12		160.593		
320		290		0.963		159.04		153.173		
340		270		0.942		154.78		145.757		
360		250		0.920		150.32		138.940		
380		230		0.899		145.63		130.907		
400		210		0.877		140.68		123.446		
410		200		0.867		138.10		119.705		
414		196		0.863		137.04		118.200		
420		190		0.856		135.43		115.941		
440		170		0.835		129.83		108.368		
460		150		0.813		123.80		100.710		
480		130		0.792		117.25		92.849		
500	110	0.770	110.04	84.784	550	60	0.717	27.40	62.664	
570		40		0.696		74.92		52.113		
590		20		0.674		57.57		38.812		
600		10		0.663		84.24		29.350		
610	0			0.653		0.00		0.000		

Table 9

Constants of equation Pi = m (Tc-T) +C

Substances	m	C	R
Be	1.7539	2136.966	0.9934
Mg	0.7331	340.999	0.9911
Ca	0.3447	169.089	0.9909
Sr	0.2902	132.599	0.9938
Ba	0.2003	99.880	0.9939
Zn	1.3904	378.968	0.9691
Cd	0.9324	282.361	0.9909
Hg	0.9638	149.139	0.9896
Cu	1.2675	1215.890	0.9933
Ag	0.8351	745.146	0.9937
Au	0.8057	868.188	0.9943
Fe	1.1505	1403.675	0.9604
CO	1.5262	1668.849	0.9922
Ni	1.5690	1562.113	0.9943
Cr	1.2017	1368.949	0.9927
MO	0.6027	1185.138	0.9948
W	1.8903	3909.816	0.9929
Al	0.7429	618.698	0.9948
Ga	0.8745	825.764	0.9938
In	0.5592	441.870	0.9958

As	1.2587	279.226	0.9833
Sb	0.7243	335.359	0.9941
Bi	0.4724	371.330	0.9965
Ge	0.5584	666.781	0.9942
Sn	0.5843	521.038	0.9961
Pb	0.3997	334.981	0.8272
Sc	0.6192	747.034	0.9929
Y	0.4401	452.052	0.9953
La	0.2632	869.356	0.8829
He	0.4698	0.5189	0.9586
Ne	1.3680	3.769	0.9793
Ar	0.7578	7.464	0.9902
Xe	0.5323	9.456	0.9895
N2	0.2616	2.926	0.9838
O_2	0.7467	9.382	0.9928
F_2	0.6249	8.132	0.9846
$C1_2$	0.4749	21.258	0.9871
Br_2	0.4300	23.894	0.9899
p-H_2	0.4403	1.411	0.9877
N-H_2	1.1504	2.302	0.9922
P-D_2	0.7382	2.554	0.9600
n-D_2	0.7273	2.9307	0.9735
H-D	0.6586	2.1285	0.9934
1-propene	0.2886	25.359	0.9974
1-Butene	0.2774	15.604	0.9918
1-Pentene	0.2422	14.577	0.9921
1-Hexene	0.2323	12.771	0.9914
1-Heptene	0.2162	13.353	0.9915
1-Octene	0.2065	14.179	0.9916
1-Nonene	0.2015	14.655	0.9909
1-Brtyne	0.3074	16.632	0.9895
1-Pentyne	0.2673	14.345	0.9903
1-Hexyne	0.2322	14.390	0.9919

1-Heptyne	0.2143	13.974	0.9907
1-Octyne	0.2052	12.191	0.9908
1-Nonye	0.1960	12.794	0.9891
Butyl alcohol	0.3852	23.377	0.9912
Amyl Alcohol	0.2609	33.975	0.8572
Hexyl alcohol	0.2615	16.897	0.9877
Heptyl alcohol	0.2319	14.983	0.9870
Decyl alcohol	0.1915	13.191	0.9899
Lauryl alcohol	0.1979	14.237	0.9857
Formaldehyde	9.5546	226.669	0.9698
Acetaldehyde	5.9917	212.999	0.9848
Propionaldehyde	5.6233	211.696	0.9782
Butyraldehyde	5.9687	225.741	0.9848
n-Vateraldehyde	7.3519	303.675	0.9869
n-Caproicaldehyde	13.1266	498.919	0.9855
Propionic acid	0.4313	29.632	0.9875
n-Butyric acid	0.3703	24.998	0.9895
n-Valeric acid	0.3248	22.775	0.9909
Caproic acid	0.3094	20.399	0.9879
Caprylic acid	0.2850	20.378	0.9882

Graph of Pi Vs (Tc-T)
for Chromium

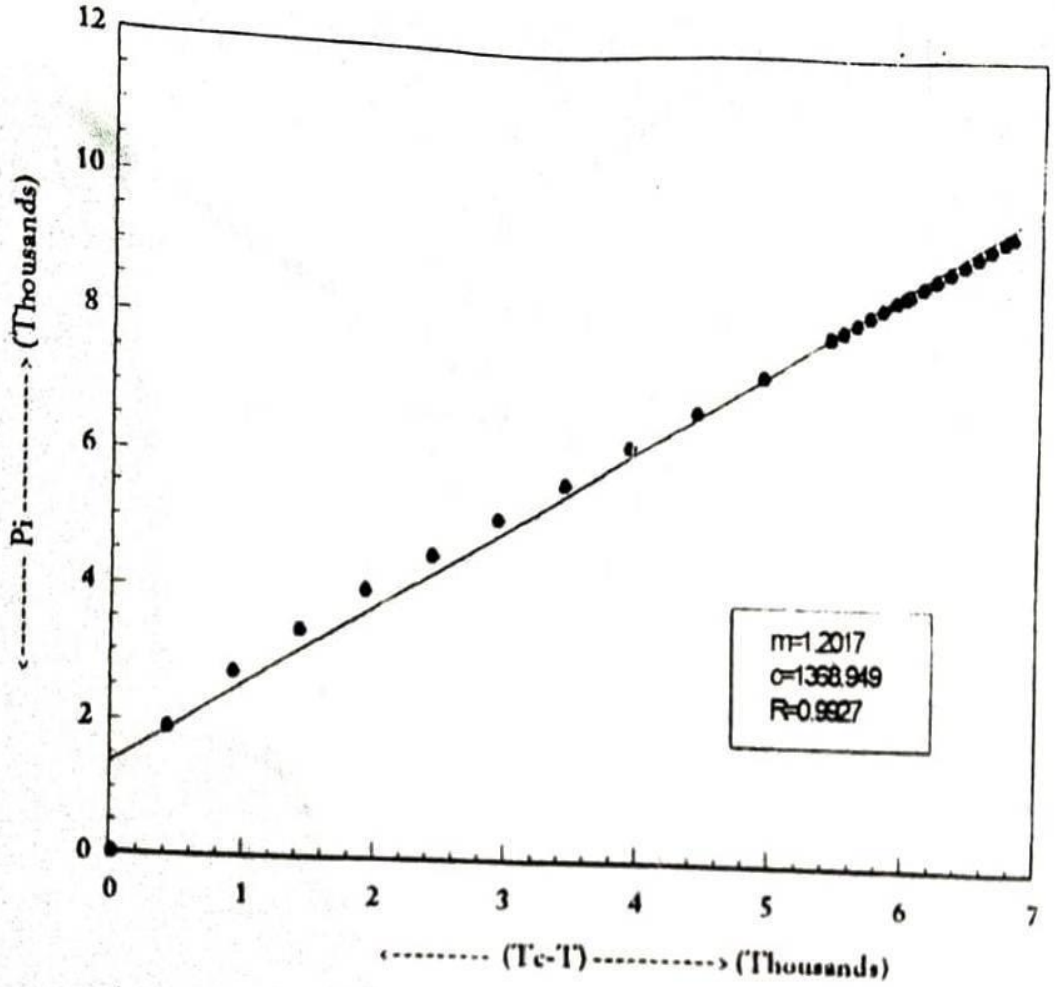

Fig 1.

Graph of Pi Vs (To-T)
for Aluminium

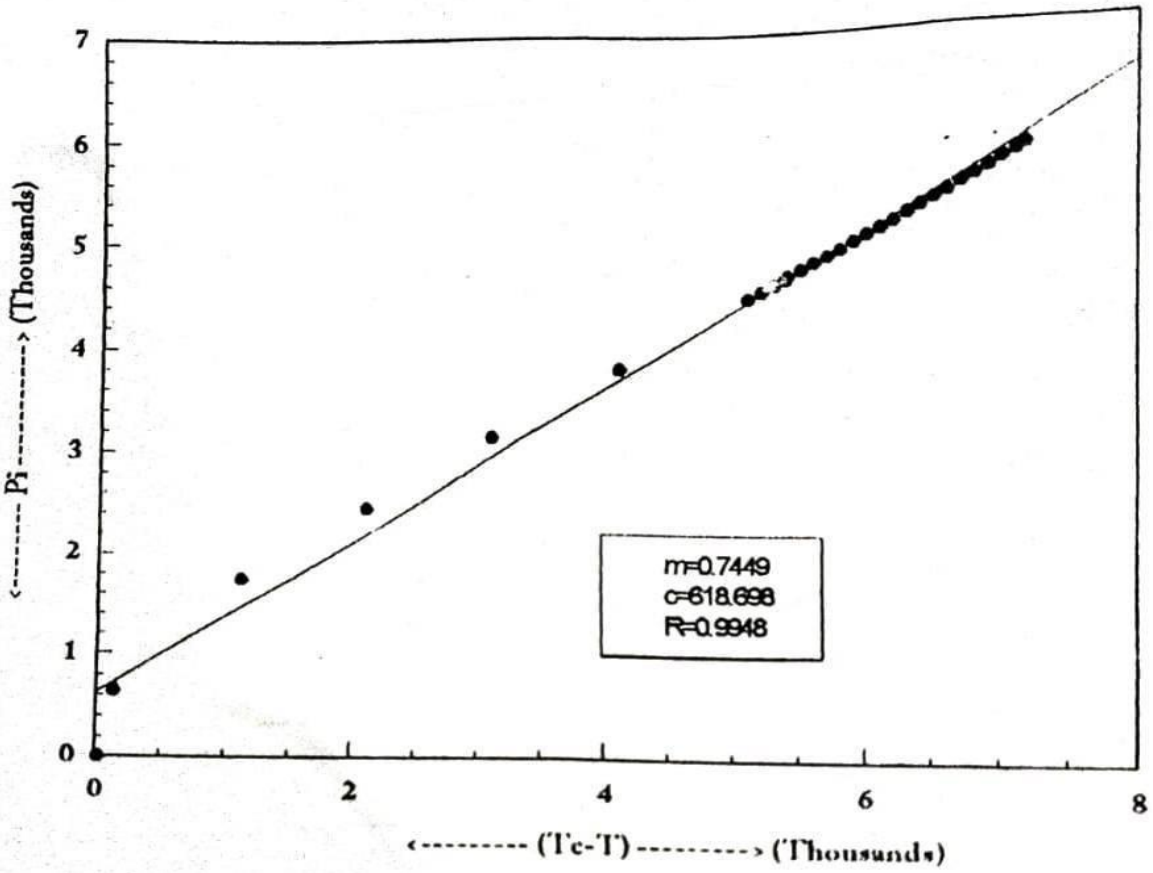

Fig 2

Graph of Pi Vs (To-T)
for Helium

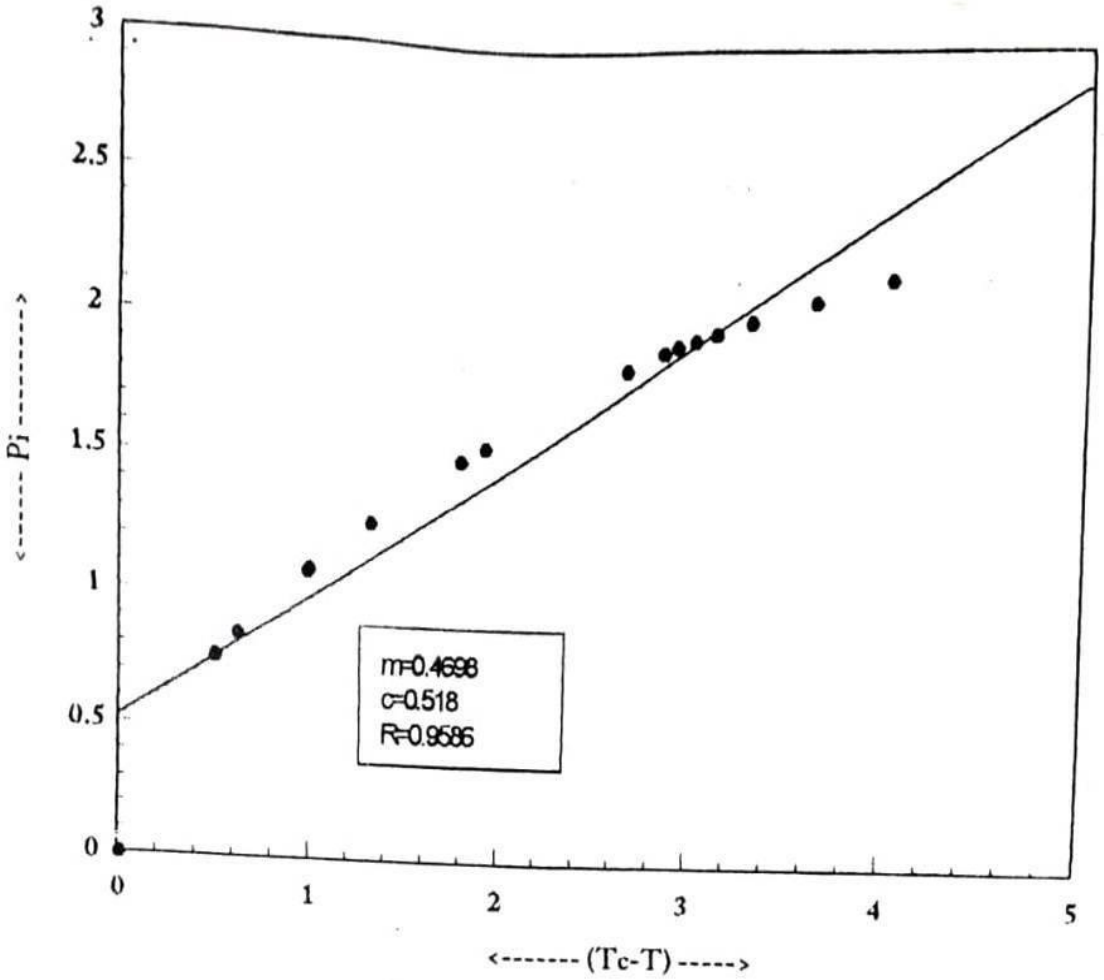

Fig 3

Graph of Pi Vs (To-T)
for 1-Propene

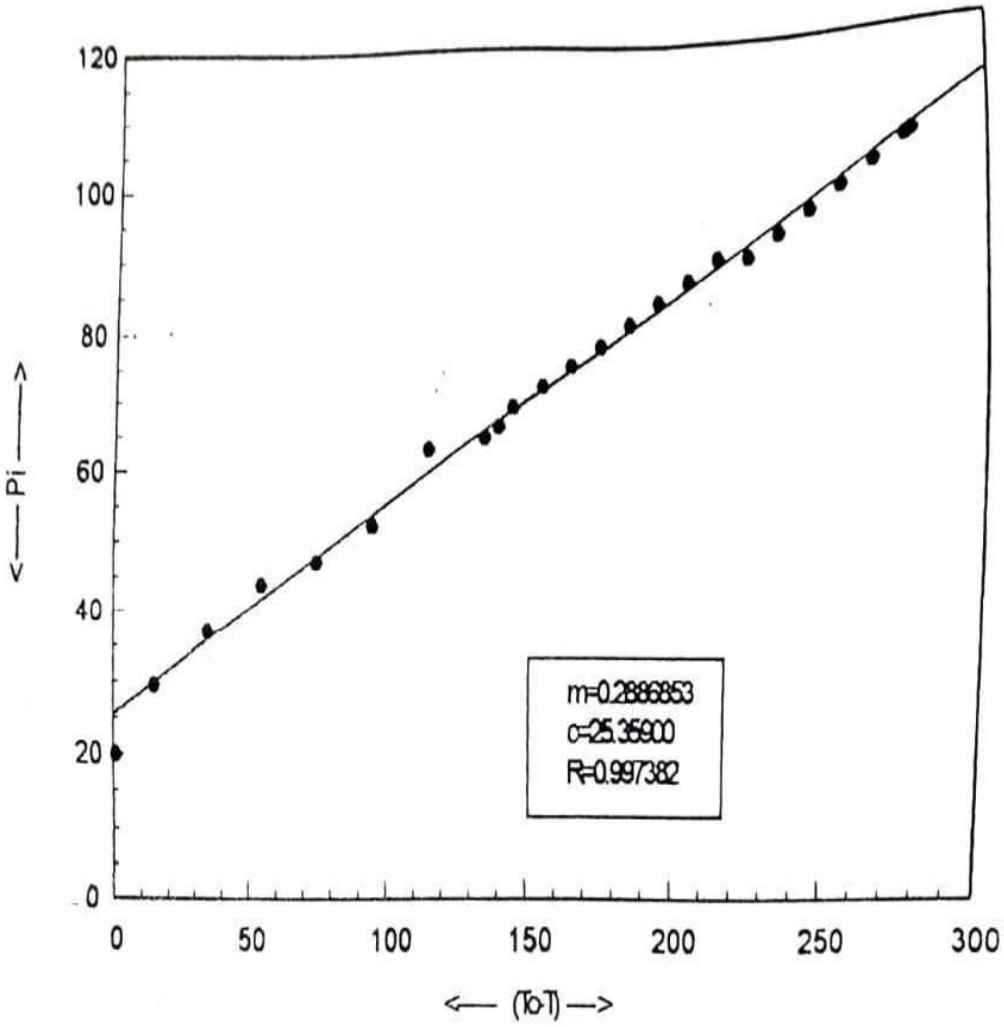

Fig 4

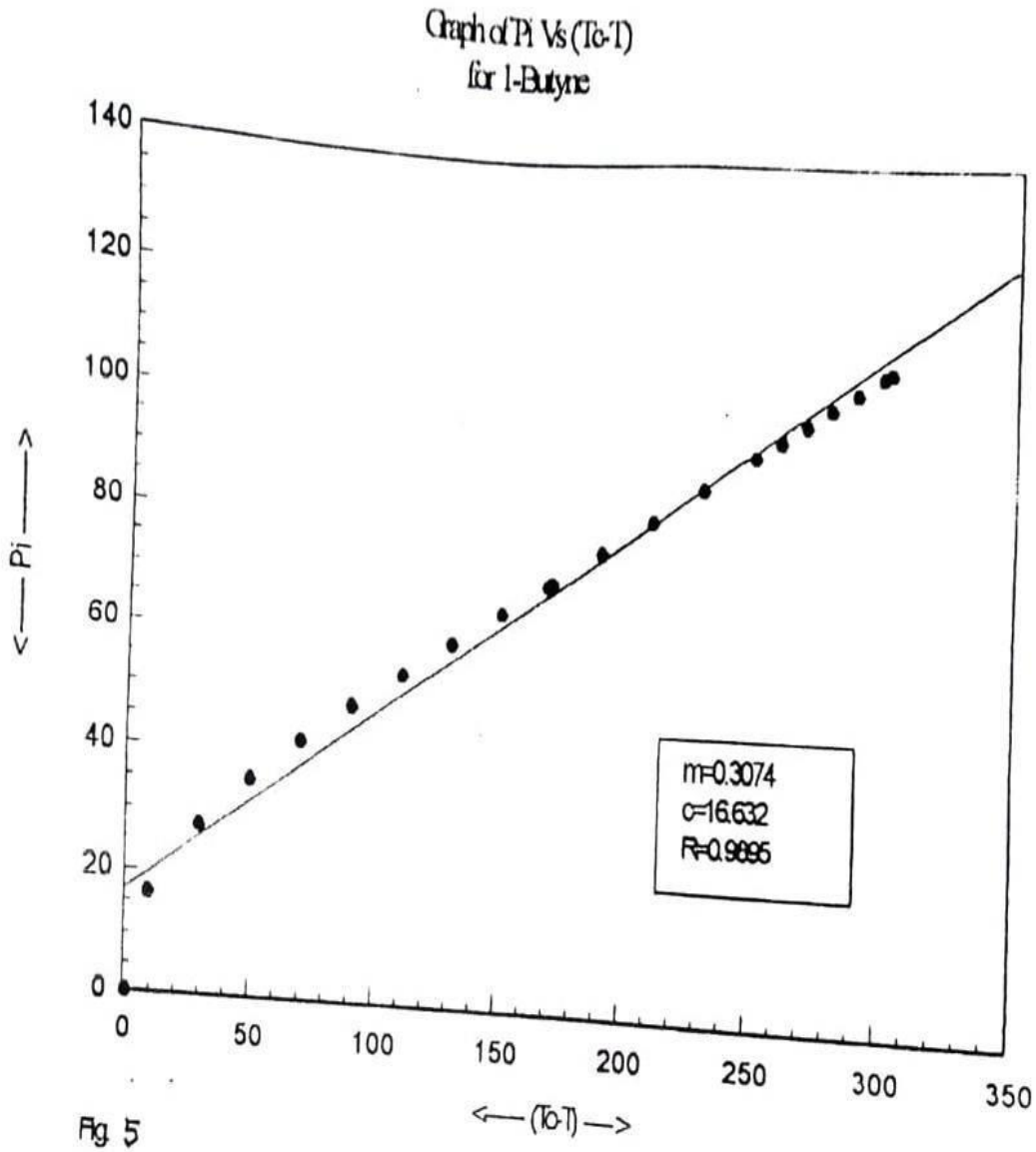
Graph of Pi Vs (To-T)
for 1-Butyne
140
120
100
80
60
40
20
0
<— Pi —>
0
50
100
150
200
250
300
350
<— (To-T) —>
m=0.3074
c=16.632
R=0.9895

Fig. 5

Graph of Pi Vs (To-T)
for n-Butyl Alcohol

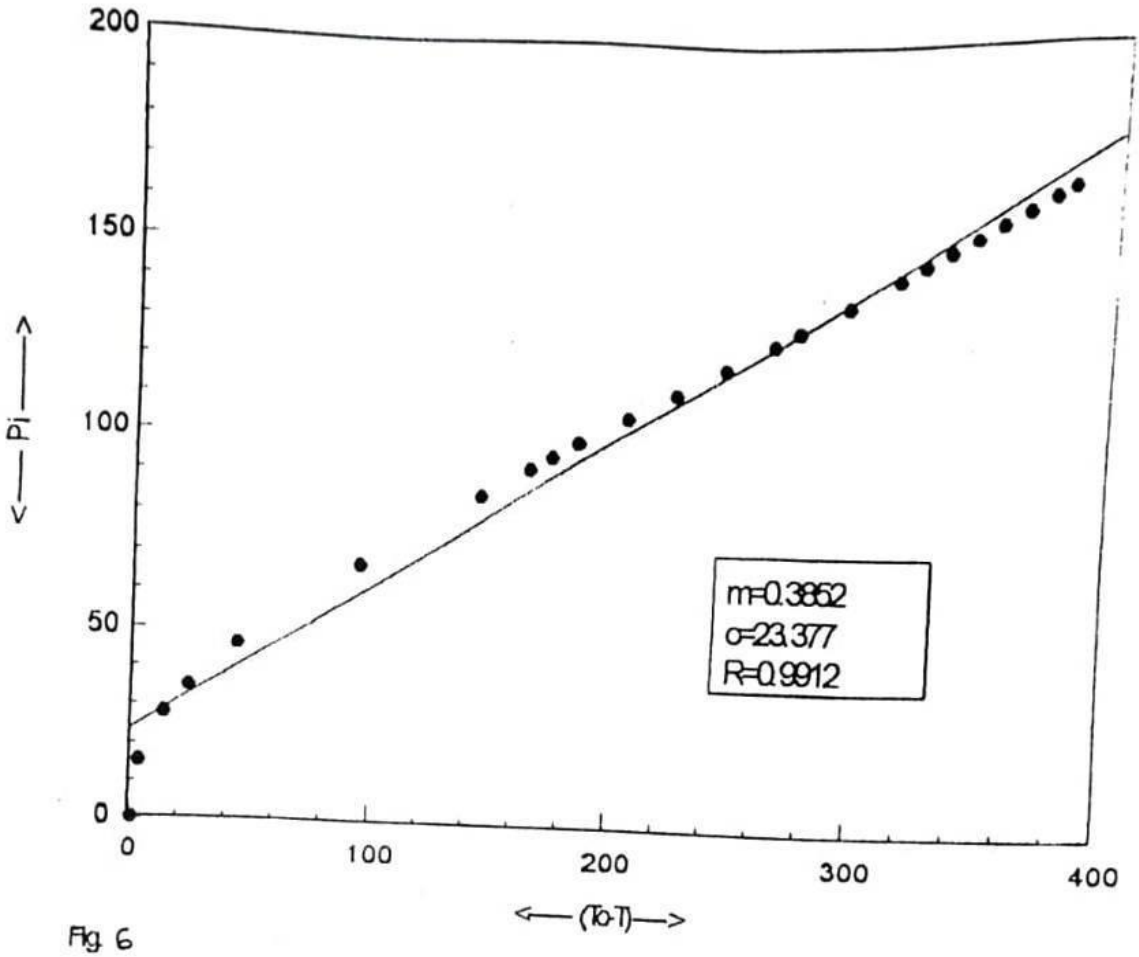

Fig. 6

Graph of Pi Vs (To-T)
for Formaldehyde

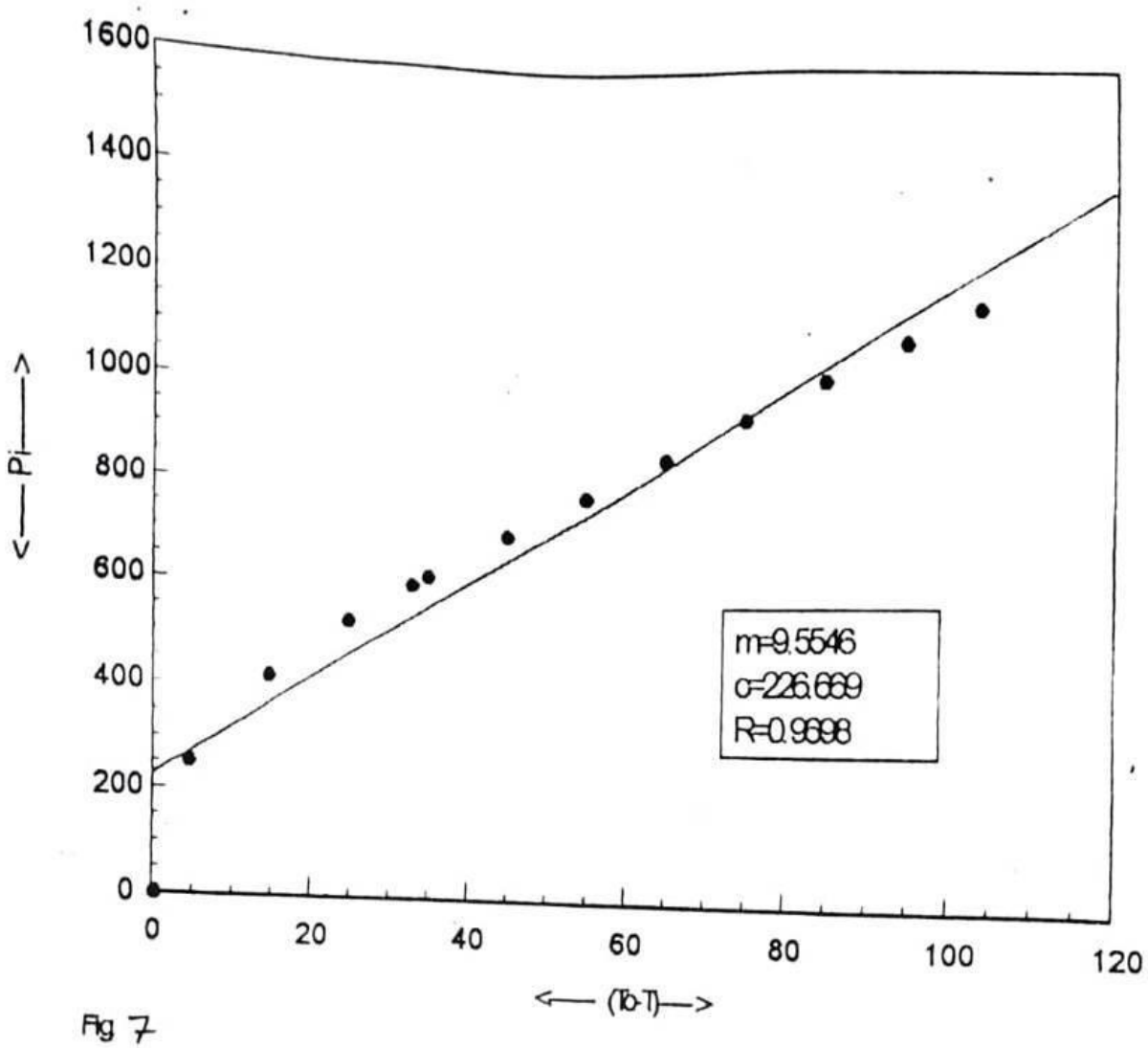

Fig 7

Graph of Pi Vs (To-T)
for Propionic acid

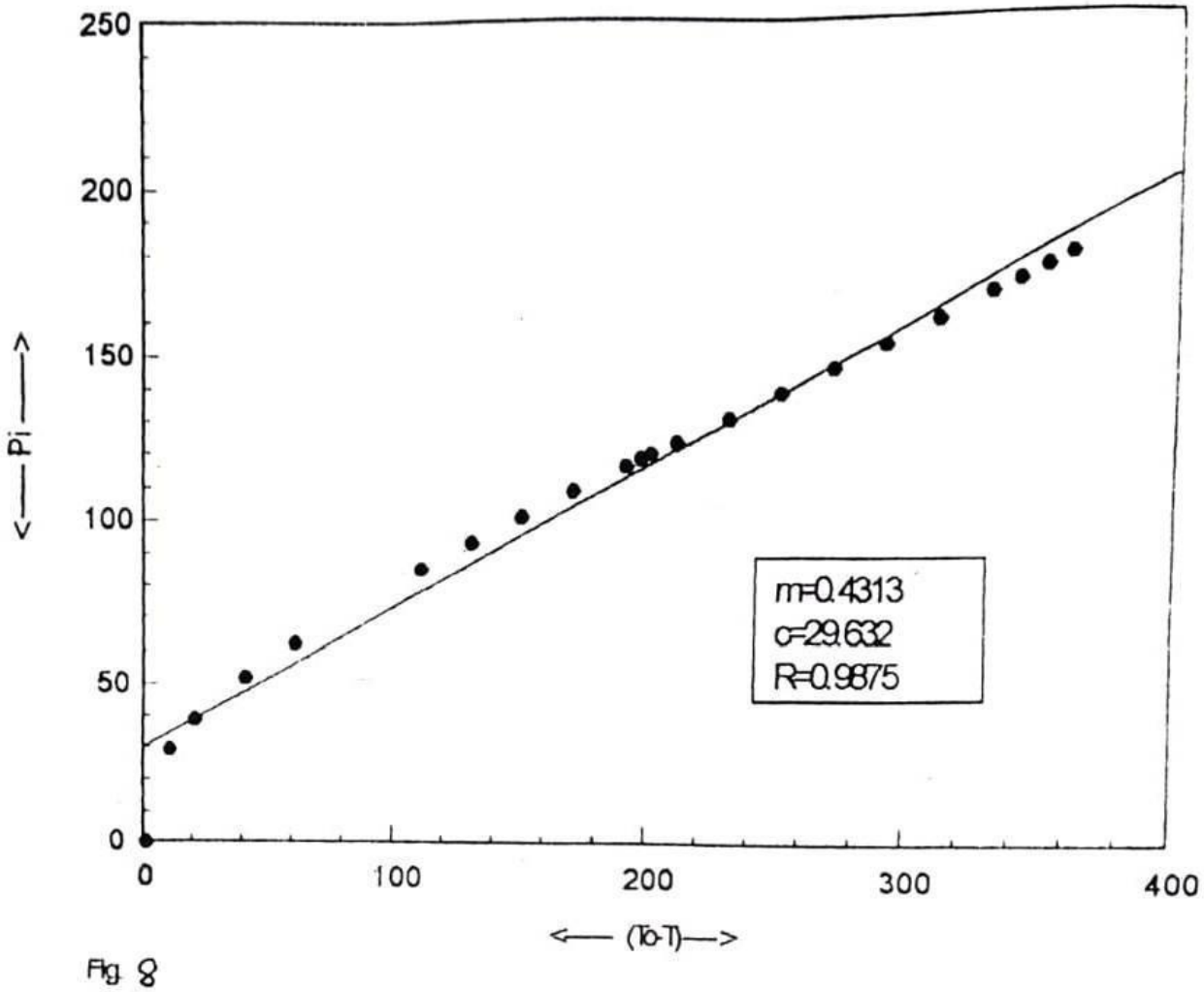

Fig. 8

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