THE USE OF IMPROVED METHODS TO CRITICALLY ASSESS AND FIT THERMODYNAMIC DATA FOR THE NEW REFRIGERANTS[1]

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[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado, U.S.A.

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ABSTRACT

As a manufacturer of the new ozone friendly refrigerants ICI needs to provide thermodynamic and physical property data on these new materials in a form suitable for the refrigeration engineer to use. To generate tables of thermodynamic data and datasheets for fluids such as R32 (CF_2H_2) and R125 (C_2F_5H) literature data for vapour pressure and liquid density are correlated to standard equations while PVT, and speed of sound data are correlated to the Martin-Hou equation of state.

The aim of any procedure for correlating experimental data should be to place the correlation within the experimental error of as many of the datapoints as possible. This can be achieved by using Maximum Likelihood fitting with appropriate analysis of the residual errors. The great advantage of this method is that the process starts with <u>all</u> the available experimental data for a property and avoids the vexed question of choosing datasets. All the data are assessed in an impartial fashion and only those datasets (or parts of datasets) that show significant inconsistencies with the bulk of the data are eliminated from the final fit.

The fitting methods will be explained using data for R32 as an example. The advantages and disadvantages of this method will be discussed and the importance of the errors supplied by the experimentalists will be emphasised.

KEY WORDS: correlation; data; errors; graphical representation; physical properties; refrigerants; thermodynamic properties.

1. INTRODUCTION

As a company committed to the marketing and manufacture of the new ozone benign refrigerants ICI is required to provide thermodynamic and physical property correlations on these new materials to aid the companies that design and manufacture refrigeration systems. For the first of these refrigerants (CF_3-CFH_2 or R134a) this information was required by our customers as early as 1990; well before extensive data had been reported in the open literature. In addition the refrigeration industry prefers a description of the superheated vapour properties which is based upon the Martin-Hou equation [1] rather than the more complex (but much more accurate) equations of state that have been developed as reference correlations for R134a [2], R32 (CF_2H_2) and R125 (C_2F_5H) [3]. Hence, in 1990, when we were required to generate thermodynamic tables and datasheets for R134a we had a limited number of PVT datasets to work with and the datasets quoting the smallest errors had been measured at relatively high temperatures (>303K). The traditional method of choosing one or two of the datasets with the smallest errors and fitting the correlation to them was felt to be inappropriate because of the limited temperature range they covered and the poor ability of the Martin-Hou equation of state to extrapolate accurately. In seeking an alternative approach we decided that our aim should be to fit as many of the data points as possible to within their experimental error. It was found that using these methods we could maximise our use of the data and overcome some of the limitations of the Martin-Hou equation of state [4,5].

Now that significantly more experimental data are available from literature sources we have decided to recorrelate the available data for the major pure refrigerants (R134a, R32, and R125) in order to update the thermophysical property datasheets and tables that we provide to our

customers and to ensure that they are in good agreement with the best data available. The methods used and an outline of the results will be reported here while the details of the fits and the correlations generated will be reported elsewhere [6].

2. THE CORRELATION OF THE DATA

As mentioned above the PVT and speed of sound data for each refrigerant are correlated to the Martin-Hou equation of state:-

$$P = \frac{RT}{V-b} + \sum_{j=1..4} \frac{A_j + B_j + C_j \, exp(-kT)}{(V-b)^{j+1}} \tag{1}$$

where P is pressure, T is temperature, V is specific volume, R is the gas constant and k, b, A_j, B_j and C_j are the fitted parameters. The resulting correlation gave the ideal gas heat capacity as well as the coefficients for the Martin-Hou equation of state.

Vapour pressure data are correlated to the Wagner equation as modified by Ambrose [7], while liquid density data are correlated to a polynomial in X;

where $X = (1-T/Tc)^{1/3}$ and the first coefficient is made equal to the critical density.

The fitting programs use the Maximum Likelihood method [8,9] which requires that all experimental data have estimates of the errors associated with each of the measured properties. For these fitting methods to work most efficiently it is important that these errors are provided by the experimentalist. This experimental error should reflect the reproducibility of the measurement (of temperature, pressure etc.) and hence the influence of random effects within the experimental apparatus.

The fitting method when applied to PVT data seeks to minimise the following objective function:-

$$OF = \sum \left[\left(\frac{T - T^*}{s_T} \right)^2 + \left(\frac{P - P^*}{s_P} \right)^2 + \left(\frac{V - V^*}{s_V} \right)^2 \right] \quad (2)$$

In equation (2) T,P,V are the experimental temperature, pressure and volume respectively while T*, P* and V* are the associated model values; σ_T, σ_P and σ_V are the standard deviations calculated from the error in the experimental values and the summation is over all the datapoints. The deviation of the correlation from the experimental point is normalised by the standard deviation (σ_T, σ_P and σ_V) which has the effect of automatically weighting the correlation towards those datasets with the smallest quoted errors. For the other correlations the objective function is of similar form to that of equation (2) but with only two terms; T, P for vapour pressure and T, ρ for a liquid density correlation.

3. STANDARDISED ERROR PLOTS

The traditional way of fitting data expresses the difference between the correlation and the datapoint in terms of percentage error in one of the properties. For example in correlating vapour pressure data the resulting fit would show the difference between the datapoint and the correlation in terms of %Error in pressure. Figure 1 shows parts of two datasets and a fit expressed in this way. In this case the points of dataset 2 are much more scattered than those of dataset 1 and despite the small errors the correlator may be tempted to fit dataset 1 and ignore dataset 2. However this type of diagram implies that all the errors are in the pressure measurement and ignores the fact that both temperature and pressure are measured experimentally and have associated errors with them. To better represent the difference between the datapoint and the correlation the overall error seen in Figure 1 has to be split into its components (error in

temperature and error in pressure) and these individual errors can then be compared to the experimental errors quoted by the author. This is demonstrated in Figure 2 where the same data have been compared to the same fit as produced by the Maximum Likelihood fitting routine. The fitting software presents the result of a fit in terms of these residual errors divided by a standard deviation derived from the quoted experimental errors given by the author. This "standardised error" in both temperature and pressure for all datapoints can then be displayed graphically. Hence the two graphs in Figure 2 together are equivalent to the graph in Figure 1 in that the data and the correlation in both cases are the same but the residual errors are expressed in different ways. The great advantage of the graphs in Figure 2 is that the correlator can tell at a glance which points have been fitted to the correlation to within their experimental error and for which points this is not true. All points within ±3 units of the x-axis on a standardised error plot for all measured properties have been fitted to within their experimental errors. As seen in Figure 2 both sets of vapour pressure data from Figure 1 can be fitted to within their experimental error using these methods.

4. THE FITTING PROCEDURE

Once all the datasets have been collected together and errors obtained for all measured quantities then each dataset is individually correlated to the equation to check for outliers and datasets that were not experimental. Each dataset should show a random scatter of points around the x-axis and if the error estimates are reasonable this scatter of points should be within ±3 units of the x-axis for all measured properties. Datasets that have been smoothed or derived from correlations are readily detected and dropped at this stage.

All the datasets are then correlated together to give a first fit which may show some points out at up to 100 units from the x-axis (the program limits the maximum standardised error to ±100

units). The most extreme datapoints are removed from the input file and the fit repeated and this typically shows a substantial improvement as a few bad points can throw the correlation seriously out. The process is repeated each time removing the points that seem to be in the most serious disagreement with the bulk of the data. The aim of the fit is to eliminate those points or sets of points that show systematic differences from the bulk of the data which can't be explained by random experimental error.

This process is illustrated in Figure 3 for the correlation of vapour pressure data for R32. The graphs show the global correlation of 20 datasets. Each dataset has been correlated on its own; as a result one set has been rejected because it was smoothed and several outliers have also been deleted. The points used in the first global fit but deleted in subsequent fits are clearly marked in Figure 3. This shows that after three fits and the deletion of a small number of datapoints a good fit is obtained with most of the points within ± 3 units of the x-axis and all within ± 4 units.

.5. RESULTS

As explained above the detailed fits for each refrigerant will be described elsewhere. Table 1 summarises our fitting work for the refrigerants and demonstrates the high proportion of the available data that could be included in the fits.

The advantages and disadvantages of these fitting methods can be summarised:-

Advantages:-

Allows all datasets to be considered for a correlation- no preselection needed.

Datasets and datapoints are deleted systematically using objective criteria.

Standardised error plots highlight points that are inconsistent.

Correlation is weighted towards those datasets with the smallest errors.

Allows the maximum use to be made of the data.

Disadvantages:-

Does require good estimates of experimental errors from the data provider.

Computationally intensive.

6. CONCLUSIONS

If it is accepted that the aim of the correlator is to use a mathematical expression to fit as many of the experimental data points as possible to within their experimental error then the method described here (or something similar) should be the method of choice.

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Table 1:- Summary of the Data Fitted for Three Refrigerants

	Datasets		Datapoints		%Datapoints
	Considered	Used	Considered	Used	Used
R32					
Vapour Pressure	22	19	583	515	88
Liquid Density	11	9	177	125	71
PVT	14	12	1612	1321	82
Speed of Sound	2	2	135	102	76
R134a					
Vapour Pressure	20	16	578	428	74
Liquid Density	15	14	228	186	82
PVT	12	11	1086	895	82
Speed of Sound	4	3	223	179	80
R125					
Vapour Pressure	15	11	500	414	83
Liquid Density	8	8	123	116	94
PVT	13	13	1044	785	75
Speed of Sound	2	2	221	210	95

FIGURE CAPTIONS

Fig. 1. The difference between experimental data and a vapour pressure correlation for R32 expressed in terms of % Error in Pressure = (P(exp)-P(corr))*100/P(corr). Partial datasets shown are:- Set 1 [10], Set 2 [11].

Fig. 2. The difference between experimental data and a vapour pressure correlation for R32 expressed as standardised error plots for both temperature and pressure. Standardised error in temperature = $(T-T^*)/\sigma_T$; standardised error in pressure = $(P-P^*)/\sigma_P$. Key to both graphs given in top diagram. Partial datasets shown are:- Set 1 [10], Set 2 [11].

Fig. 3. Standardised error plots for the fitting of R32 vapour pressure data showing the sequential dropping of outlying datapoints until a good fit is obtained. Key to both graphs is given in the lower diagram. The key shows which points were dropped after the specified fit with the remaining data (19 datasets) being correlated in the fourth and final fit to within experimental error.

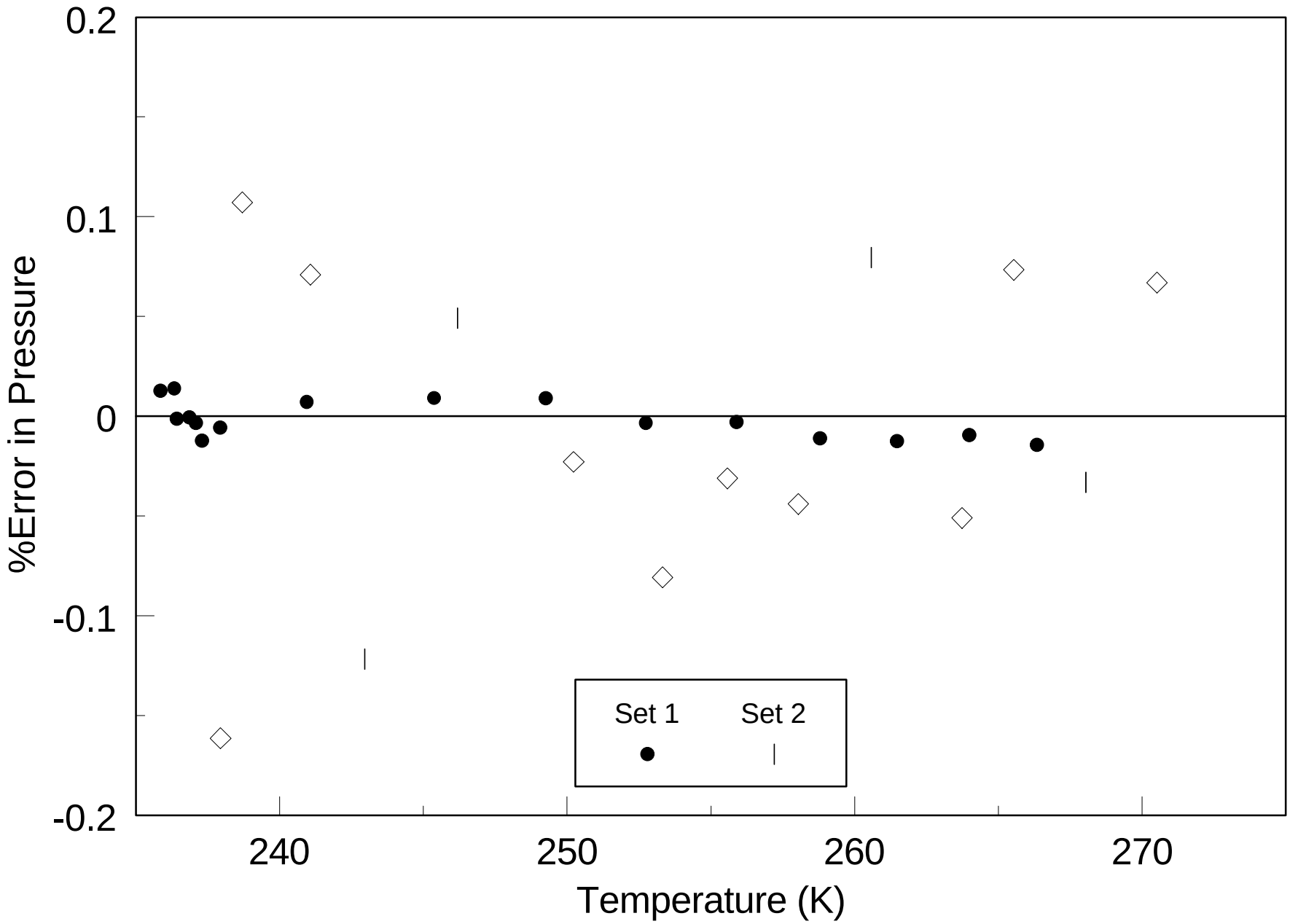
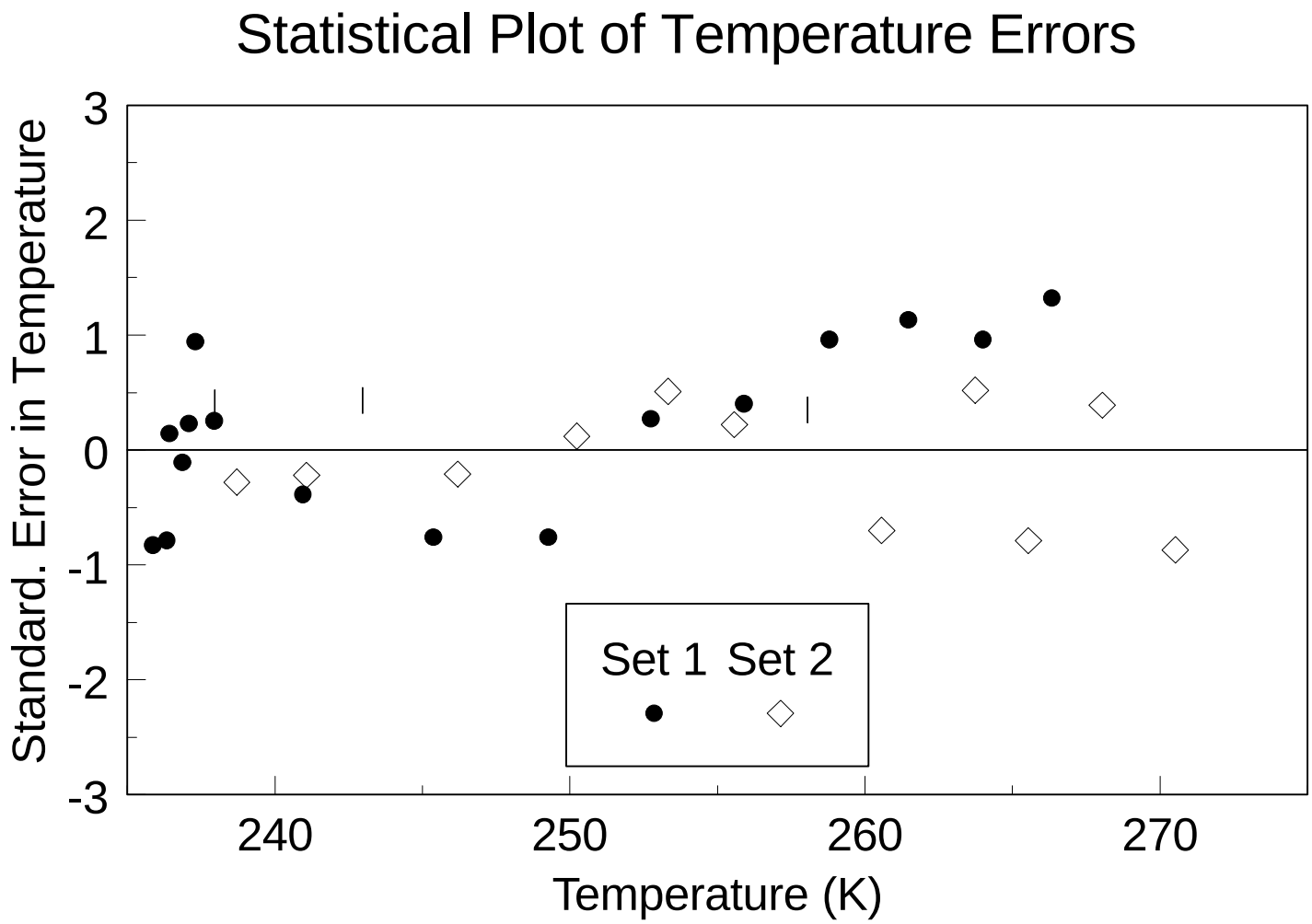

0.2
0.1
0
-0.1
-0.2
%Error in Pressure
240
250
260
270
Temperature (K)
Set 1
Set 2

Figure 1


Statistical Plot of Temperature Errors
Standard. Error in Temperature
3
2
1
0
-1
-2
-3
240
250
260
270
Temperature (K)
Set 1
Set 2

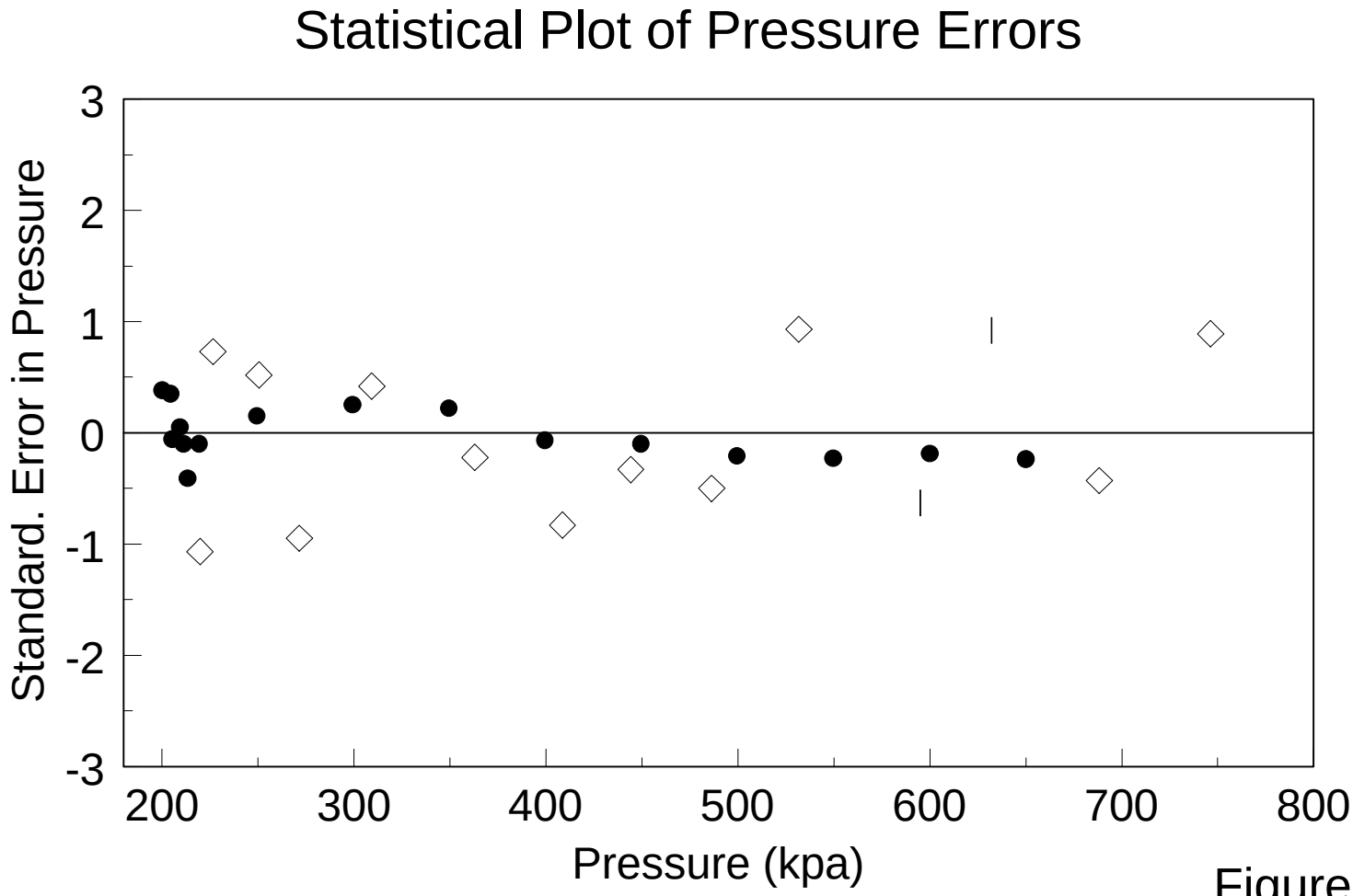
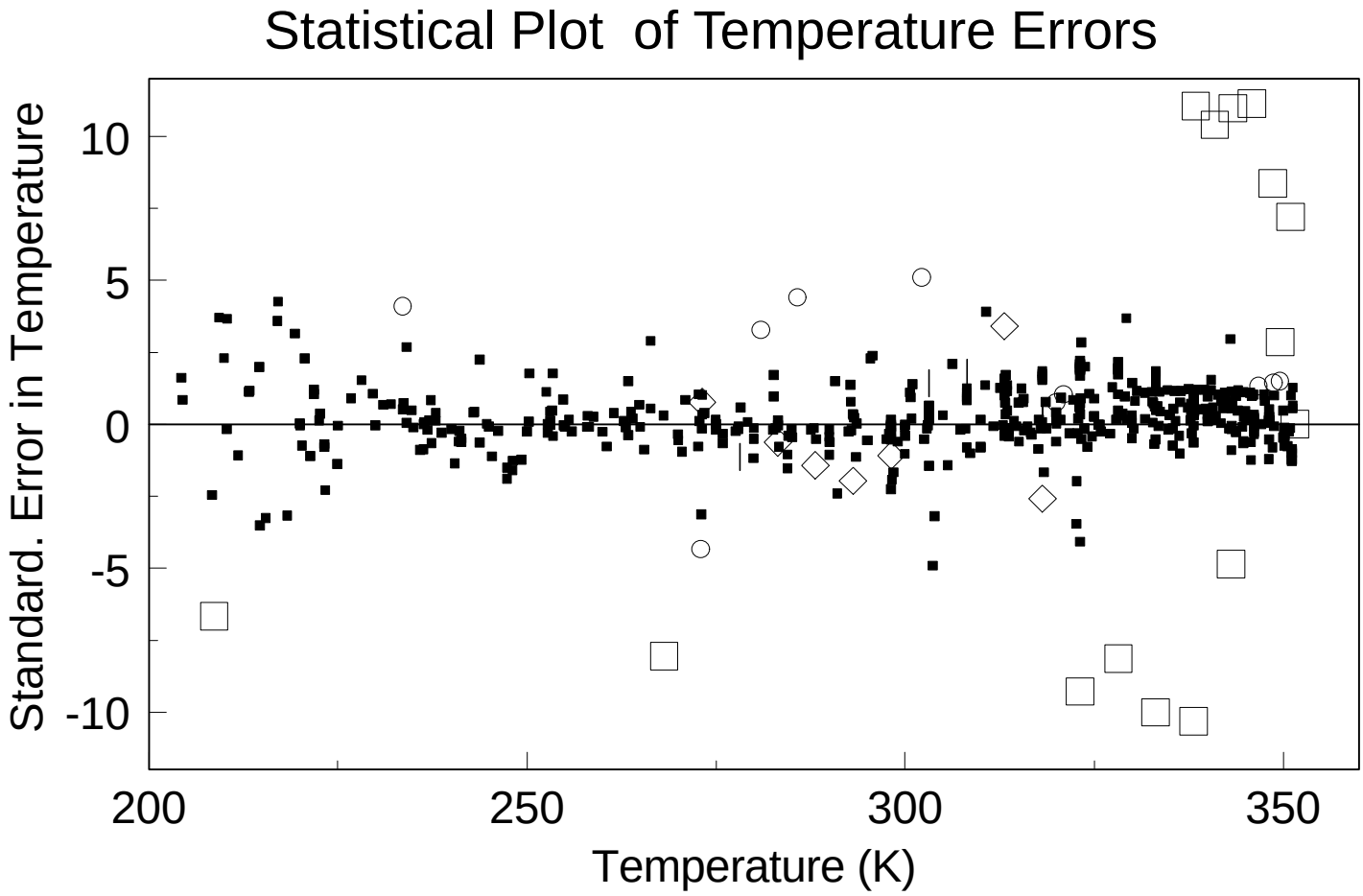

Statistical Plot of Pressure Errors
Standard. Error in Pressure
3
2
1
0
-1
-2
-3
200
300
400
500
600
700
800
Pressure (kpa)

Figure 2


Statistical Plot of Temperature Errors
Standard. Error in Temperature
10
5
0
-5
-10
200
250
300
350
Temperature (K)

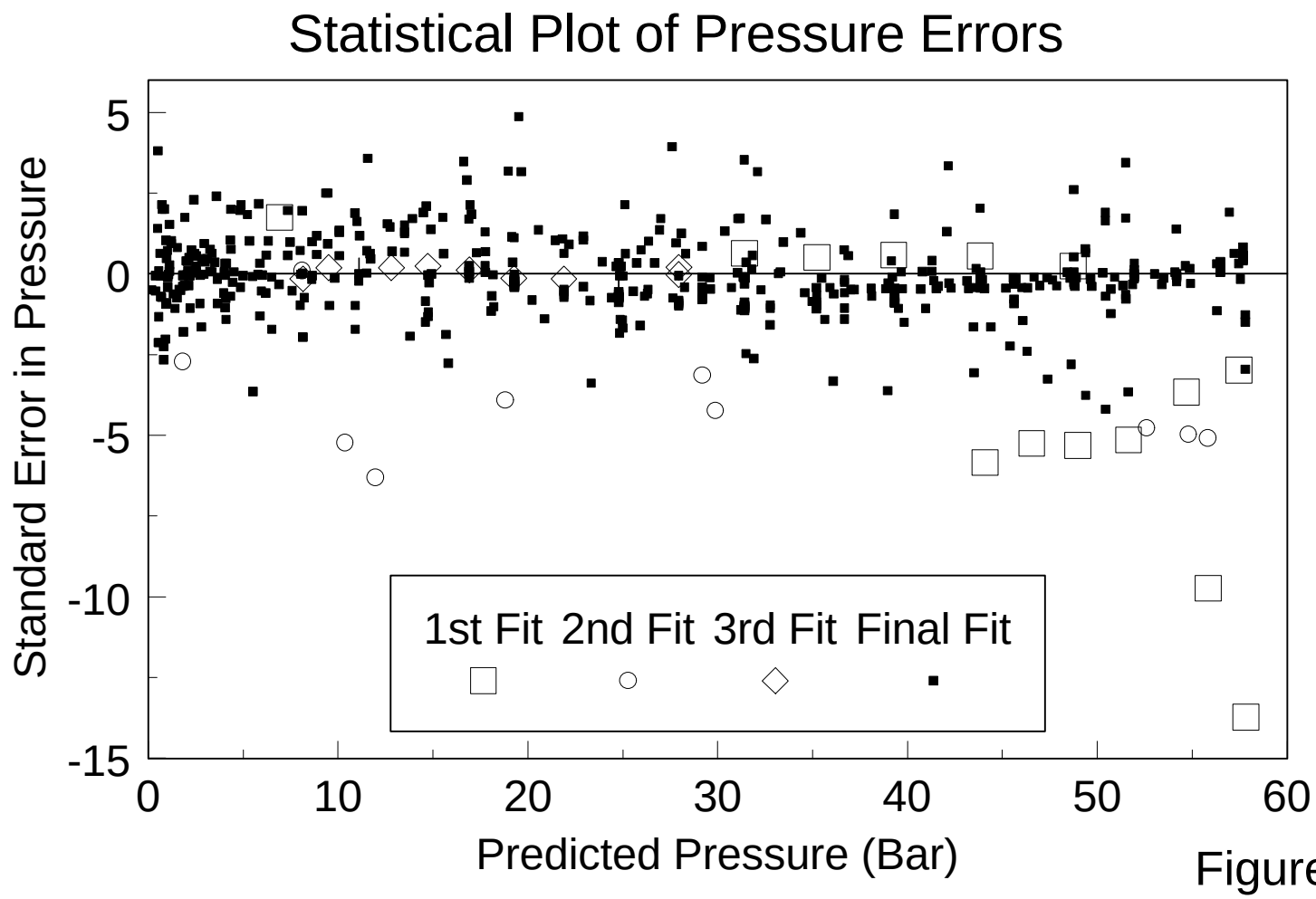

Statistical Plot of Pressure Errors
Standard Error in Pressure
5
0
-5
-10
-15
0
10
20
30
40
50
60
Predicted Pressure (Bar)
1st Fit
2nd Fit
3rd Fit
Final Fit

Figure 3