CALCULATION OF ASTM CURVES FROM TRUE BOILING POINT CURVES

By

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PREFACE

A semitheoretical method for the calculation of ASTM distillation curves from true boiling point curves is presented in this thesis. The method works well both for pure component blends and for continuous true boiling point curves.

A comparison of the results using this new method was made with the results of the empirical methods of Edmister and of Geddes.

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CHAPTER I

INTRODUCTION

Petroleum fractions are characterized by two types of standard laboratory distillations; the true-boiling-point (TBP) distillation (29, 31) and the ASTM distillation (1). The TBP distillation is a batch distillation process involving an efficient column fractionation of a sample. The ASTM distillation is a simple batch distillation process except for a slight amount of reflux from condensation on the neck of the flask. The TBP distillation is required for equilibrium calculations of petroleum oils (20, 24, 35). Design of crude distillation units and calculation of gasoline blends requires the TBP distillation. Finished products, however, are sold on the basis of the simpler ASTM distillations. For this reason, a relation between TBP distillation curves and ASTM distillation curves is necessary (20).

Existing methods for calculating ASTM curves from TBP curves (5,6,7,8,10,14,18,19,21,22,34) are empirical methods based on slopes of the distillation curves, with one exception (14). The accuracy of the exisiting methods is usually poor, especially for mixtures which are considerably different from those for which the correlation was developed. These methods are not applicable for "step" distillation curves; i.e., blends of a small number of pure components.

The purpose of this work was to develop a semitheoretical method for calculating ASTM distillation curves from TBP distillation curves which can be used both for continuous TBP curves and for step TBP curves. An IBM 7094 computer was used for making all calculations.

CHAPTER II

BATCH DISTILLATION PHENOMENA

Simple batch distillation is a process in which the vapors formed are removed continuously with no partial condensation of the vapors or refluxing of condensate to the still. The mathematical analysis of this type of distillation was first made by Rayleigh (28, 32).

The best known form of the Rayleigh equation is derived as follows(33):

Let W_O represent the total mols of a mixture containing x_A mol fraction of component A. If a differential quantity of the mixture $-$ dW of composition y_A is vaporized, a material balance for component A gives

$$-y_A dW = -d\,(x_A W) = -x_A dW - W dx_A \tag{1}$$

Collecting terms,

$$\frac{dW}{W} = \frac{dx_A}{y_A - x_A} \tag{2}$$

Integrating between limits,

$$\ln \frac{W_1}{W_O} = \int_{x_{AO}}^{x_{A1}} \frac{dx}{y_A - x_A} \tag{3}$$

This form of the Rayleigh equation can be graphically integrated if experimental data giving the relationship between x and y are available.

Equation (3) is convenient to use for binary mixtures. For multicomponent mixtures, a knowlege of y as a function of x is generally not available.

An alternate form of the Rayleigh equation which is more convenient to use for multicomponent mixtures is derived as follows (28):

Let A, B, C, D, etc., represent the total mols of the respective components in a multicomponent mixture. If a differential quantity of the mixture is vaporized,

$$\frac{-dA}{-dB} = \frac{y_A}{y_B} = \frac{K_A x_A}{K_B x_B} \tag{4}$$

Since $x_A = A/(A + B + C + D)$ and $x_B = B/(A + B + C + D)$,

$$(-dA)/(-dB) = (K_A/K_B)(A/B) = \alpha(A/B) \tag{5}$$

where $\alpha = K_A/K_B$. Equation (5) can be integrated for the case where relative volatility (α) is constant to give

$$\ln (A_0/A_1) = \alpha \ln (B_0/B_1) \tag{6}$$

where subscript 0 indicates the total mols of the component in the original mixture and subscript 1 indicates the total mols of the component remaining in the liquid after the batch distillation operation.

Equation (6) can be written for each pair of components in the mixture. When relative volatilities and the composition of the original mixture are known, if the amount of one component in the residual liquid is fixed, the composition of the residual liquid can be calculated from equation (6).

The ASTM distillation procedures and apparatus are similar to those for simple batch distillation. They are different from simple batch distillation operations in that some reflux is obtained from partial condensation in the neck of the flask. The apparatus and method, including the rate at which heat is supplied, are specified by the ASTM. The complete procedure is given in reference 1. The ASTM distillation temperature is measured by a thermometer. The bulb of the thermometer is located in the vapor at the point at which it leaves the distillation flask. The reading of the thermometer when the first drop of liquid falls into the receiver is recorded as the initial boiling point. The temperature and the total volume of distillate taken overhead is recorded at specified distillate volumes or specified temperatures. The per cent of the initial charge that has been taken overhead at any point in the distillation is called volume per cent overhead. The maximum temperature observed on the thermometer is recorded as the end point. Thermometer stem corrections are not applied to the temperature readings. Temperatures were not corrected to standard atmospheric pressure except in case of dispute until recently. The latest test method requires specifications to be based on 760 mm atmospheric pressure and requires temperatures to be corrected to 760 mm pressure when comparing test data or when judging complicance with specifications (1).

The ASTM temperature might be expected to be approximately the bubble point of the liquid in the flask. Further consideration will show that this is not the case. During an ASTM distillation, a film of liquid will form on the thermometer bulb. The temperature of the film will be dependent on the vapor temperature (which is approximately equal to the bubble point of the kettle liquid), the bubble point of the film, the temperature and concentration gradients between the vapor and the liquid film on the thermometer bulb, and the thermal lag of the thermometer.

The TBP distillation is a batch distillation process in which a large reflux ratio and number of theoretical plates are used to separate a mixture into its components. The temperatures on a true boiling point curve are essentially the actual boiling points of the components in the mixture. TBP apparatus are not standardized; any equipment that accomplishes a good degree of fractionation is termed "true-boiling-point" equipment (21). Therefore, a number of TBP distillation curves are possible for the same sample. The best known types of equipment are those of the Peters (29) type and the Podbielniak (31) fractional distillation equipment (21).

CHAPTER III

SURVEY OF THE LITERATURE

A number of methods for estimating ASTM distillation curves from TBP curves have been published. Most of these methods are empirical correlations based on slopes of the two distillation curves, and can be used for continuous curves only. The single exception is the method of Lewis and Robinson (14).

In 1922, Lewis and Robinson presented a theoretical method for calculating the simple distillation curve for multicomponent mixtures (14). This method assumes Raoult's law applies, constant relative volatility and no reflux. Lewis and Robinson assumed that the Engler (essentially the same as the ASTM) distillation curve is represented by the bubble point curve of the liquid during simple batch distillation of the liquid. For a binary mixture, Lewis and Robinson used the Rayleigh equation to calculate composition of the liquid for a given volume per cent overhead, then used a boiling point curve to obtain the temperature of the kettle liquid. For a multicomponent mixture, a graphical method was used. A plot of molecular weight as a function of boiling point is required. Use of this method requires construction of ten graphs, several of which must be obtained by graphical integration.

The first empirical method was published in 1939 by Nelson and Hansburg (22). This method correlates the slope of the TBP curve between the 20 and 80 per cent points with the slope of the ASTM curve between the same points. The temperatures at the 50 per cent point is obtained from a curve relating TBP temperature to ASTM temperatures. The zero per cent point is obtained from a plot of "log slope" of the TBP curve between the zero and 20 per cent points as a function of "log slope" of the ASTM curve between the same points. The "log slope" is defined as $(\log (T_{20}) - \log (T_{10}))/(\log (20) - \log (10))$, where T_{20} and T_{10} indicate temperatures at the 20 and 10 per cent points, respectively. The 90 and 99 per cent points are obtained from a curve showing TBP temperatures as a function of ASTM temperatures.

Geddes (10) published a method in 1941 in which the curves were broken into six segments. A correlation between the 50 per cent temperatures of the ASTM and TBP curves establishes one temperature point. The remaining points are estimated from correlations of comparative temperature differences for similar portions of the two curves. For all points but the 50 per cent point, an additional correlating parameter was required. This method appears to be the most accurate of all the methods published. However, it is also the least convenient of the empirical methods to use. It is described in detail in Appendix B.

In 1948, Edmister and Pollock (6, 8) published a method similar to Geddes' method except that a third correlating parameter was not used. The original method correlated ASTM slope with TBP slope. Later revisions (5, 7) correlated ASTM temperature difference with TBP temperature difference. This method is probably the most widely known of all methods considered. It is more convenient to use than the method of Geddes, but appears to be less accurate. This method is described in detail in Appendix C.

A simple method was presented in 1951 by Schwarzenbek, Slejngstad, Atteridg and Jewell (34). They noted that the 80 per cent point on an ASTM distillation is nearly equal to the 80 per cent on the TBP curve provided all temperatures are corrected for stem emergence. A graphical correlation of difference in temperatures between the 80 and 20 per cent points of the two curves was used to obtain the 20 per cent point. This method was designed to predict TBP 80 and 20 per cent temperatures from ASTM temperatures. It can be used in reverse to estimate ASTM temperatures from TBP temperatures between 20 and 80 per cent if a straight line distillation curve between the two points is assumed.

Nelson (18) presented a correlation of TBP and Saybolt distillation curves in 1952 which was based mainly on crude oils. The measured Saybolt vapor temperature was correlated as a function of TBP slope between 400 and 700°F, with TBP boiling point temperature and the mid-boiling point on the TBP curve as correlating parameters. A plot of slope of the TBP curve as a function of the slope of other distillation curves was later published by Nelson (19) to show that the above correlation method was similar to previous correlation methods by other authors. Nelson later suggested (21) that this plot of slopes be used with a table of relationships between 50 per cent points of the curves as an estimation method for the central portion of the distillation curves.

A number of methods have been published for predicting equilibrium flash vaporization (EFV) curves from ASTM distillation curves or from TBP distillation curves (3, 16, 17, 23, 25, 26, 27, 30). These methods may be used to approximate the ASTM curve from the TBP curve by estimating the EFV curve from the TBP curve, then using a correlation in reverse to estimate the ASTM curve from the estimated EFV curve.

CHAPTER IV

DISCUSSION AND EXPLANATION OF NEW METHOD

The method developed in this thesis is not similar to any of the existing methods published in the literature. It resembles the Lewis and Robinson method in the sense that batch distillation calculations are made. However, Lewis and Robinson used a graphical method for continuous TBP curves, and they assumed that the temperature of the kettle liquid was equal to the ASTM temperature. The method developed in this thesis does neither.

Continuous TBP curves are broken in pseudocomponent increments with the normal boiling point of the pseudocomponent set equal to the average temperature of the increment. Step TBP curves are already in component form.

Batch distillation calculations are made using the Rayleigh equation (equation 6 of Chapter II). The relative volatilities (α) used in the Rayleigh equation are raised to the power (1 - .001 (T - 100)) to empirically account for the increasing reflux and sharper separation obtained at higher temperatures. Bubble point temperatures of the liquid and bubble point temperatures of the vapor in equilibrium with the liquid are calculated for various percentage volume removals during the distillation. The ASTM distillation temperature is calculated as a weighted average of the bubble point of the kettle liquid and the bubble point of the vapor in equilibrium with the liquid. The weighting factor is a logarithmic function of the volume per cent overhead. Two distinct weighting factors are found; one for vapor temperatures above 150°F and one for vapor temperatures below 70°F. A logarithmic average of the two is used for temperatures between 70°F and 150°F. Two different factors are required because at temperatures below 70°F, little or no condensation on the thermometer bulb will take place and the ASTM temperature will be closer to the temperature of the vapor. Above 150°F, condensation on the thermometer bulb will occur readily. The region between 70°F and 150°F is a transition zone between the two. Selection of 150°F as the upper temperature was somewhat arbitrary, but a definite break point exists, and the temperature of 150°F works satisfactorily.

The initial boiling point is estimated from the bubble point of the vapor in equilibrium with the kettle liquid. If the vapor bubble point at zero volume per cent overhead is 300°F or above, it is used as the initial boiling point of the ASTM. If it is below 300°F, the vapor bubble point temperature at 16 volume per cent overhead is used as the ASTM initial boiling point.

The end point of the ASTM is estimated by calculating the dew point of the kettle liquid remaining after 99+ per cent has been distilled overhead, then adding ten degrees to account for superheat.

A stem correction in reverse is applied to the calculated results to compensate for the fact that actual ASTM distillations are not corrected for stem emergence.

All physical and thermodynamic properties required are estimated from the boiling point of the components or pseudocomponents. Details of the estimation methods are given in Appendix A.

The calculation sequence follows:

Data necessary: Pressure

Type of liquid (for molal densities. Curve fits are available for normal hydrocarbons, and for hydrocarbon fractions belonging to groups I, III, and V (characterization factors 12.1 to 12.6, 11.7 to 12.0 and 11.3 to 11.6, respectively)).

Fraction of key component to be taken overhead per increment.

Maximum fraction of key component overhead before changing key components.

For step input:
Number of components
Volume per cent of components in mixture
Normal boiling point of components

For TBP curve input:
Number of data points
Volume per cent overhead
Temperature at the above per cent overhead

1. If the input is in TBP curve form the curve is broken into 100 pseudocomponent increments of one volume per cent. The normal boiling point of each component is calculated as the average of the temperatures at the beginning and end of the increment. Linear interpolation between supplied TBP data points is used. Any number of TBP data points (temperature and volume per cent overhead) not exceeding 100 may be supplied. The initial boiling point must be supplied; the end point will be

estimated by linear extrapolation if not supplied.

2. Vapor pressure equation constants are calculated for each component.

3. Molal densities are calculated for each component.

4. Solubility parameters are calculated for each component.

5. The liquid composition is converted from a volume basis to a molal basis using the molal densities calculated in step 3.

6. The bubble point of the mixture, the composition of the vapor in equilibrium with the liquid, and the bubble point of the vapor are calculated.

7. The lowest boiling component is selected as the key component. Fraction of the key component distilled overhead is set.

8. The quantity and composition of the residual liquid remaining after distilling the specified quantity of key component overhead are calculated using the Rayleigh equation.

9. The volume of the condensed overhead vapor is calculated from component molal densities and the above.

10. The bubble point of the residual liquid and of the vapor in equilibrium with the residual liquid are calculated.

11. The fraction of the key component taken overhead is increased and steps 8 through 11 are repeated until the maximum fraction of key component overhead is exceeded.

12. The next higher boiling component is selected as the key component, and steps 8 through 12 are repeated until the maximum fraction of the highest boiling component in the mixture is exceeded.

13. If the total volume overhead is less than 99 per cent steps 8 through 10 are repeated with half of the remaining key component

taken overhead each time until the total volume overhead exceeds 99 per cent.

14. The dew point of the remaining material is calculated.

15. ASTM temperatures are calculated as the weighted average of the bubble point temperatures of the residual liquid and the vapor in equilibrium with the liquid:

$$T_{ASTM} = \frac{T_{BL} + f(V)\ T_{BV}}{1 + f(V)}$$

The weighting factor f(V) is calculated as follows:

T_{BV} greater than 150°F:

$$f(V) = 2.40\ V^{(-0.640)},\ V \neq 0$$

T_{BV} less than 70°F:

$$f(V) = 0.419\ V^{(-0.695)},\ V \neq 0$$

For T_{BV} between 70 and 150°F, a logarithmic interpolation between the two equations is used:

$$f(V) = \frac{(T_{BV}-70)\ \ln f(V)_{150} + (150-T_{BV})\ \ln f(V)_{70}}{80}$$

16. The initial boiling point is set equal to the bubble point of the vapor in equilibrium with the initial feed liquid if this temperature is 300°F or above. If it is below 300°F, the bubble point of the vapor in equilibrium with the residual liquid at 16 volume per cent overhead is used.

17. A stem correction is subtracted from the calculated ASTM temperatures to give uncorrected thermometer reading. The stem correction is estimated from the equation

$$T_S = 0.870\ (T-100)^{0.1586}$$

where T_S is the stem correction to be subtracted from the actual temperature to obtain thermometer reading. The above equation will reproduce the actual stem corrections for both the 30 to 580°F and the 30 to 760°F standard ASTM thermometers with a maximum error of less than 5 degrees.

CHAPTER V

ACCURACY OF THE NEW METHOD

Comparison of New Method with Experimental Data

The new method was developed from data on pure component blends obtained from Erbar (9). The calculated and actual ASTM curves and the estimated TBP curves (approximated as the normal boiling points of the components in the blend) for these pure component blends are shown in Figures 1 through 13. Deviations of the calculated ASTM temperatures from actual ASTM temperatures are shown in Table I.

The method was tested by calculating ASTM curves from the continuous TBP curve data published by Geddes (10). The TBP data used for the calculations are tabulated in Table II. ASTM curves for the same samples are tabulated in Table III. The calculated and actual ASTM curves are shown in Figures 14 through 41. Deviations of the calculated ASTM temperatures from actual ASTM temperatures are shown in Table IV.

For step input data, the new method duplicated experimental data well. The average absolute deviation for all points calculated is 2.8°F, and standard deviation for all points calculated is 3.7 °F. The ASTM temperature data for the step curves were obtained under carefully controlled conditions at a pressure of 760 millimeters of mercury (9). A second ASTM distillation was available on eleven of the thirteen samples. The average deviation of the second distillation from the

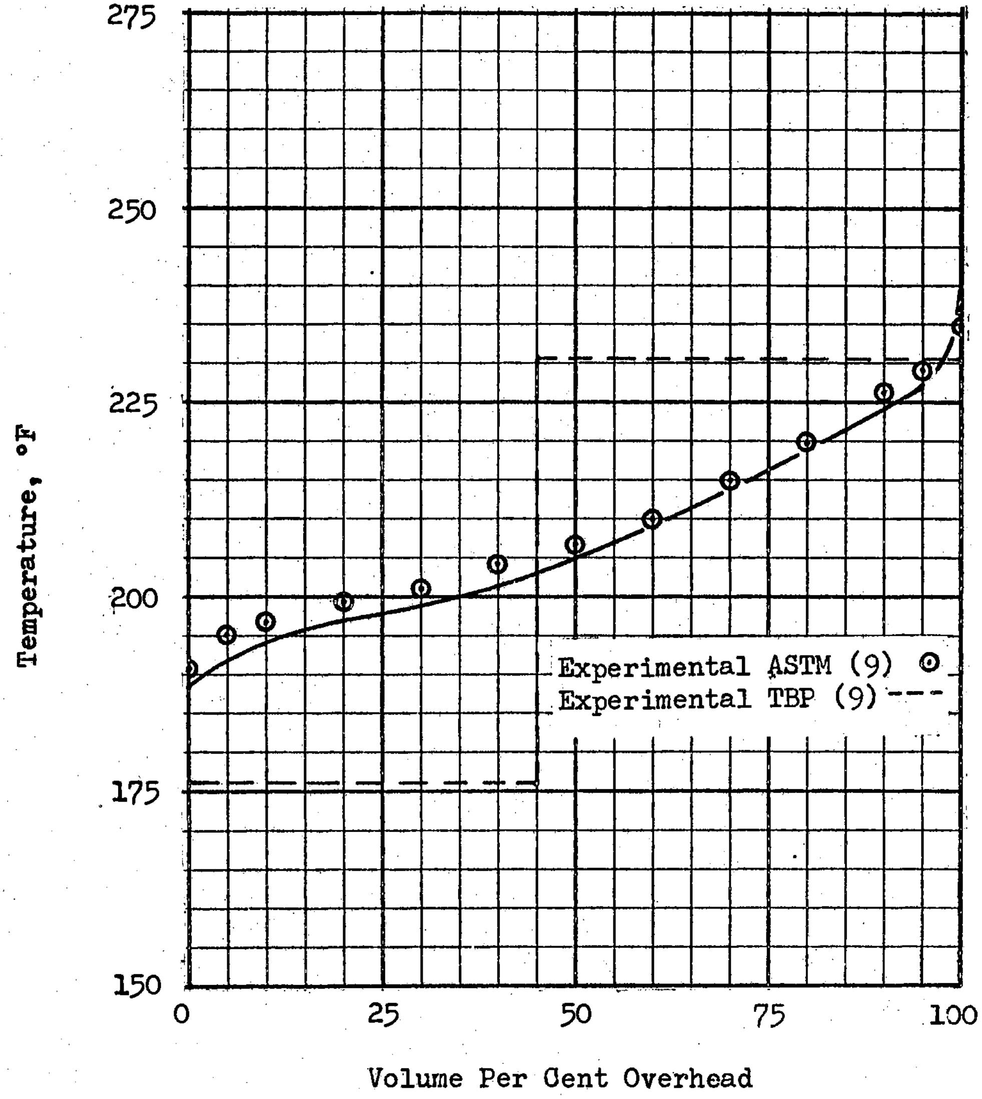


Figure 1. Experimental Points, Calculated ASTM Curve and TBP Curve for Sample No. 101

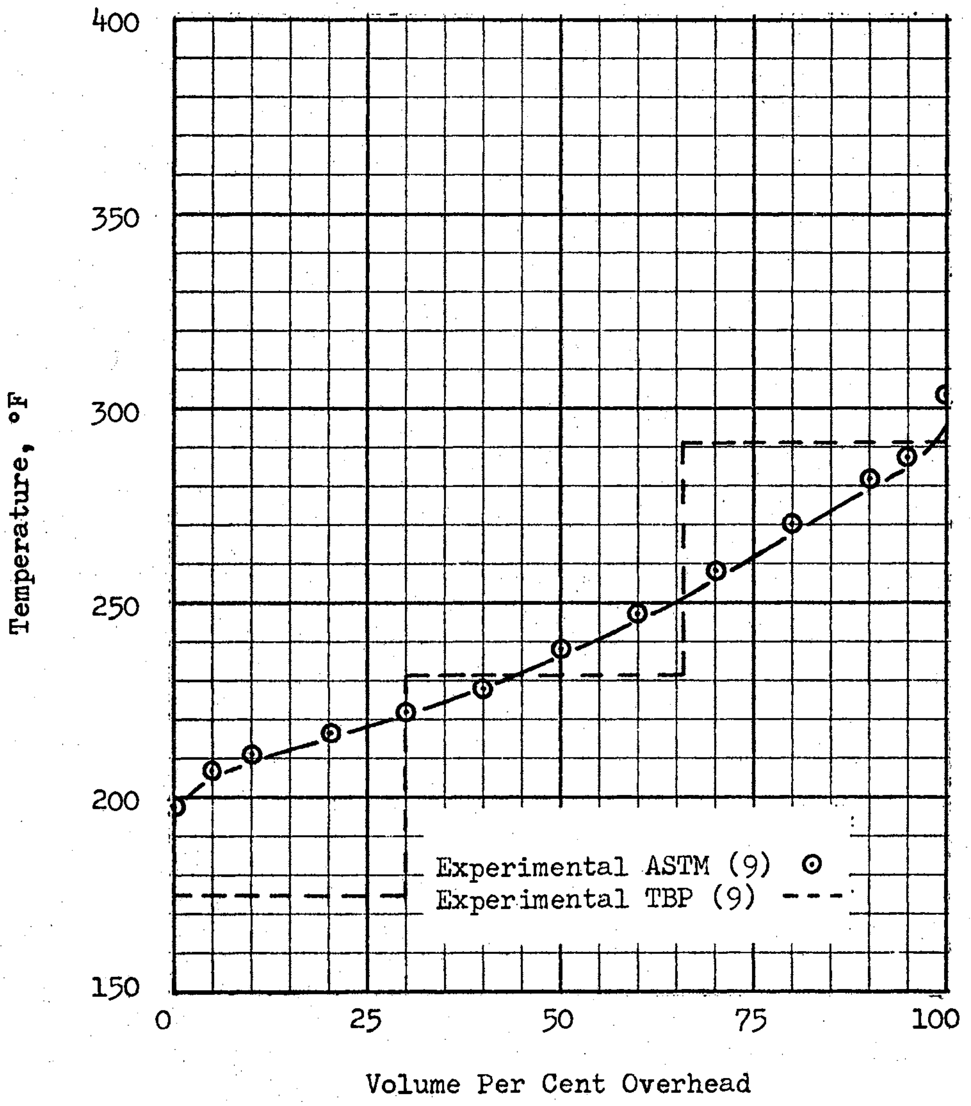


Figure 2. Experimental Points, Calculated ASTM Curve and TBP Curve for Sample No. 102

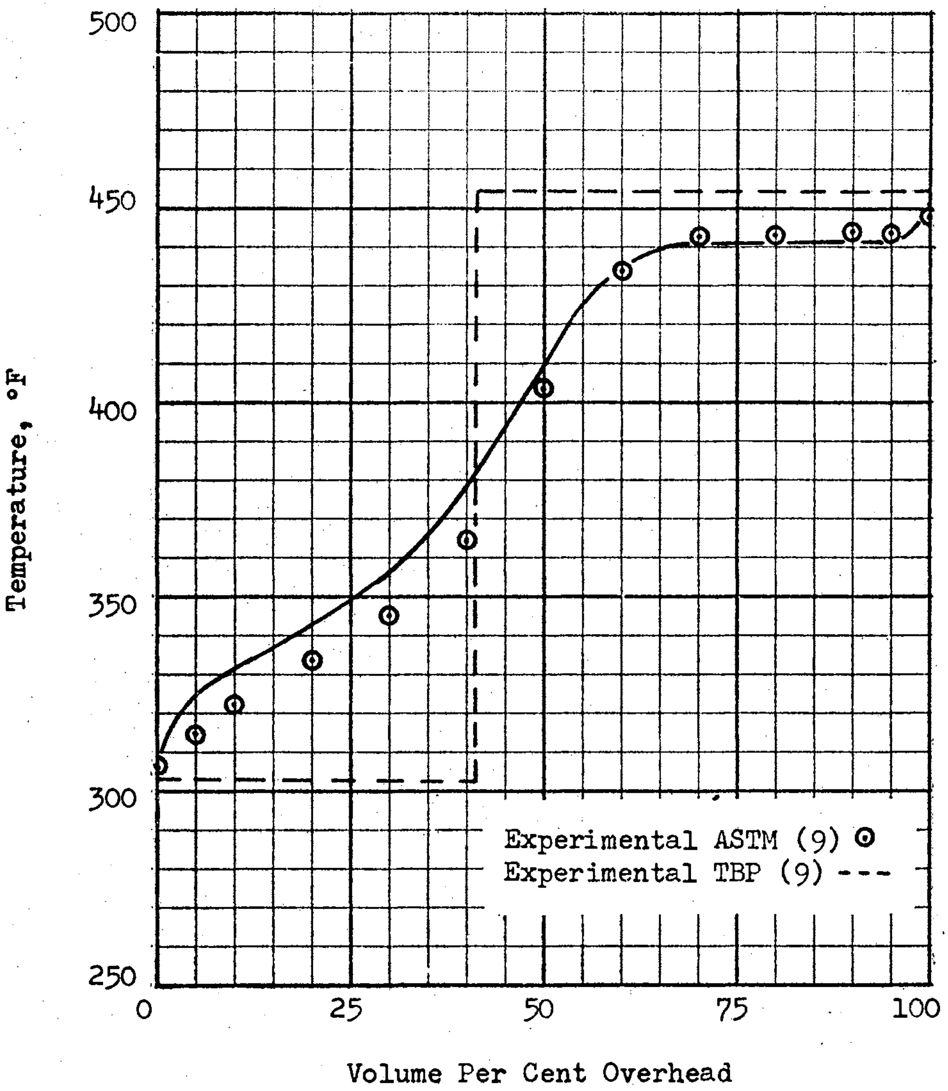


Figure 3. Experimental Points, Calculated ASTM Curve and TBP Curve for Sample No. 103

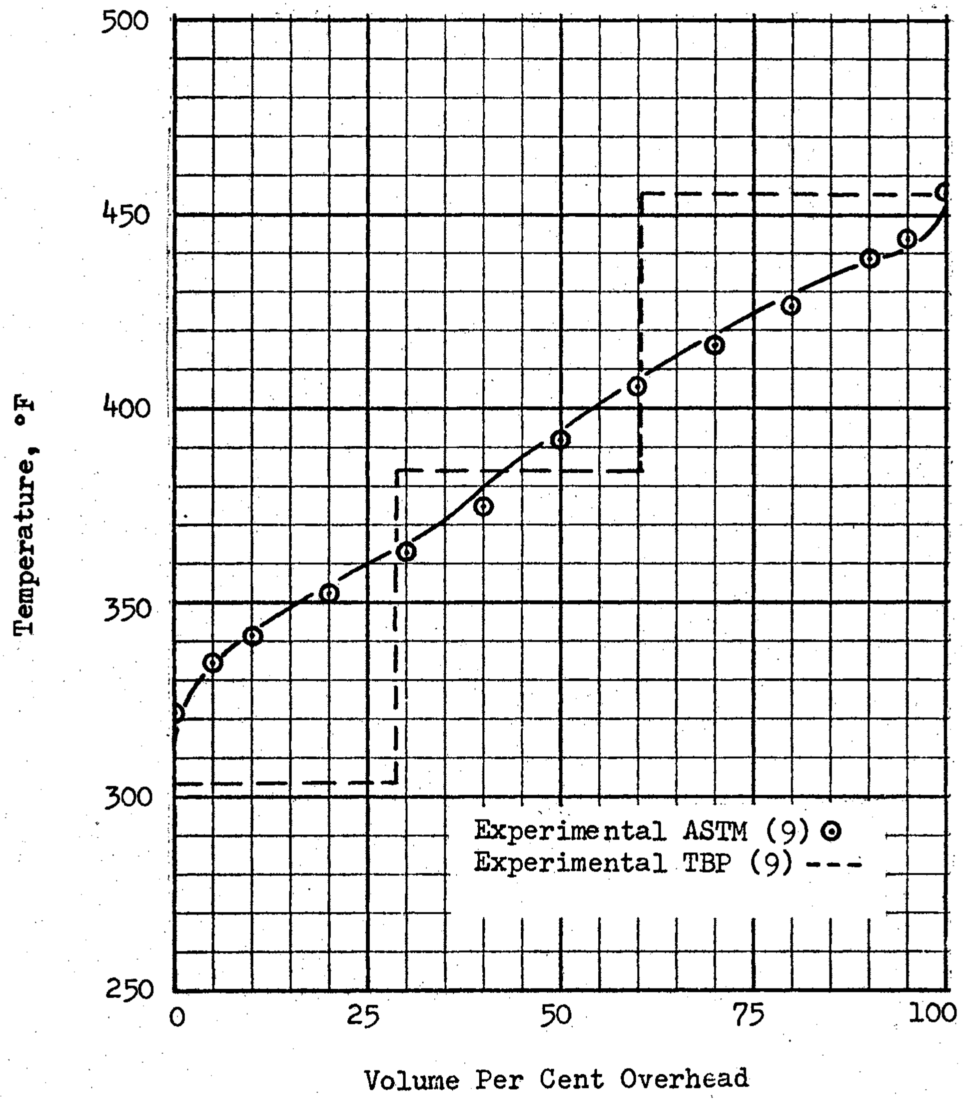


Figure 4. Experimental Points, Calculated ASTM Curve and TBP Curve for Sample No. 104

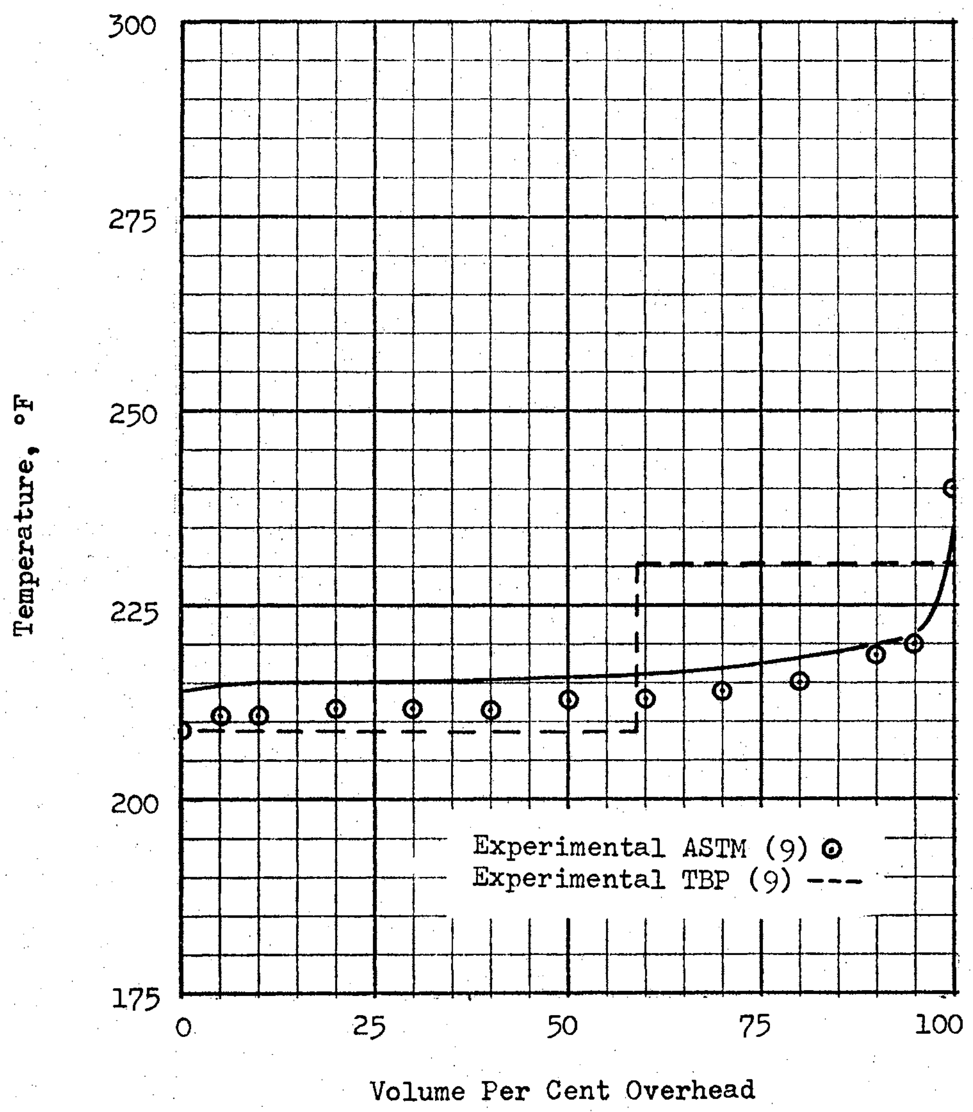


Figure 5. Experimental Points, Calculated ASTM Curve and TBP Curve for Sample No. 105

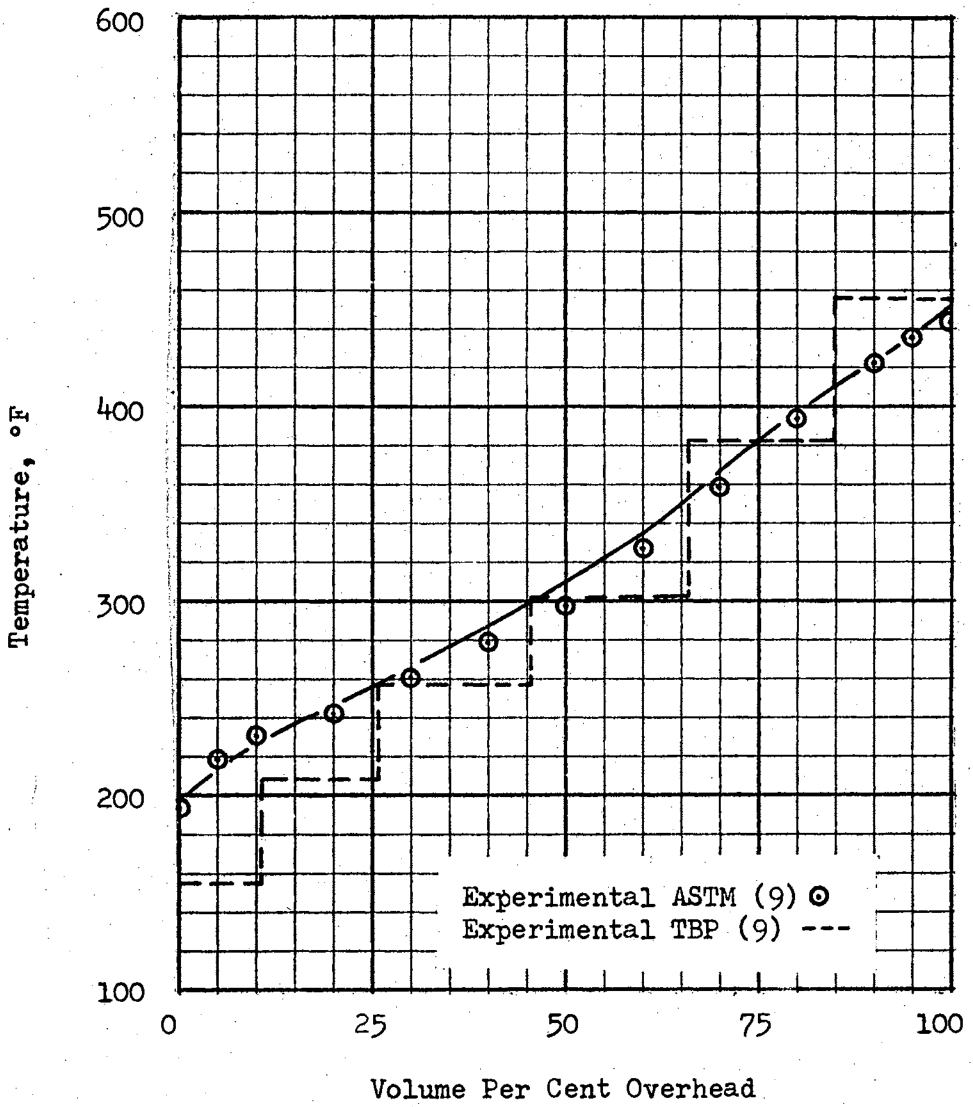


Figure 6. Experimental Points, Calculated ASTM Curve and TBP Curve for Sample No. 106

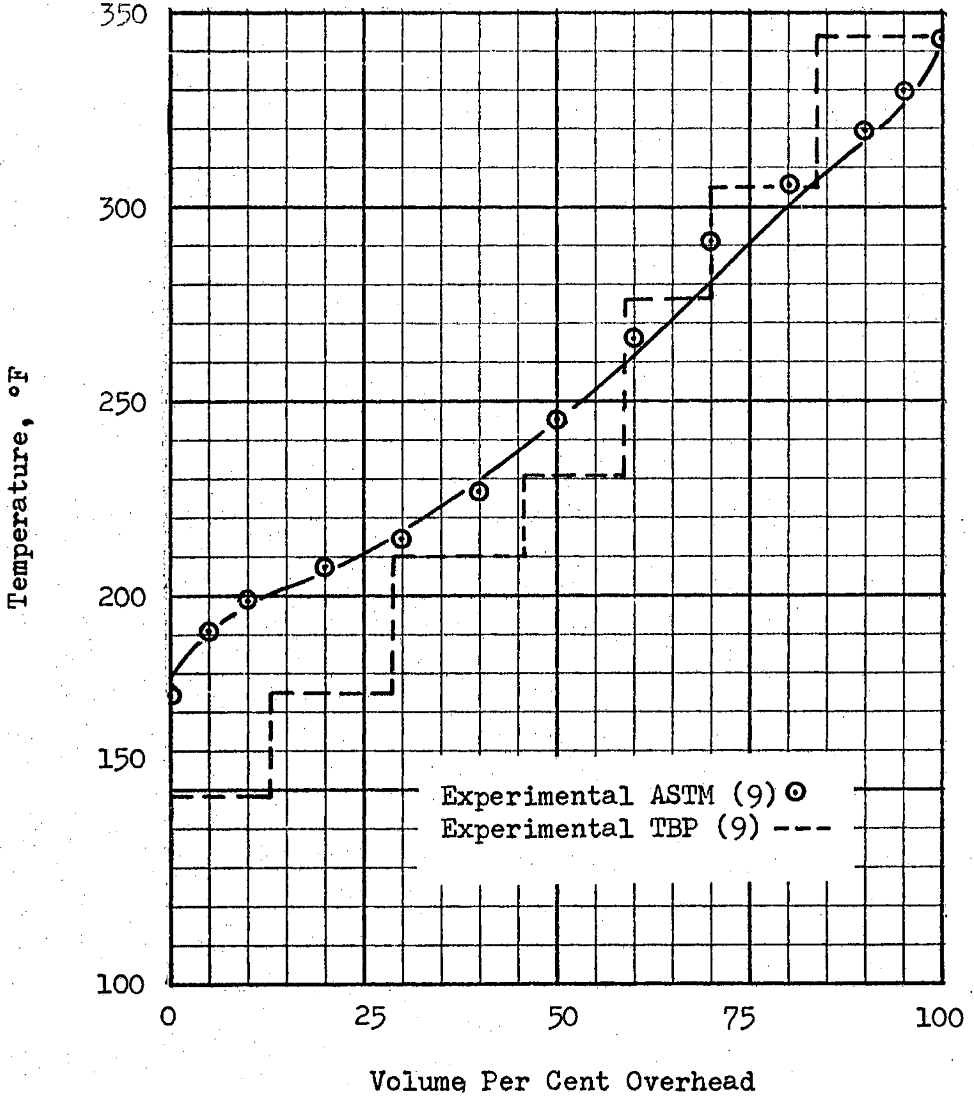


Figure 7. Experimental Points, Calculated ASTM Curve and TBP Curve for Sample No. 107

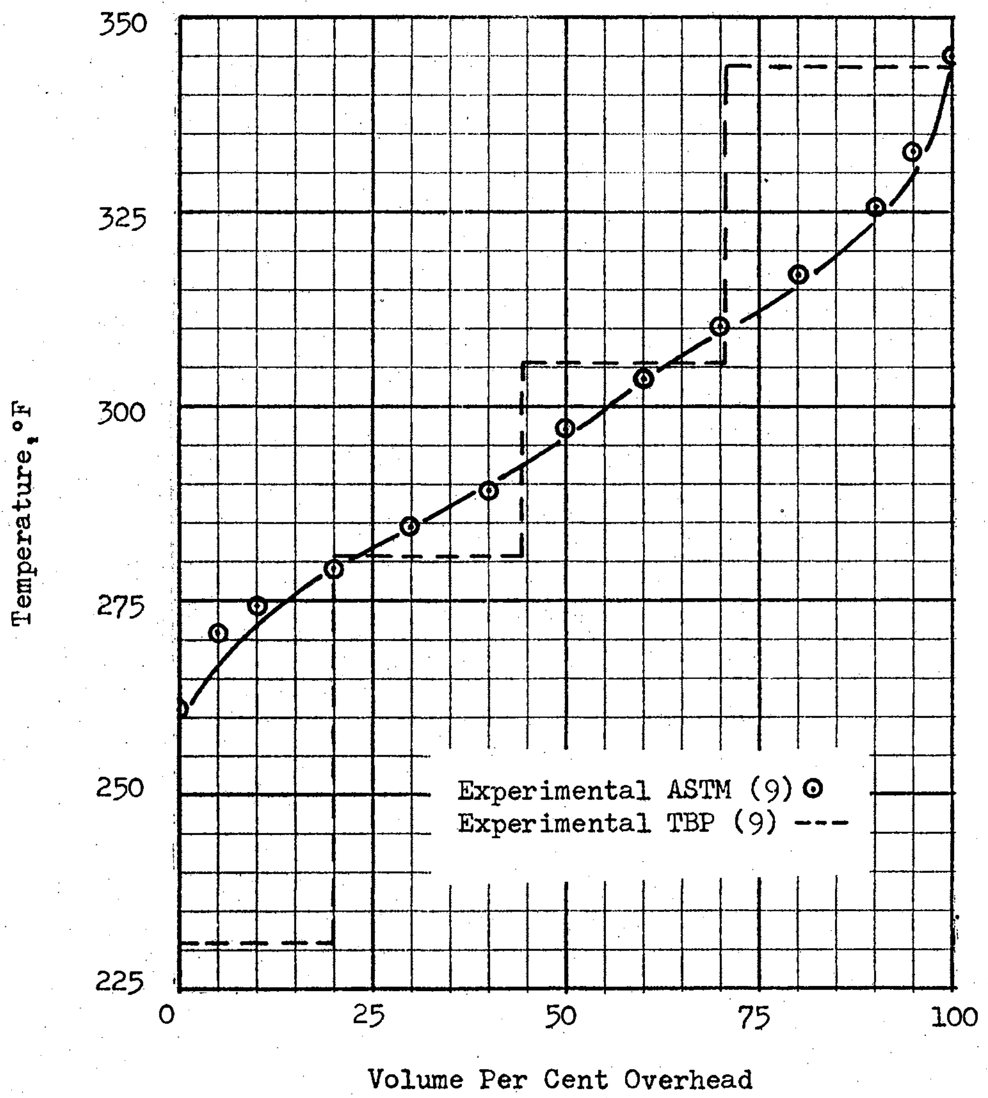


Figure 8. Experimental Points, Calculated ASTM Curve and TBP Curve for Sample No. 108

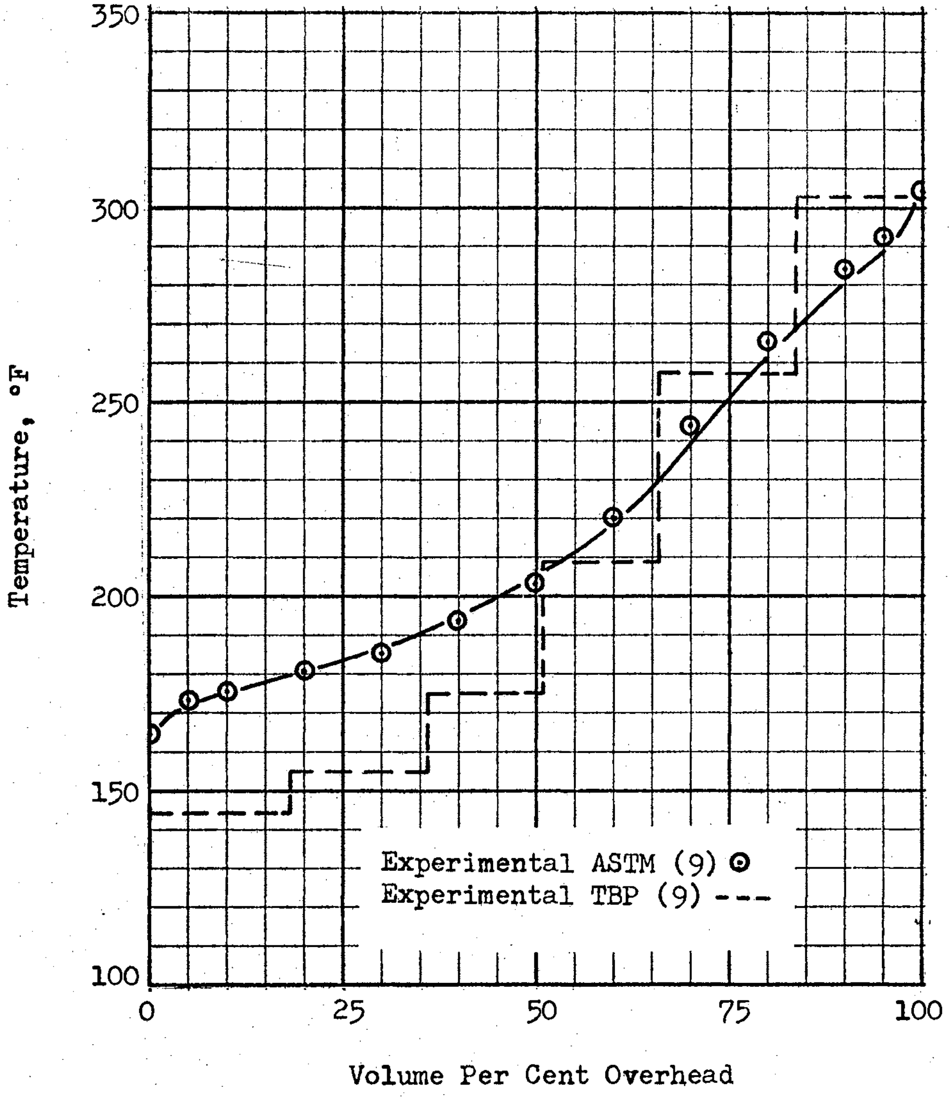


Figure 9. Experimental Points, Calculated ASTM Curve and TBP Curve for Sample No. 109

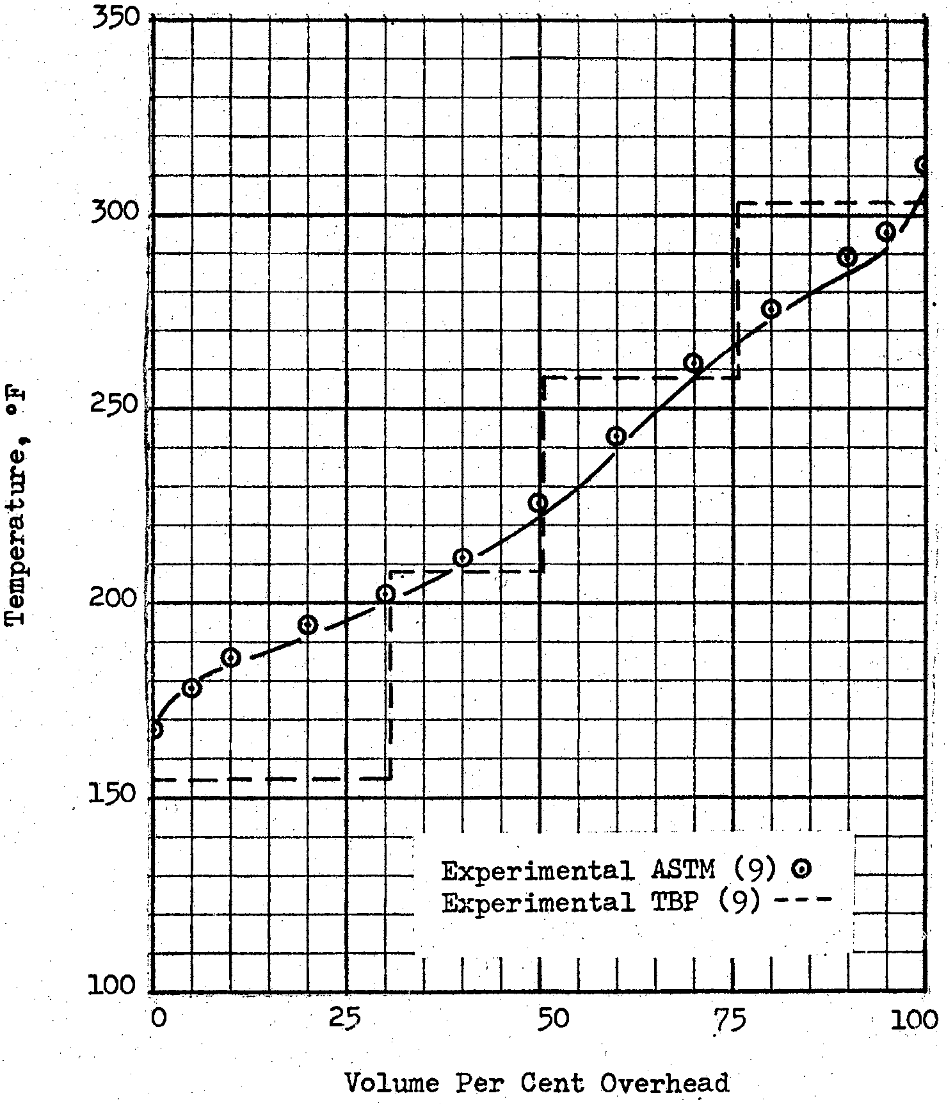


Figure 10. Experimental Points, Calculated ASTM Curve and TBP Curve for Sample No. 110

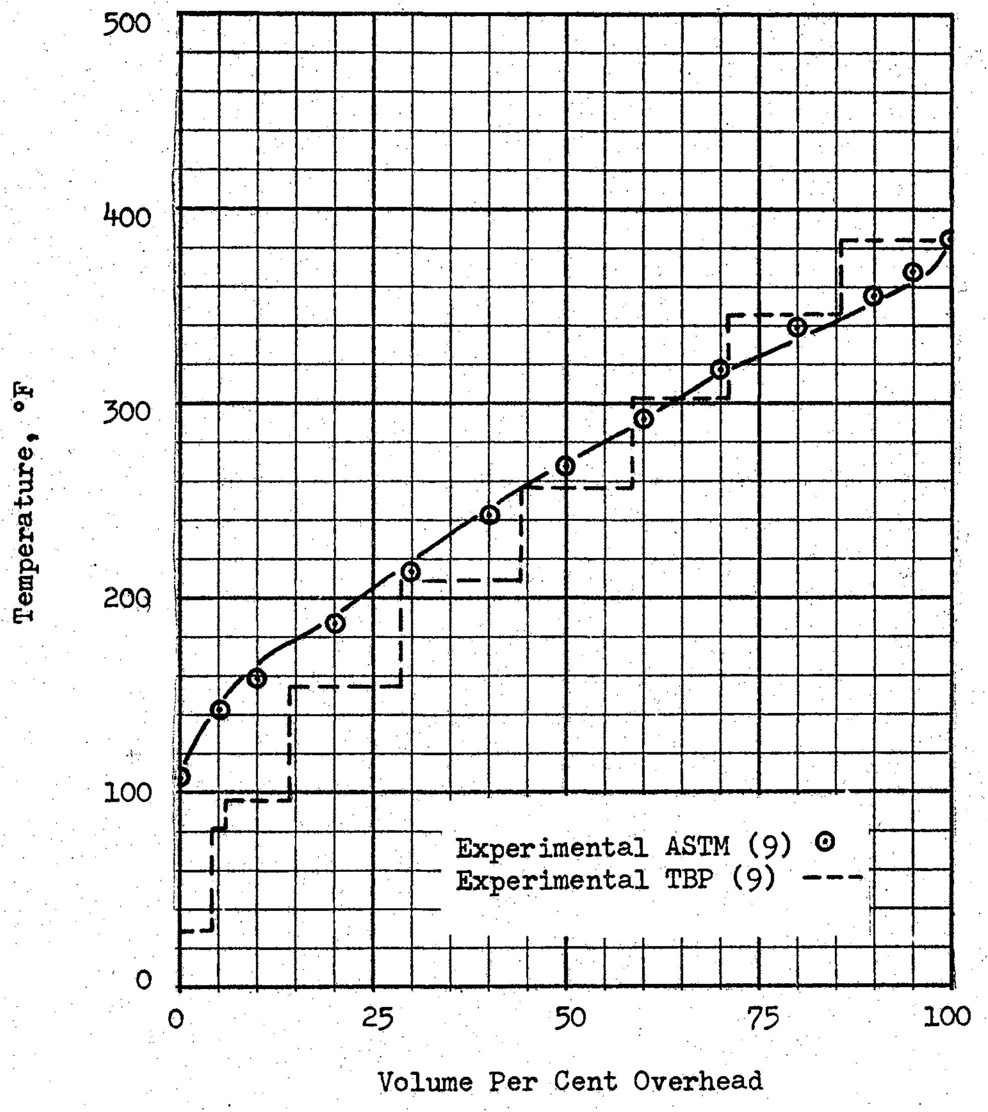


Figure 11. Experimental Points, Calculated ASTM Curve and TBP Curve for Sample No. 111

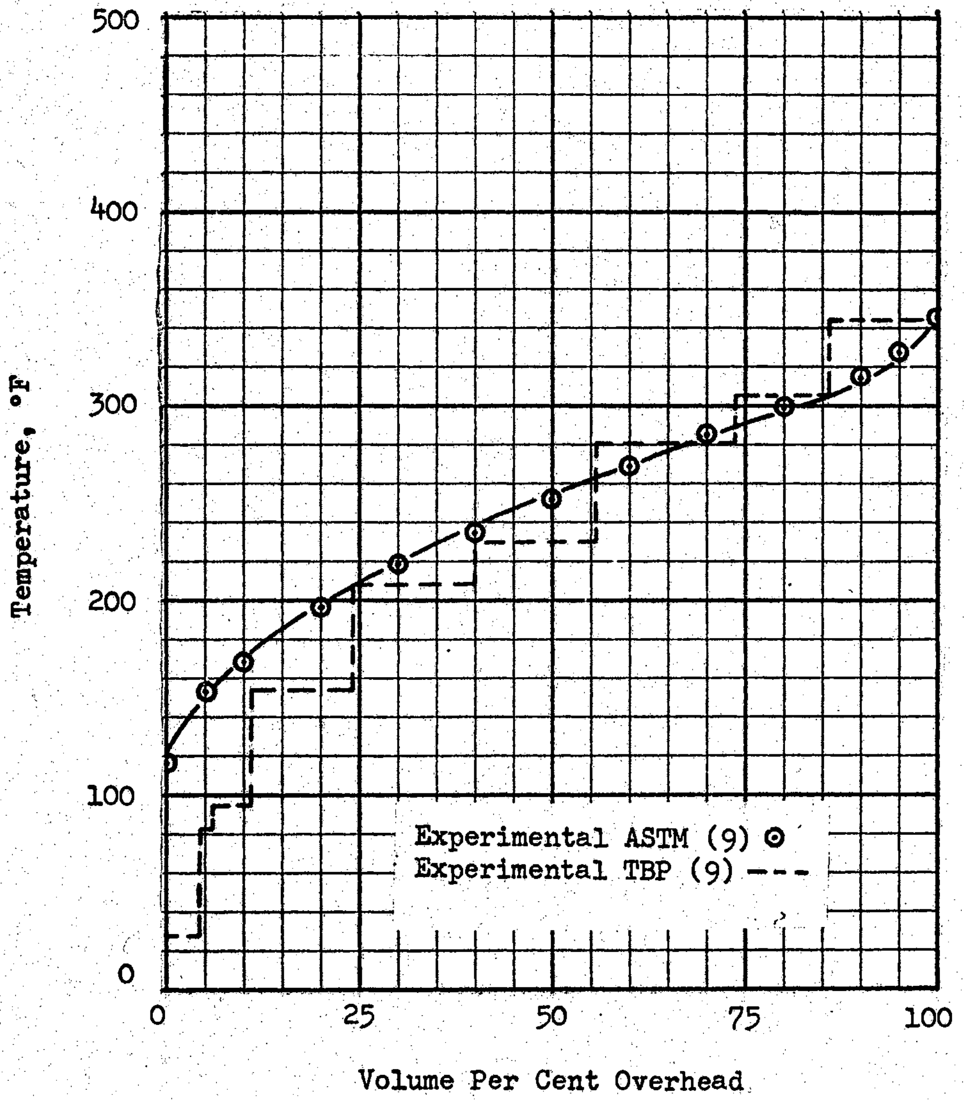


Figure 12. Experimental Points, Calculated ASTM Curve and TBP Curve for Sample No. 112

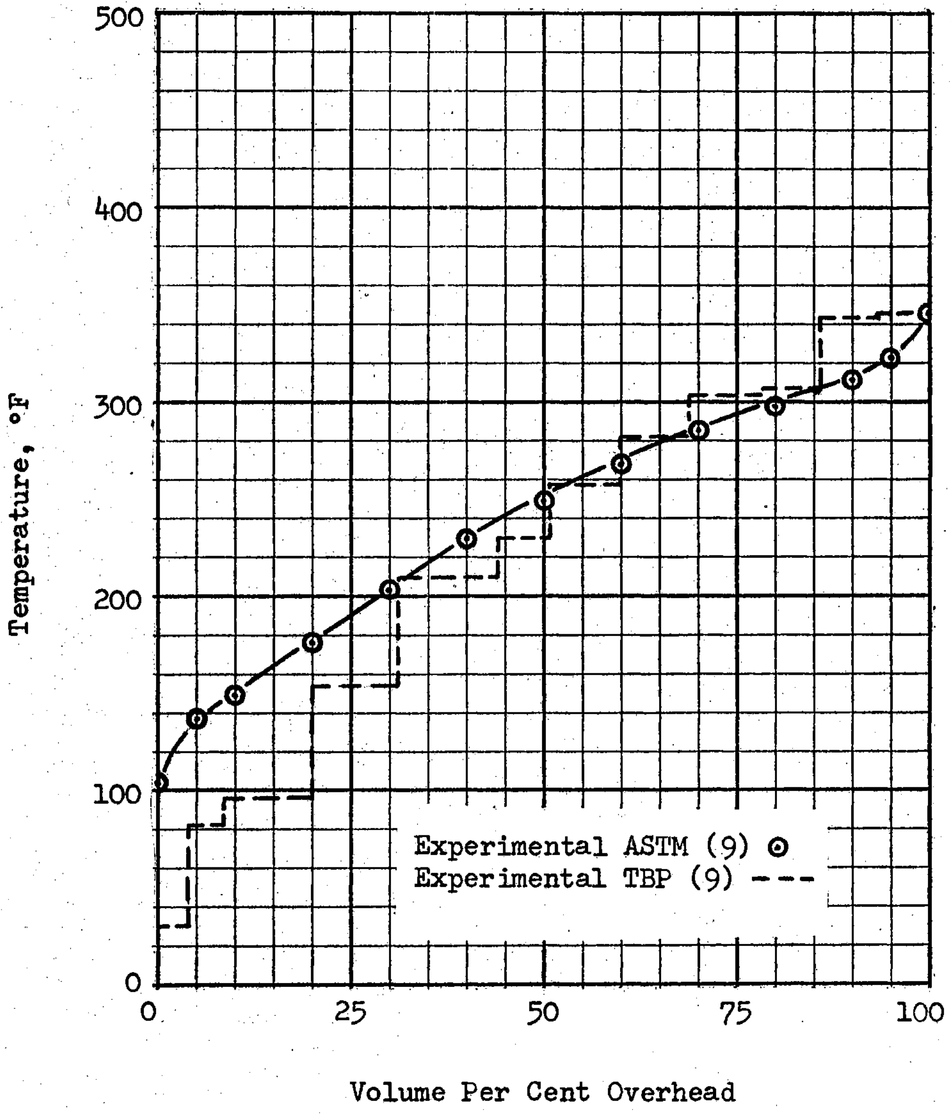


Figure 13. Experimental Points, Calculated ASTM Curve and TBP Curve for Sample No. 113

TABLE I

DEVIATION OF CALCULATED ASTM TEMPERATURES FROM ACTUAL ASTM TEMPERATURES FOR PURE COMPONENT BLEND DATA

Sample	Deviation, °F												
Number	IBP	5%*	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%	EP
101	-2	-3	-3	-2	-2	-2	-2	-1	+2	-2	-3	-2	+3
102	-2	+2	-3	-2	-1	0	-2	-1	-2	-2	-3	-3	-7
103	-2	+10	+9	+10	+11	+14	+5	+2	-1	-1	-1	-1	+4
104	-7	0	+1	+2	+2	+5	+2	+2	+2	+2	0	-2	-4
105	+5	+3	+4	+3	+3	+4	+3	+4	+3	+3	+2	+1	-5
106	+2	-6	-3	+3	+5	+9	+11	+8	+6	+2	0	+1	-1
107	+3	0	-1	-1	+2	+3	-1	-6	-10	-6	-3	-5	+1
108	-2	-4	-2	0	0	+1	-1	0	-1	-1	-2	-4	0
109	-2	-1	0	0	+1	+1	+2	-2	-5	-3	-3	-4	+2
110	0	+1	-1	-2	-2	-2	-3	-4	-5	-4	-5	-4	-6
111	+3	+2	+6	+5	+3	+3	+1	0	-2	-5	-4	-5	0
112	+5	-2	+2	+1	+1	+4	+1	0	-1	-2	-2	-4	+1
113	-7	-1	+1	+1	0	+1	+2	+2	+1	+2	+2	0	+2

* Volume per cent overhead

TABLE II

CONTINUOUS TBP DISTILLATION CURVES-DATA OF GEDDES (10)

Sample	True Boiling Point Distillation, °F												
Number	IBP	1%*	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%	98%
1	30	34	100	131	151	167	180	197	214	231	252	268	282
2	95	103	137	160	176	190	203	214	227	242	258	268	282
3	150	166	214	222	240	252	260	266	271	284	306	316	326
4	250	280	309	317	327	341	351	358	368	385	397	404	414
5	-40	-27	109	161	190	212	230	249	262	281	301	320	347
6	268	280	307	317	326	333	340	347	356	365	379	394	413
7	317	340	367	388	400	412	422	434	449	460	478	495	512
8	390	410	465	482	496	506	516	532	546	568	600	635	672
9	-40	-22	132	177	212	235	257	278	301	323	345	364	383
10	-40	-10	162	217	255	293	330	364	395	420	455	472	496
11	-40	0	197	252	305	357	401	438	473	503	544	580	617
12	310	340	391	415	434	457	476	493	511	536	571	603	645
13	240	300	351	380	409	435	460	481	502	522	562	597	638
14	240	285	330	353	371	387	405	417	430	452	470	492	502
15	32	52	142	179	211	238	267	290	316	342	374	391	403
16	32	43	121	152	173	193	211	240	247	262	280	291	310
17	140	178	238	264	291	307	316	339	353	361	382	400	408
18	200	235	286	300	210	320	329	339	349	358	374	392	412
19	230	275	361	377	396	407	415	430	441	455	474	489	512
20	260	300	429	462	478	492	504	517	534	550	589	622	662
21	360	395	488	514	538	563	591	619	652	685	711	729	742
22	170	235	297	312	322	327	333	338	346	353	364	373	383
23	182	270	366	383	395	406	422	434	446	460	475	487	500
24	300	302	450	474	487	496	505	518	534	551	575	588	598
25	360	400	491	529	550	570	585	599	614	630	653	682	709
27	124	170	251	279	304	317	330	339	350	364	383	393	403
30	0	27	97	140	163	183	203	225	249	277	335	390	435
58	145	300	436	452	462	484	502	513	527	548	576	606	640

*Volume per cent overhead

TABLE III

EXPERIMENTAL ASTM DISTILLATION CURVES-DATA OF GEDDES (10)

Sample Number	ASTM Distillation, °F										
	IBP	10%*	20%	30%	40%	50%	60%	70%	80%	90%	EP
1	117	143	153	162	171	180	188	198	210	227	279
2	158	181	186	192	198	203	210	217	226	242	283
3	220	240	244	250	254	260	265	270	278	288	316
4	324	334	337	342	346	351	356	362	370	382	411
5	100	162	189	208	222	233	246	257	270	287	322
6	318	328	331	334	337	340	344	348	354	364	392
7	381	397	405	410	416	422	429	437	449	465	497
8	456	484	491	498	505	512	521	534	550	577	648
9	113	183	210	230	246	259	275	290	306	327	374
10	126	214	250	278	302	329	353	379	404	431	471
11	139	353	296	335	370	400	433	461	491	523	597
12	387	421	431	442	455	468	481	498	518	552	622
13	340	387	401	416	432	451	468	486	509	541	616
14	332	354	362	370	379	389	400	412	425	444	480
15	128	179	202	223	244	265	286	308	329	352	385
16	117	160	173	185	196	208	219	229	242	259	292
17	238	269	280	291	303	313	324	334	346	362	390
18	287	308	313	317	321	325	328	333	339	350	382
19	339	375	385	392	398	405	412	420	431	448	481
20	349	456	474	484	494	503	512	524	541	567	636
21	465	536	555	572	586	601	616	635	656	683	736
22	296	316	321	324	328	331	334	338	344	351	379
23	345	387	398	404	412	419	425	433	444	459	483
24	352	470	485	495	502	508	515	522	531	545	586
25	469	527	542	552	564	573	583	595	609	633	681
27	231	286	300	309	319	328	335	346	356	372	415
30	100	157	178	194	216	222	238	261	292	335	404
58	382	471	485	492	500	508	516	524	538	565	613

*Volume per cent overhead

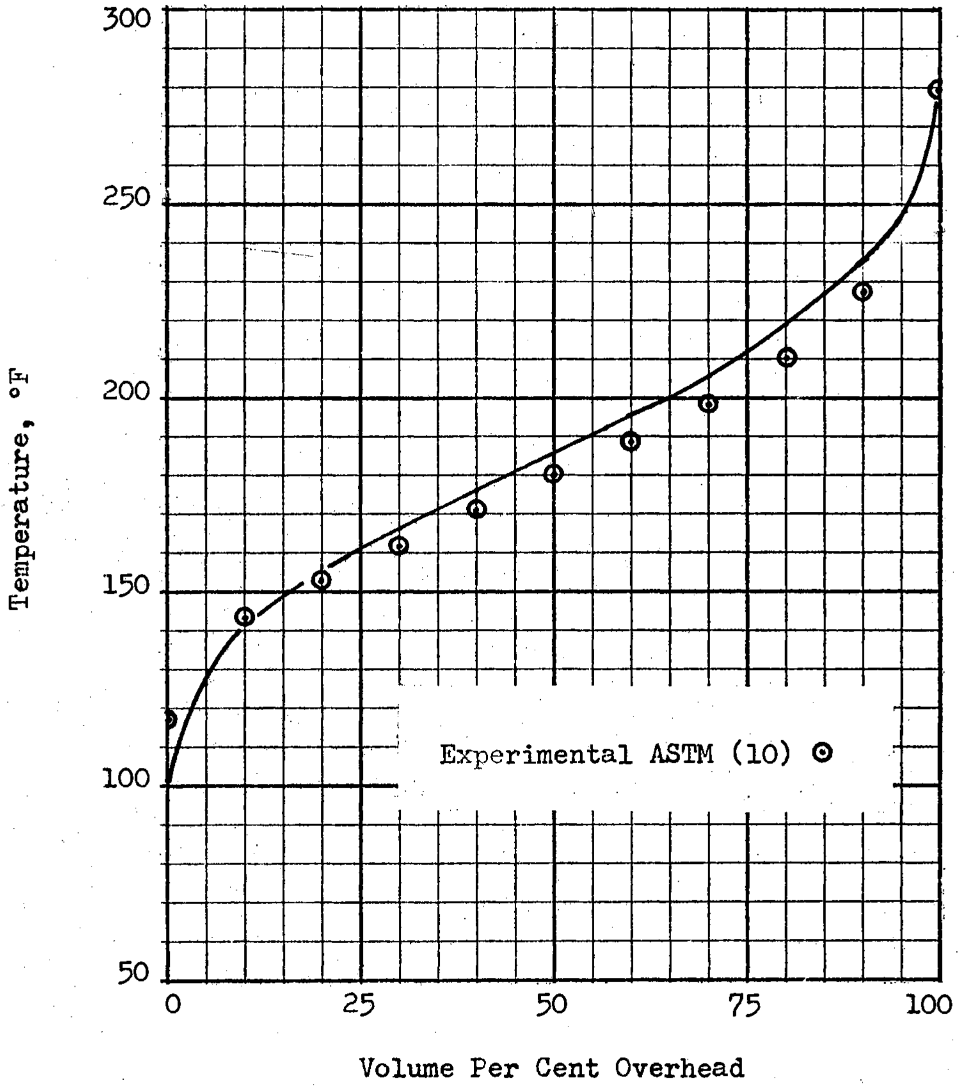


Figure 14. Experimental Points and Calculated ASTM Curve for Sample No. 1

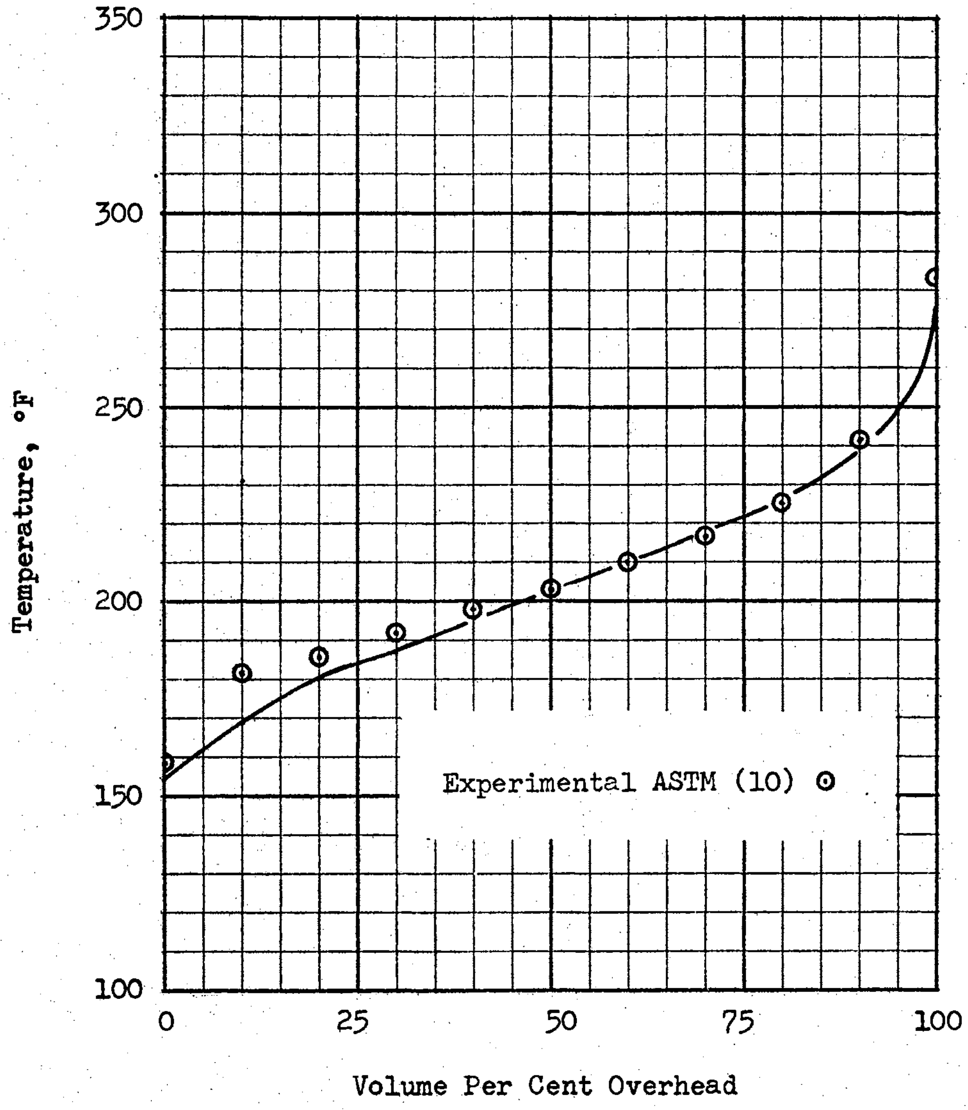


Figure 15. Experimental Points and Calculated ASTM Curve for Sample No. 2

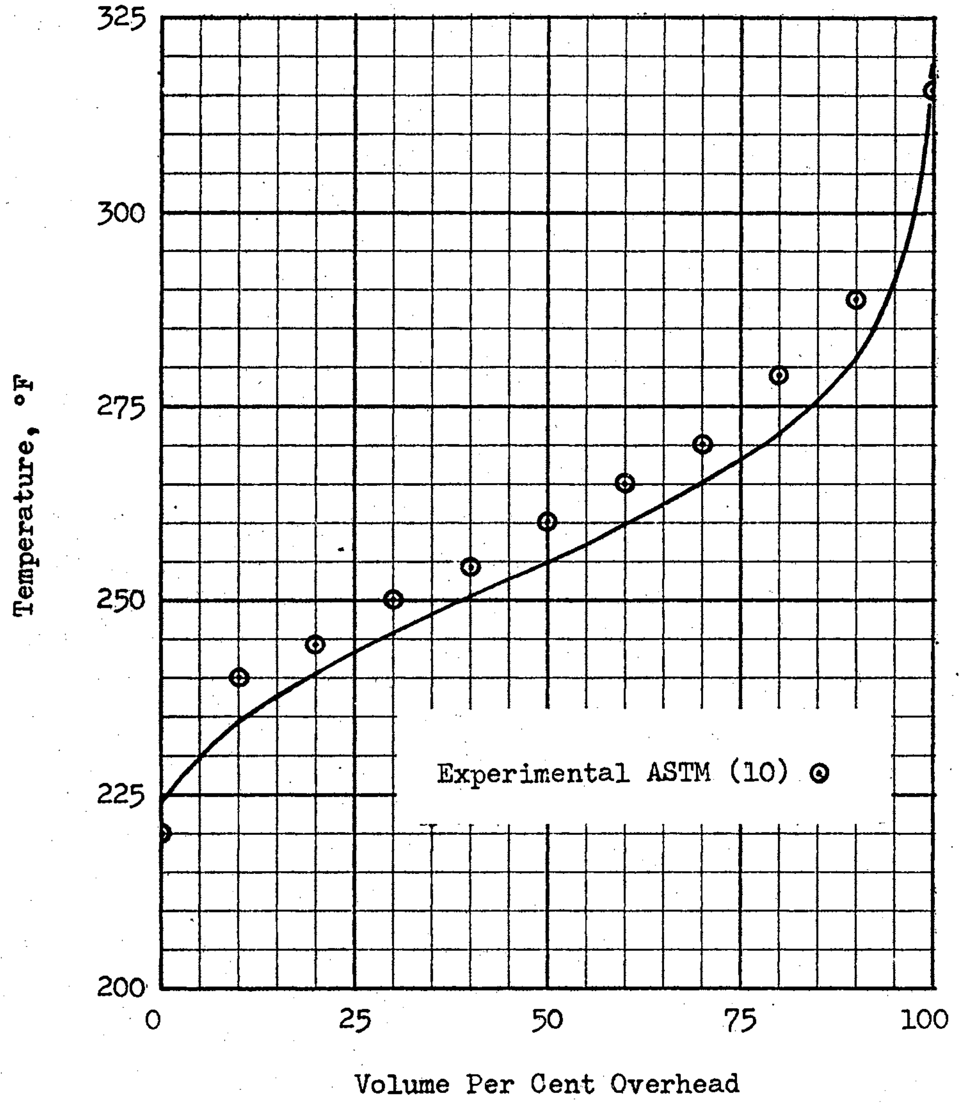


Figure 16. Experimental Points and Calculated ASTM Curve for Sample No. 3

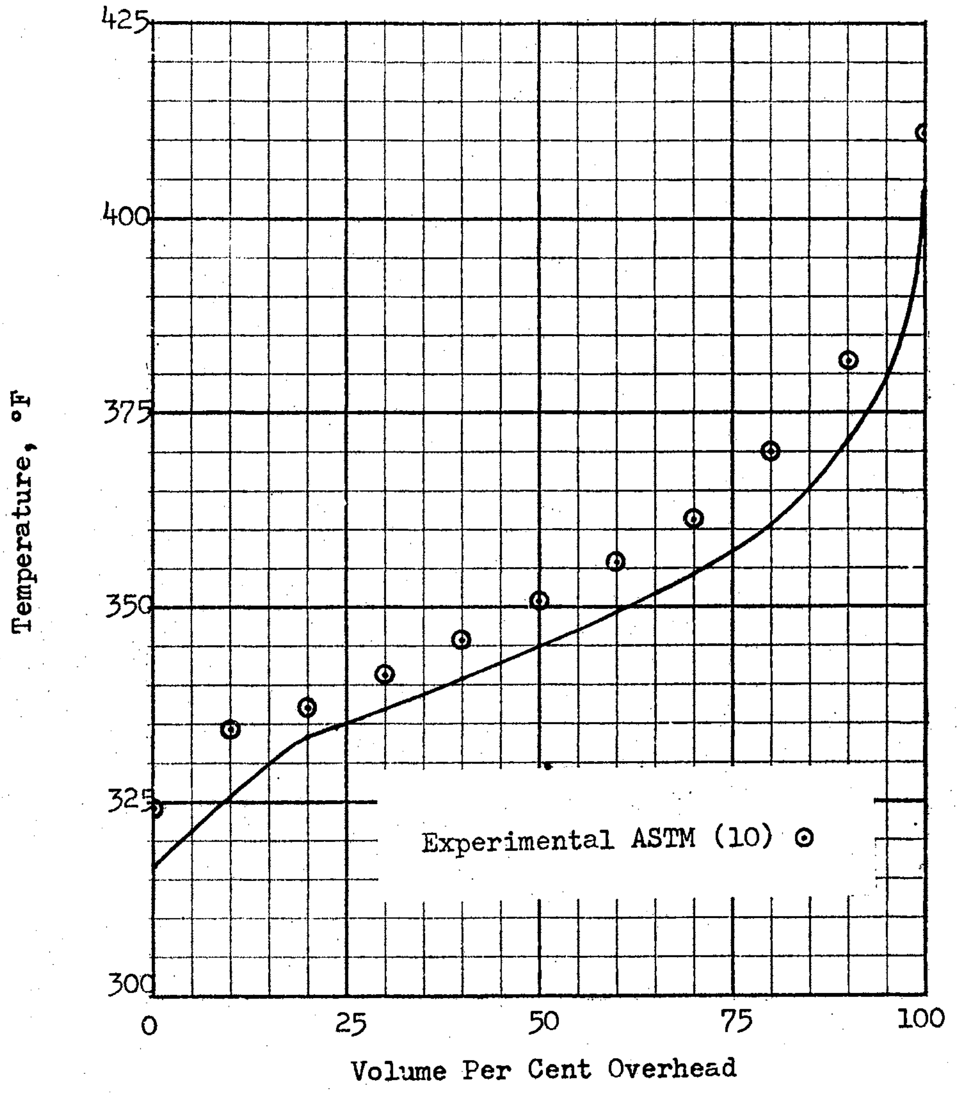


Figure 17. Experimental Points and Calculated ASTM Curve for Sample No. 4

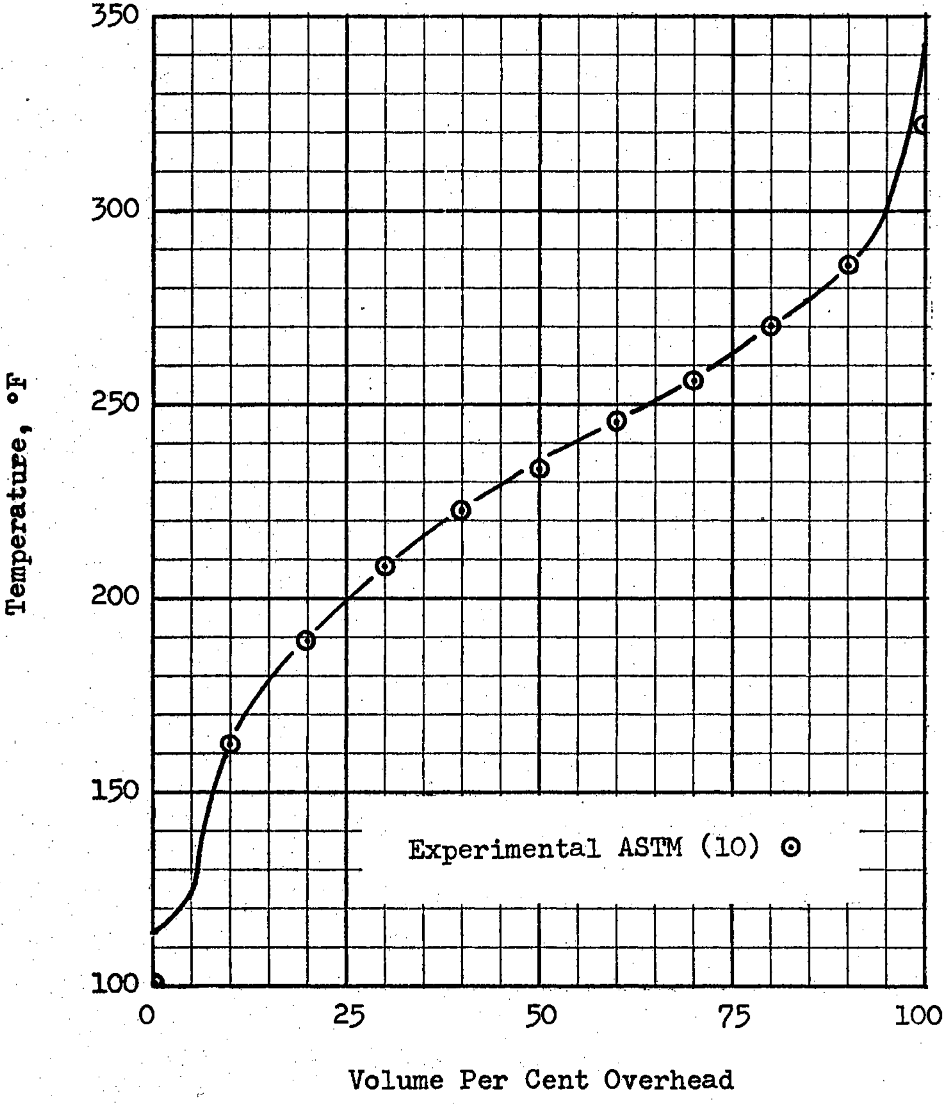


Figure 18. Experimental Points and Calculated ASTM Curve for Sample No. 5

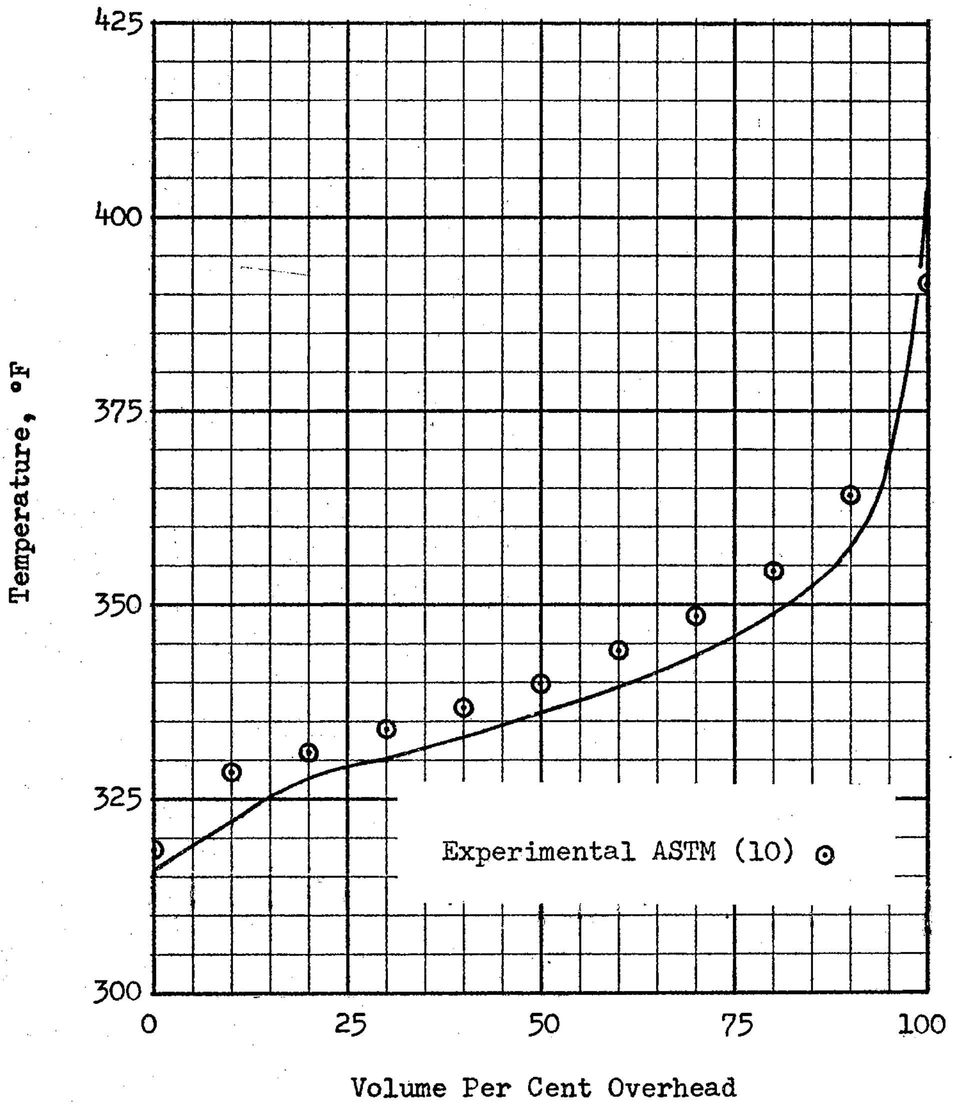


Figure 19. Experimental Points and Calculated ASTM Curve for Sample No. 6

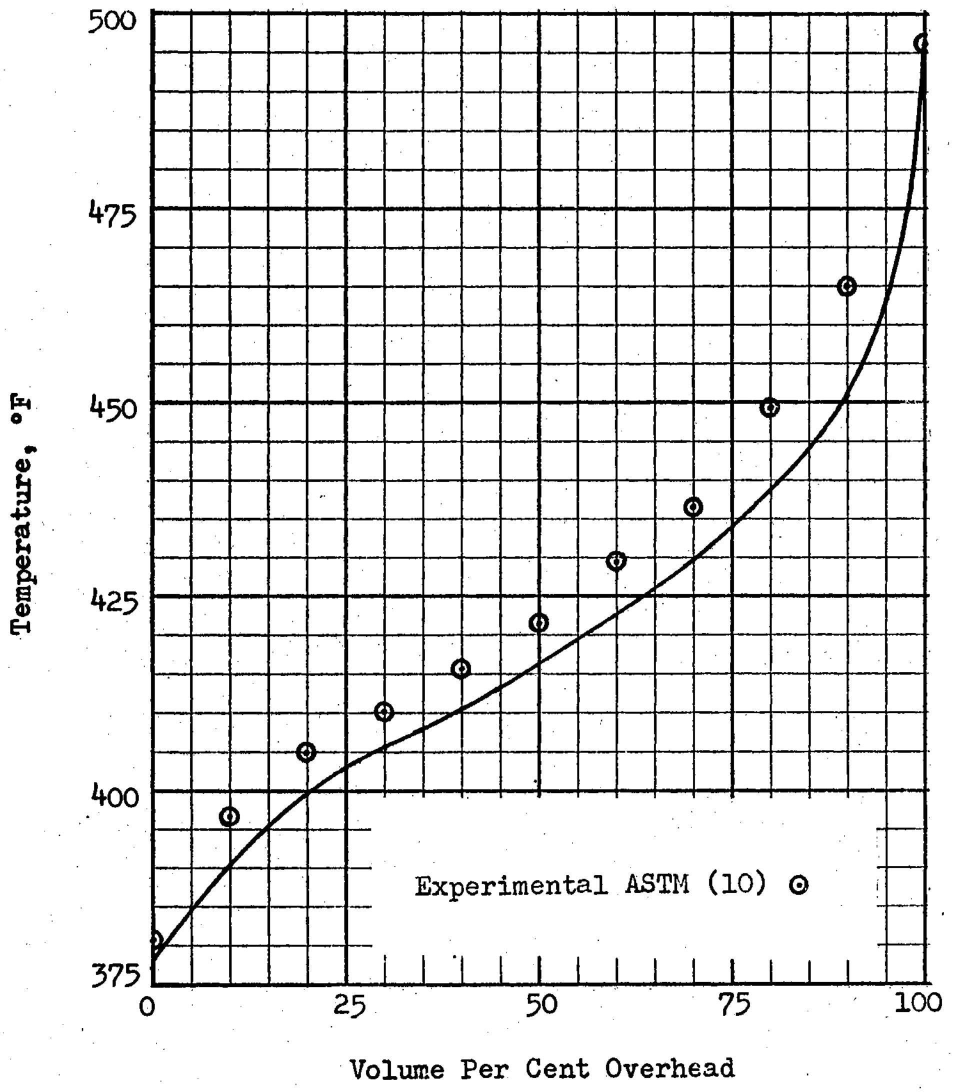


Figure 20. Experimental Points and Calculated ASTM Curve for Sample No. 7

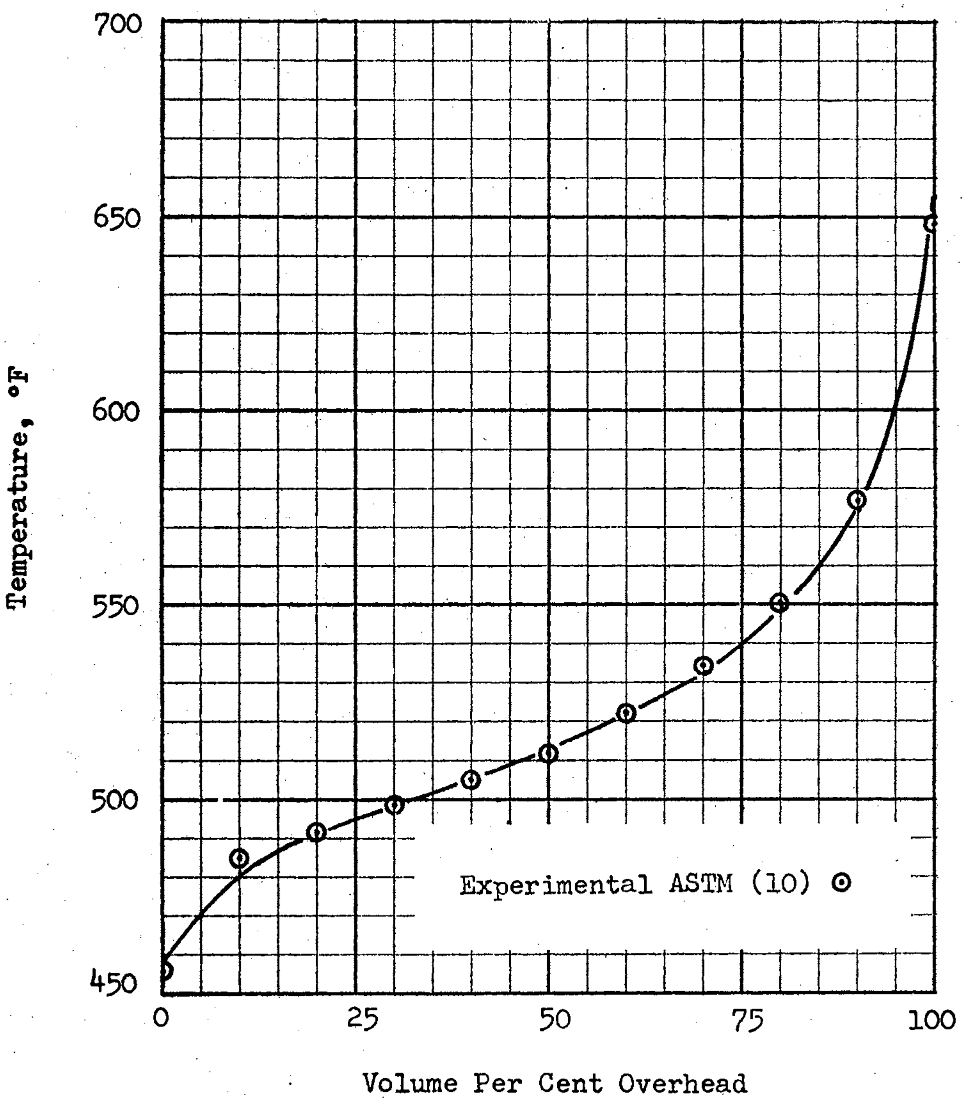


Figure 21. Experimental Points and Calculated ASTM Curve for Sample No. 8

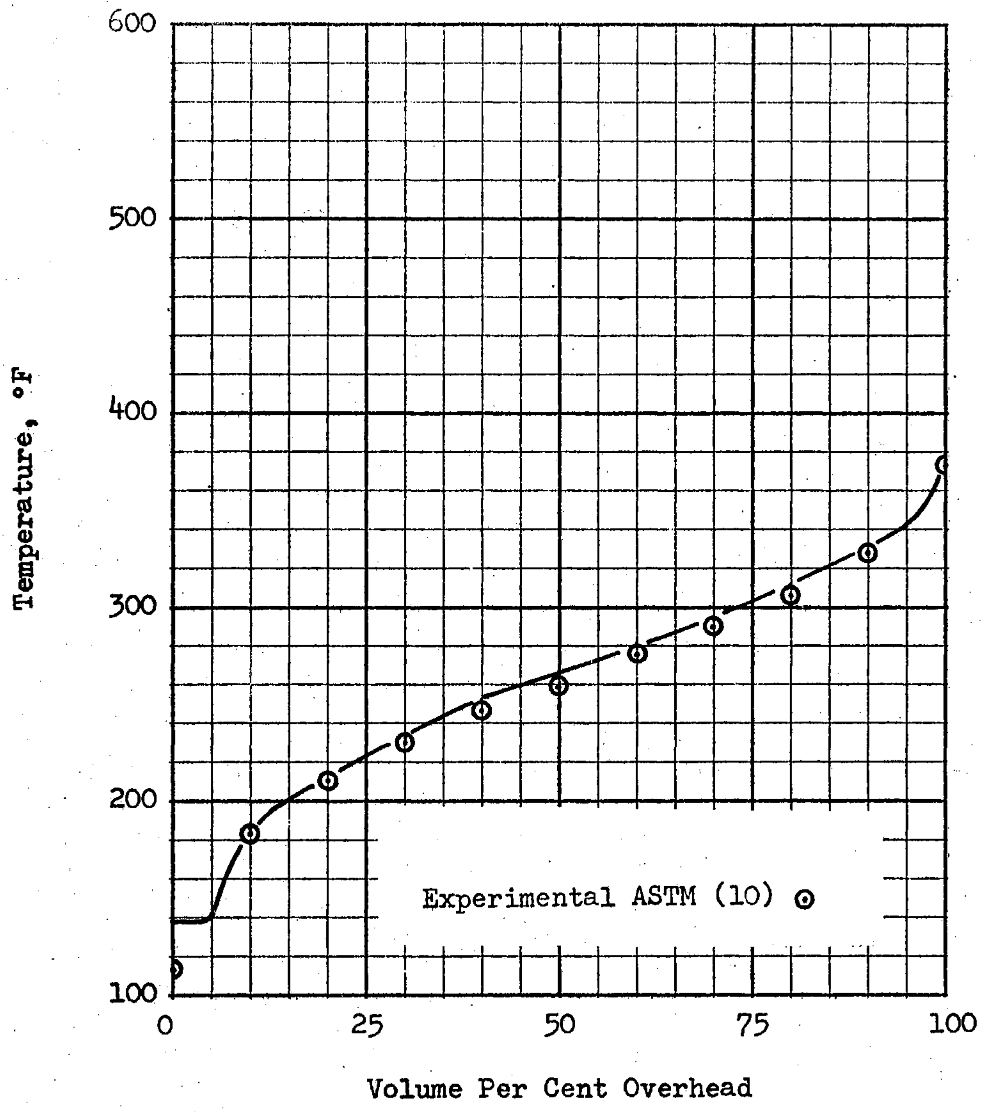


Figure 22. Experimental Points and Calculated ASTM Curve for Sample No. 9

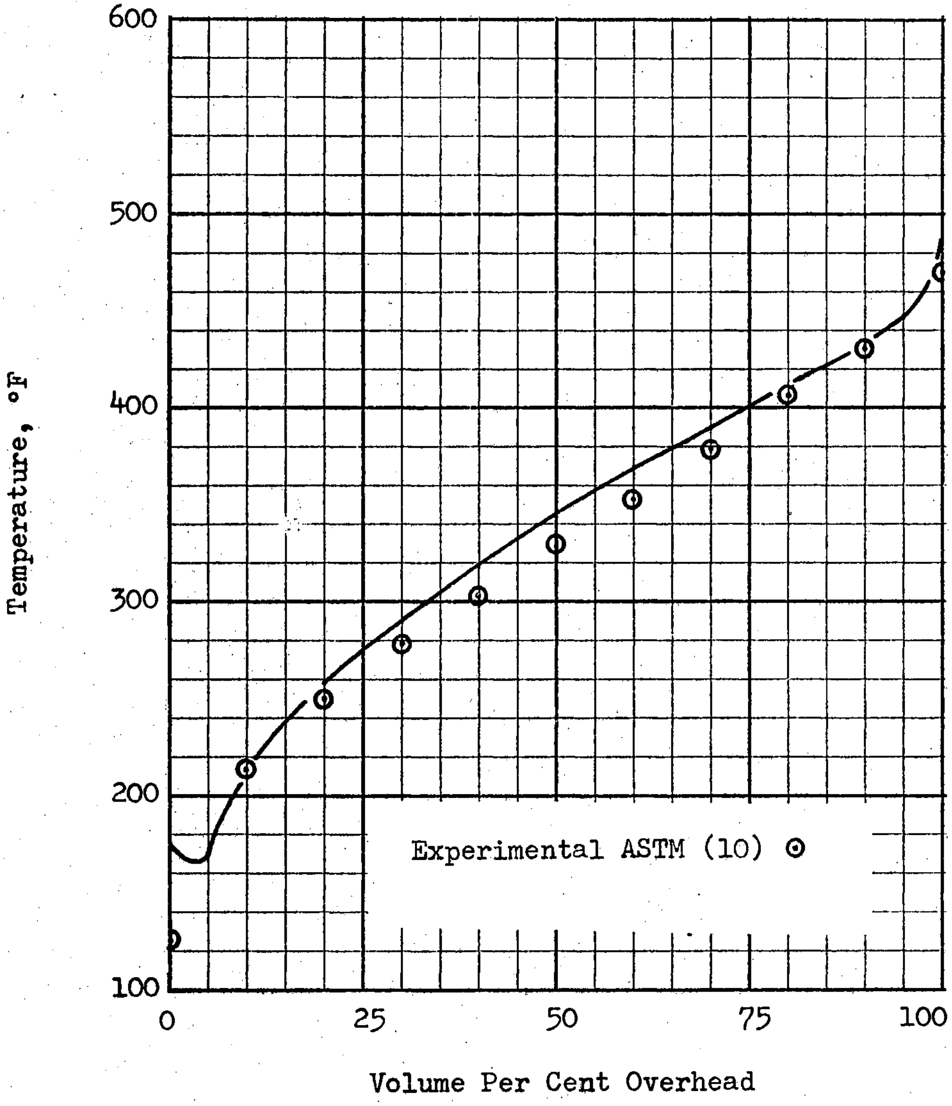
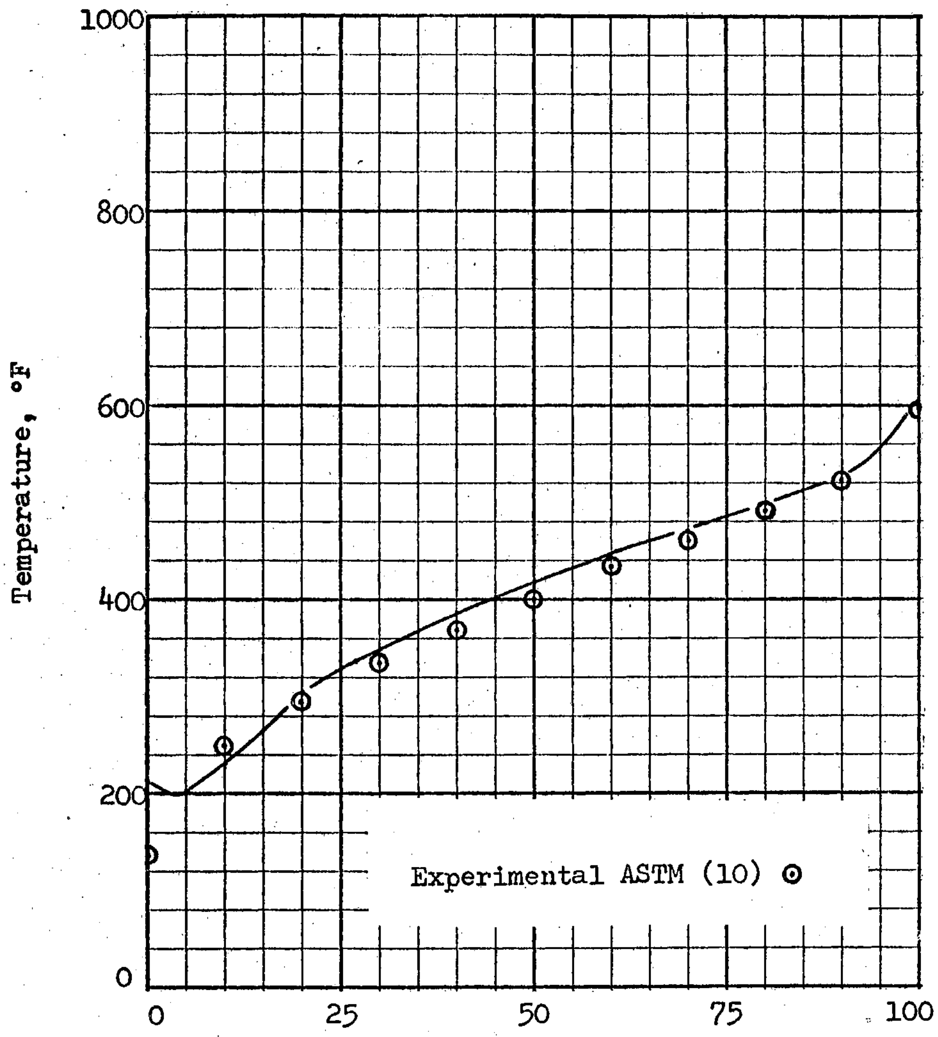


Figure 23. Experimental Points and Calculated ASTM Curve for Sample No. 10



Volume Per Cent Overhead

Figure 24. Experimental Points and Calculated ASTM Curve for Sample No. 11

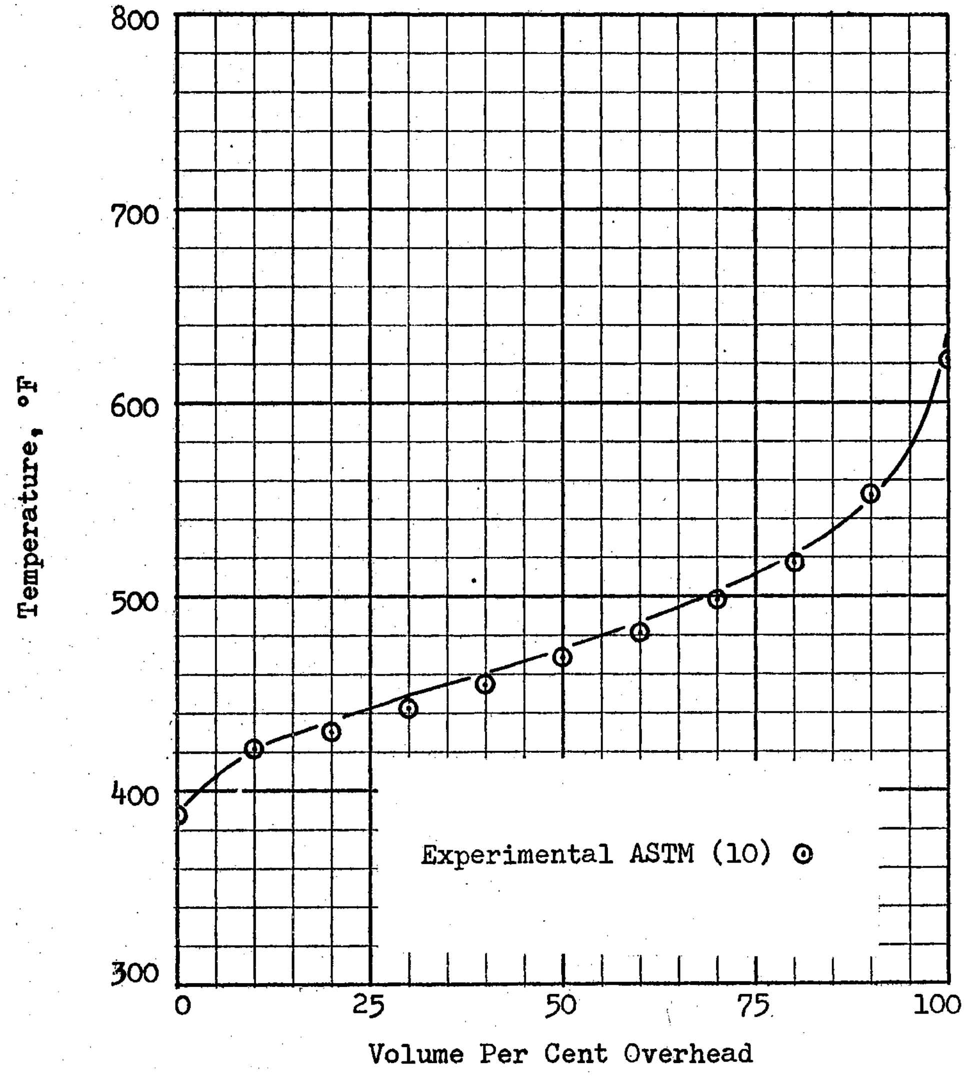


Figure 25. Experimental Points and Calculated ASTM Curve for Sample No. 12

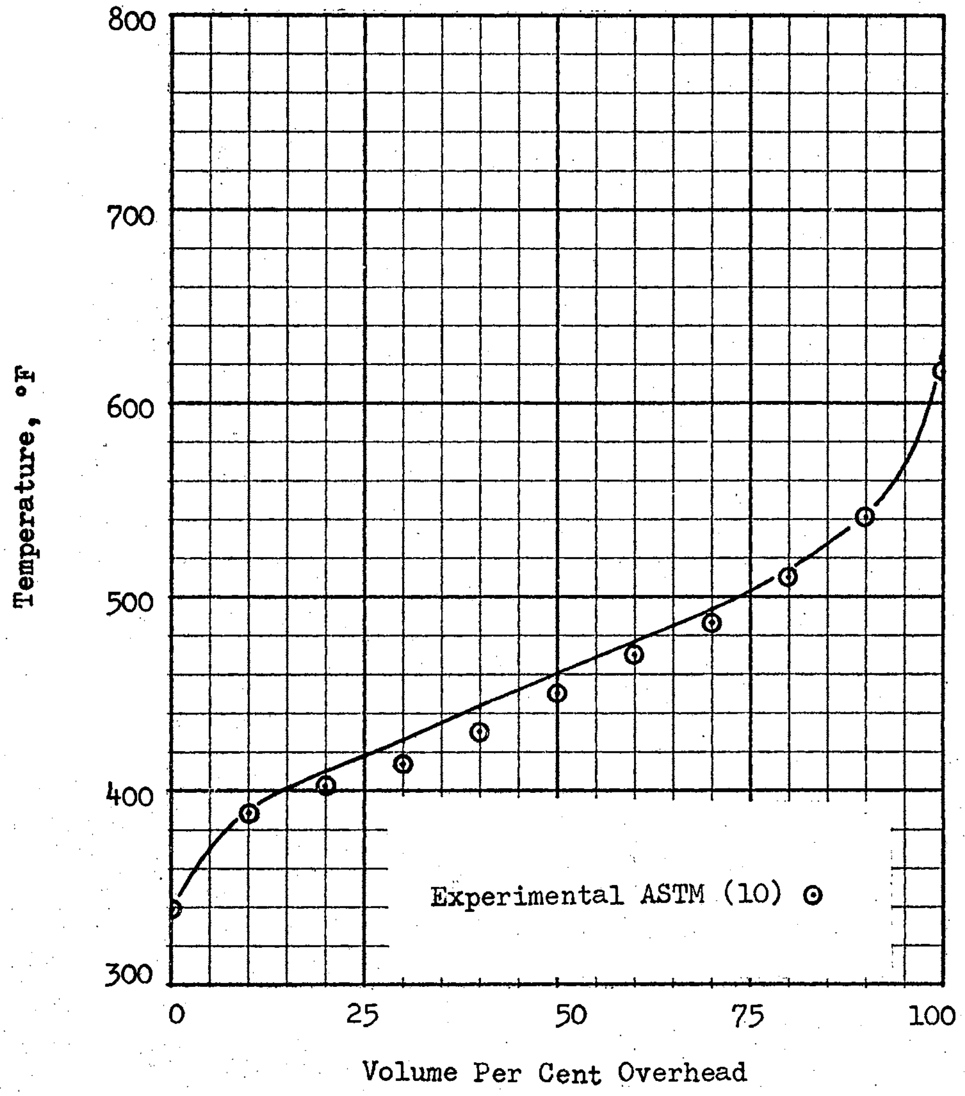


Figure 26. Experimental Points and Calculated ASTM Curve for Sample No. 13

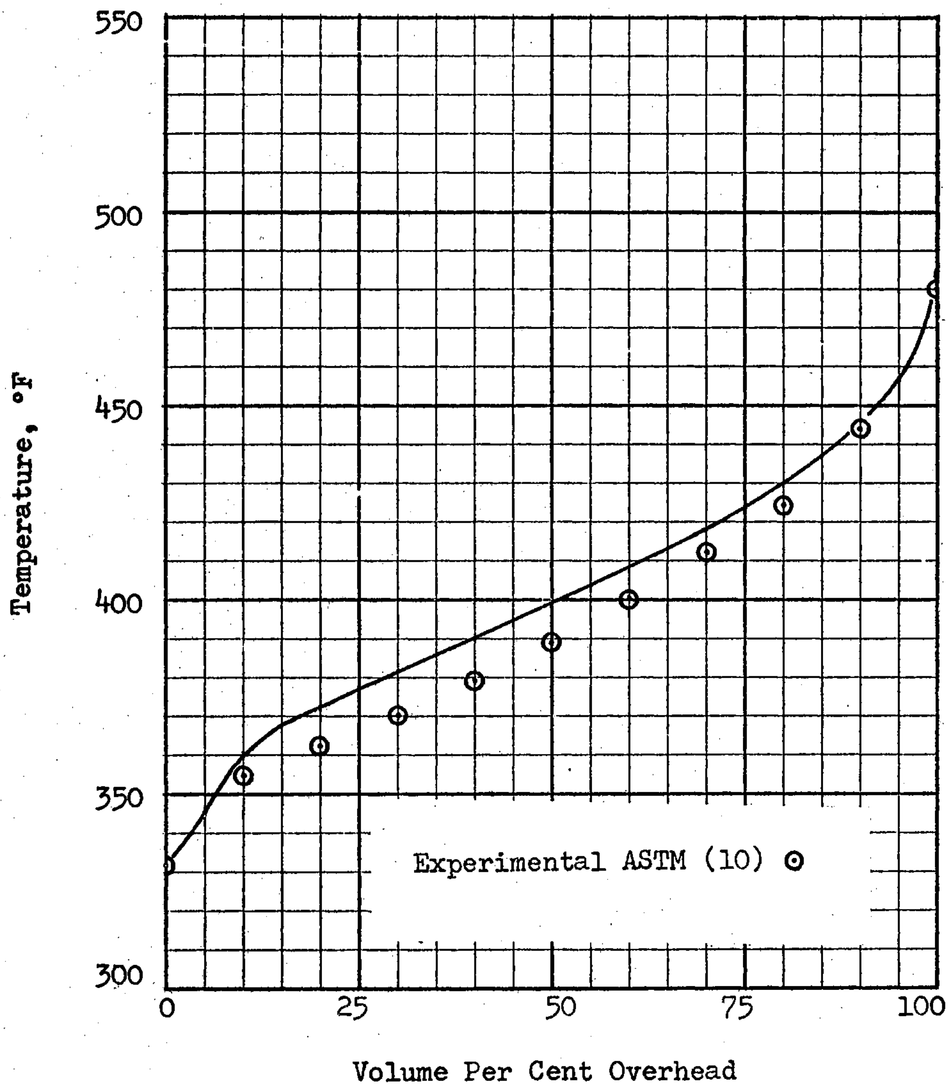


Figure 27. Experimental Points and Calculated ASTM Curve for Sample No. 14

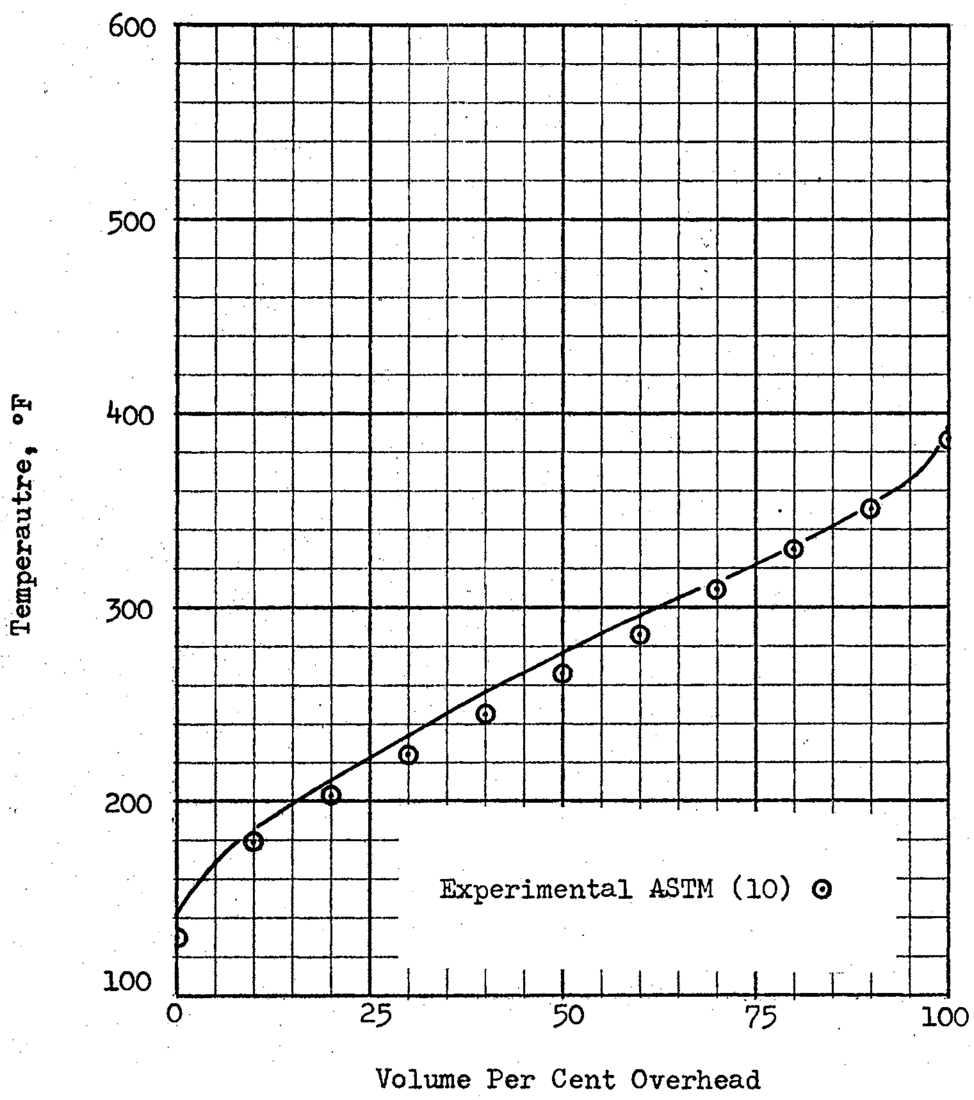


Figure 28. Experimental Points and Calculated ASTM Curve for Sample No. 15

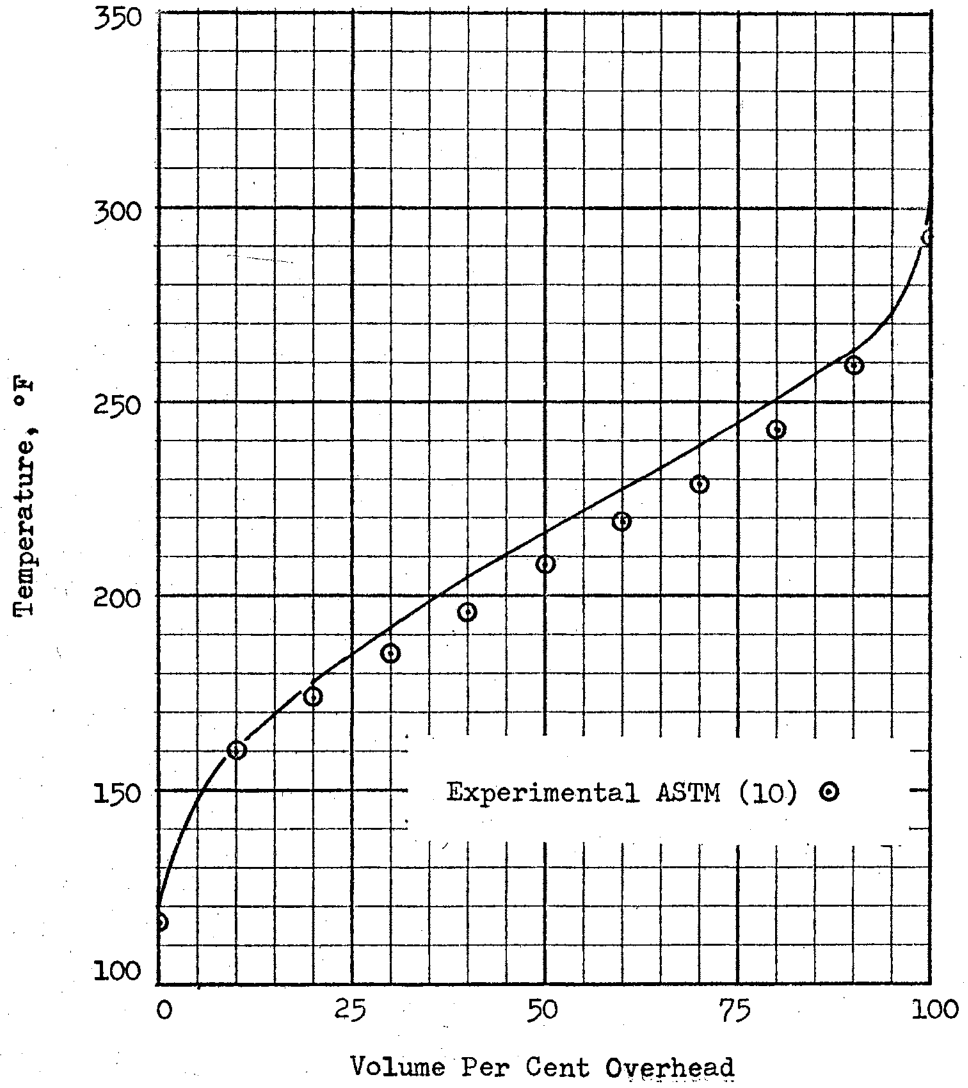


Figure 29. Experimental Points and Calculated ASTM Curve for Sample No. 16

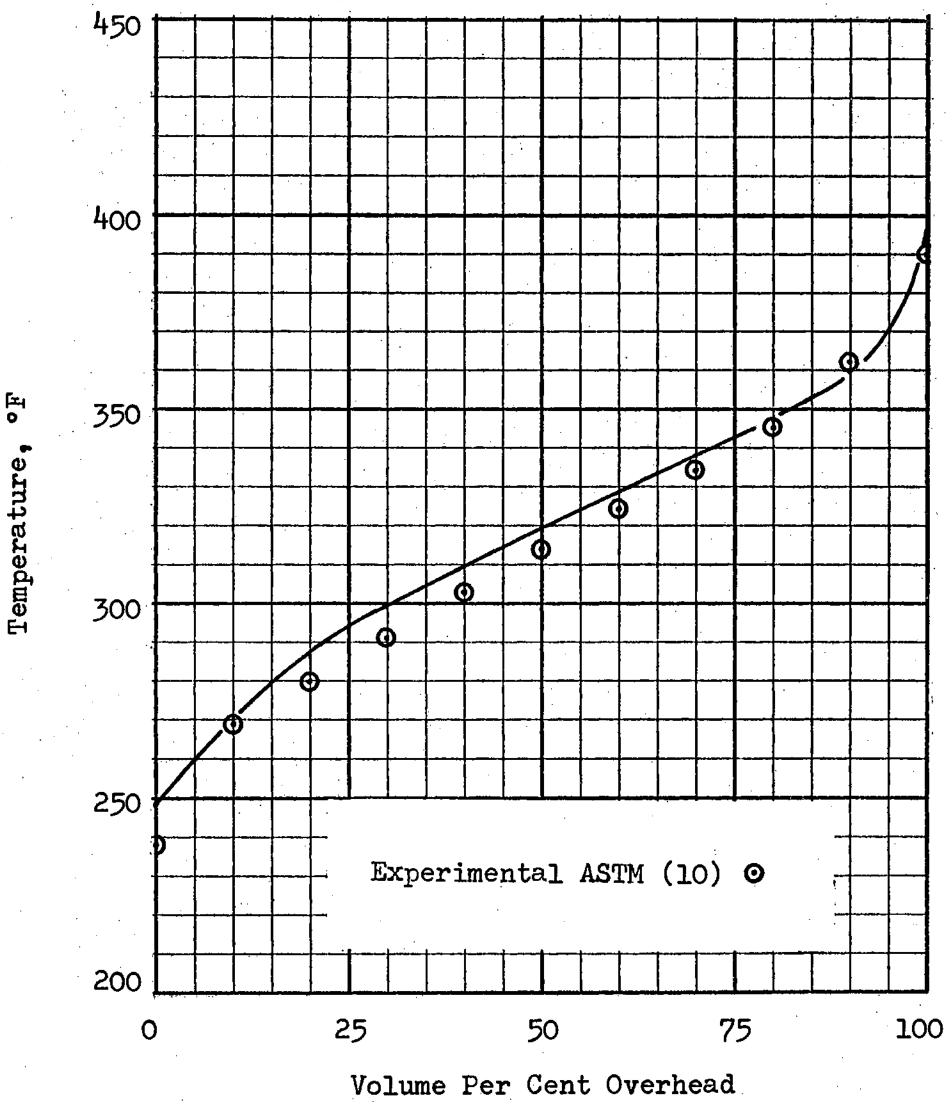


Figure 30. Experimental Points and Calculated ASTM Curve for Sample No. 17

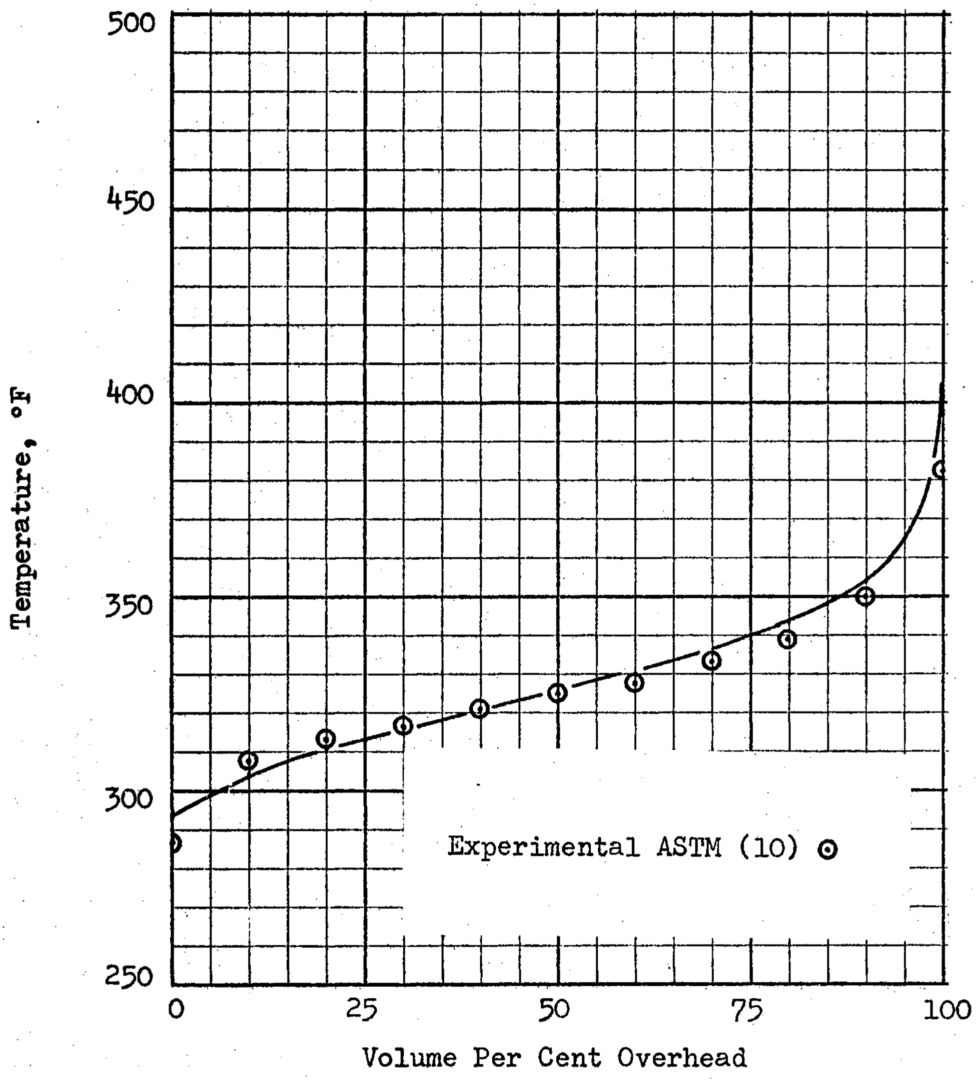


Figure 31. Experimental Points and Calculated ASTM Curve for Sample No. 18

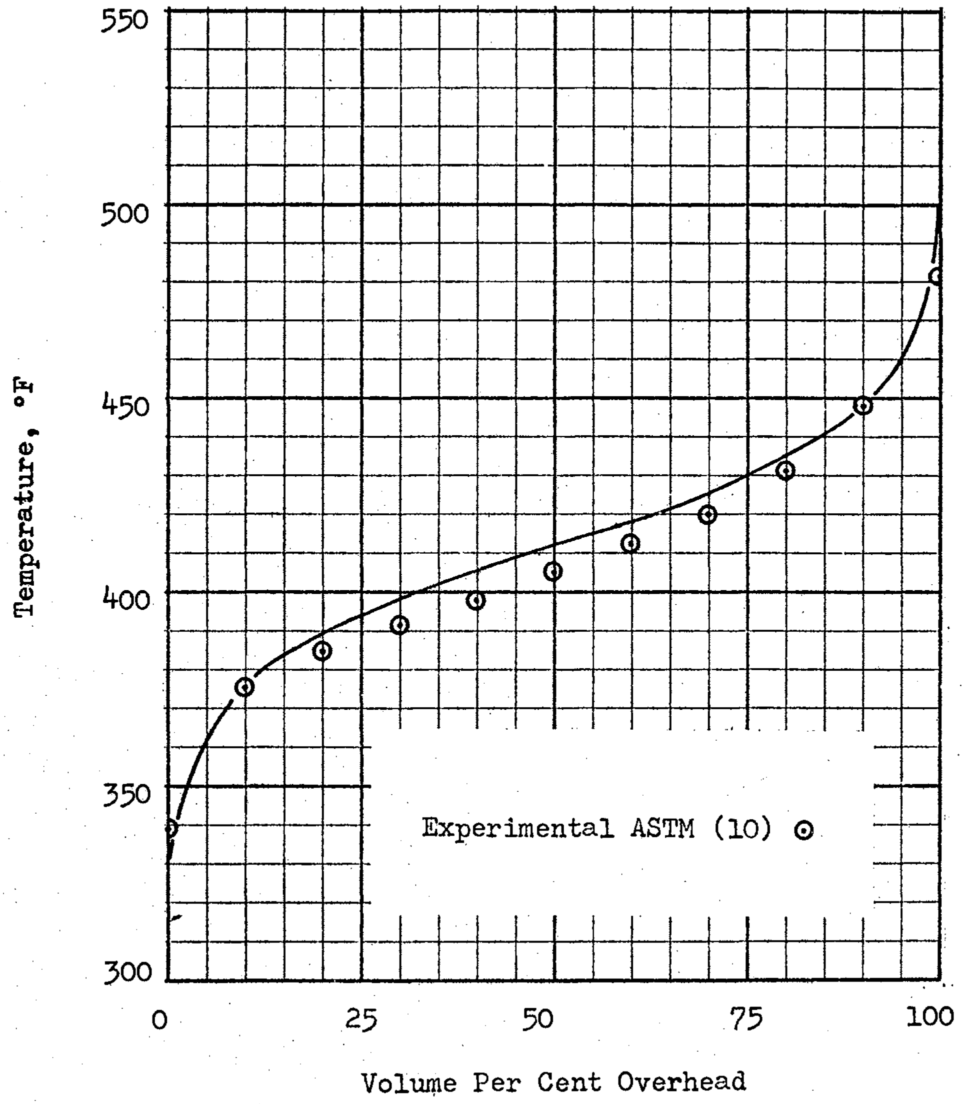


Figure 32. Experimental Points and Calculated ASTM Curve for Sample No. 19

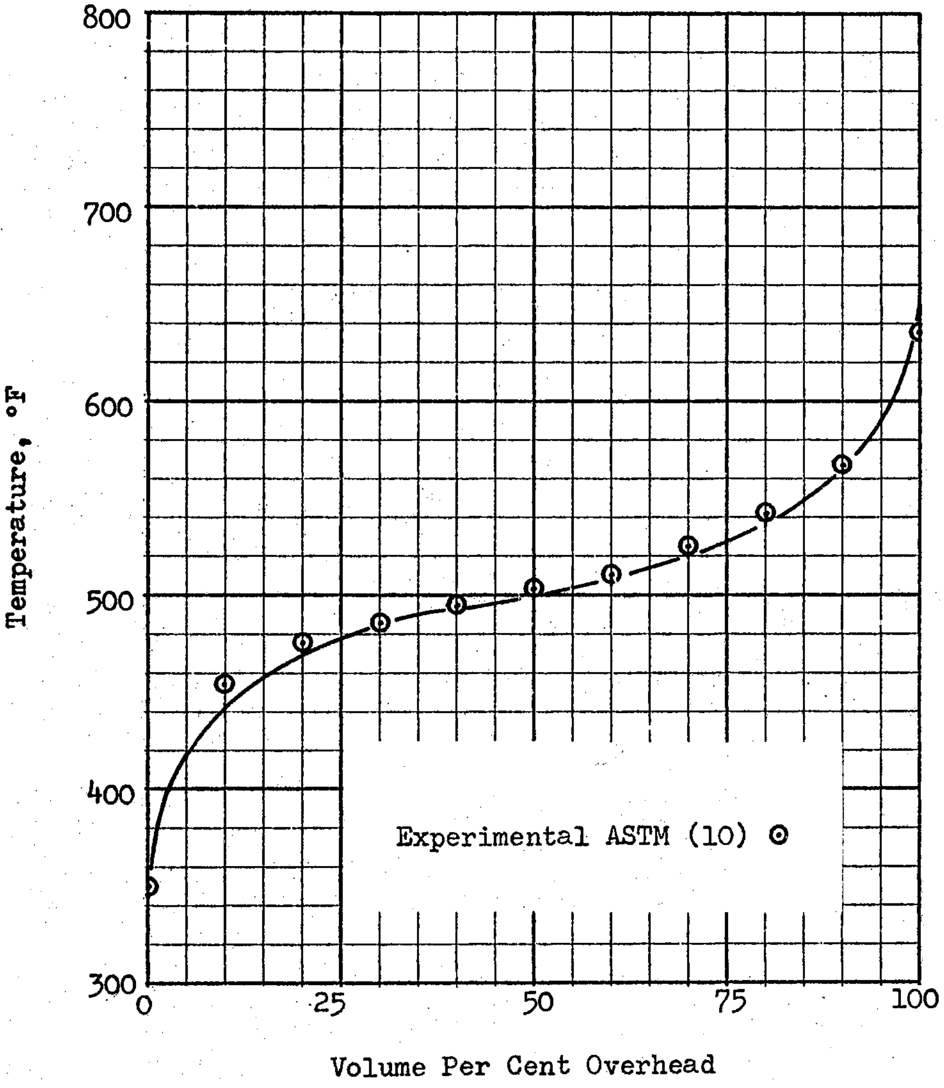


Figure 33. Experimental Points and Calculated ASTM Curve for Sample No. 20

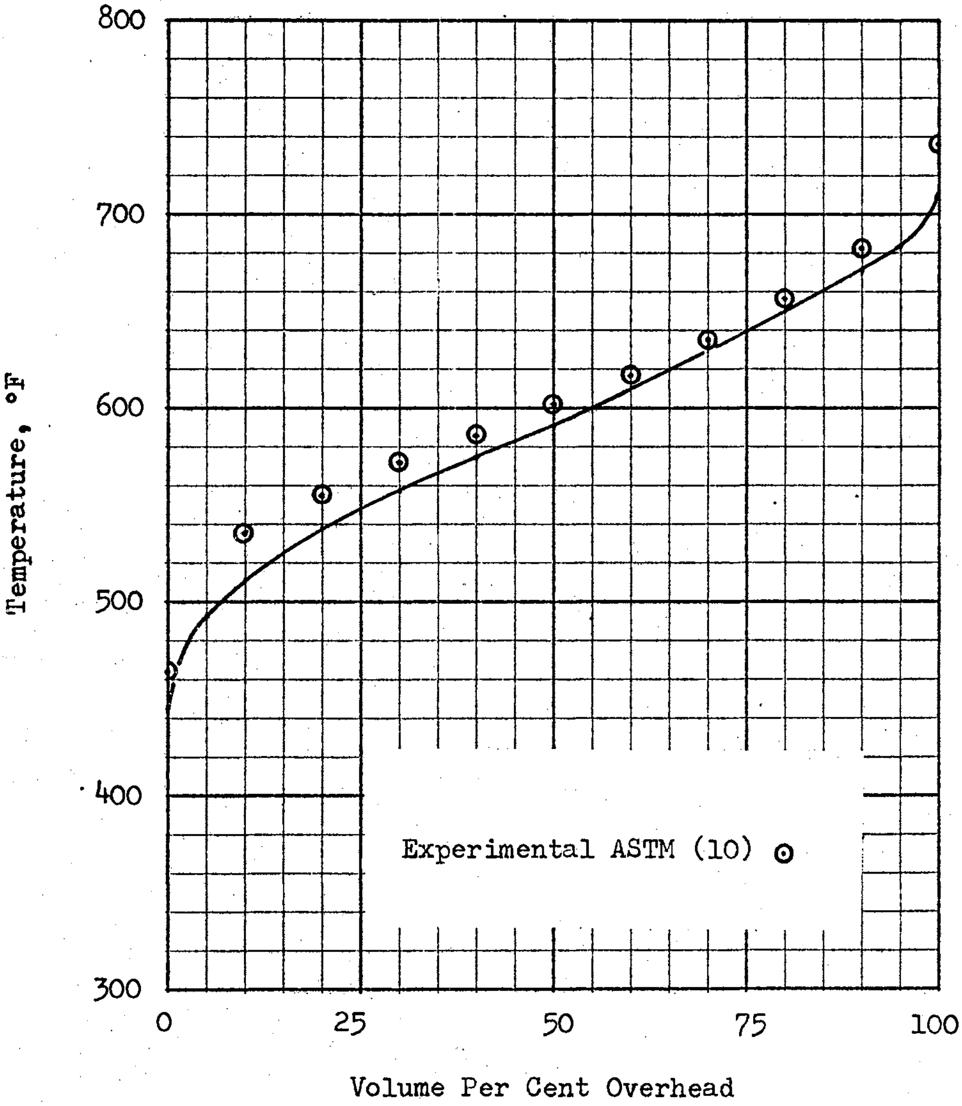


Figure 34. Experimental Points and Calculated ASTM Curve for Sample No. 21

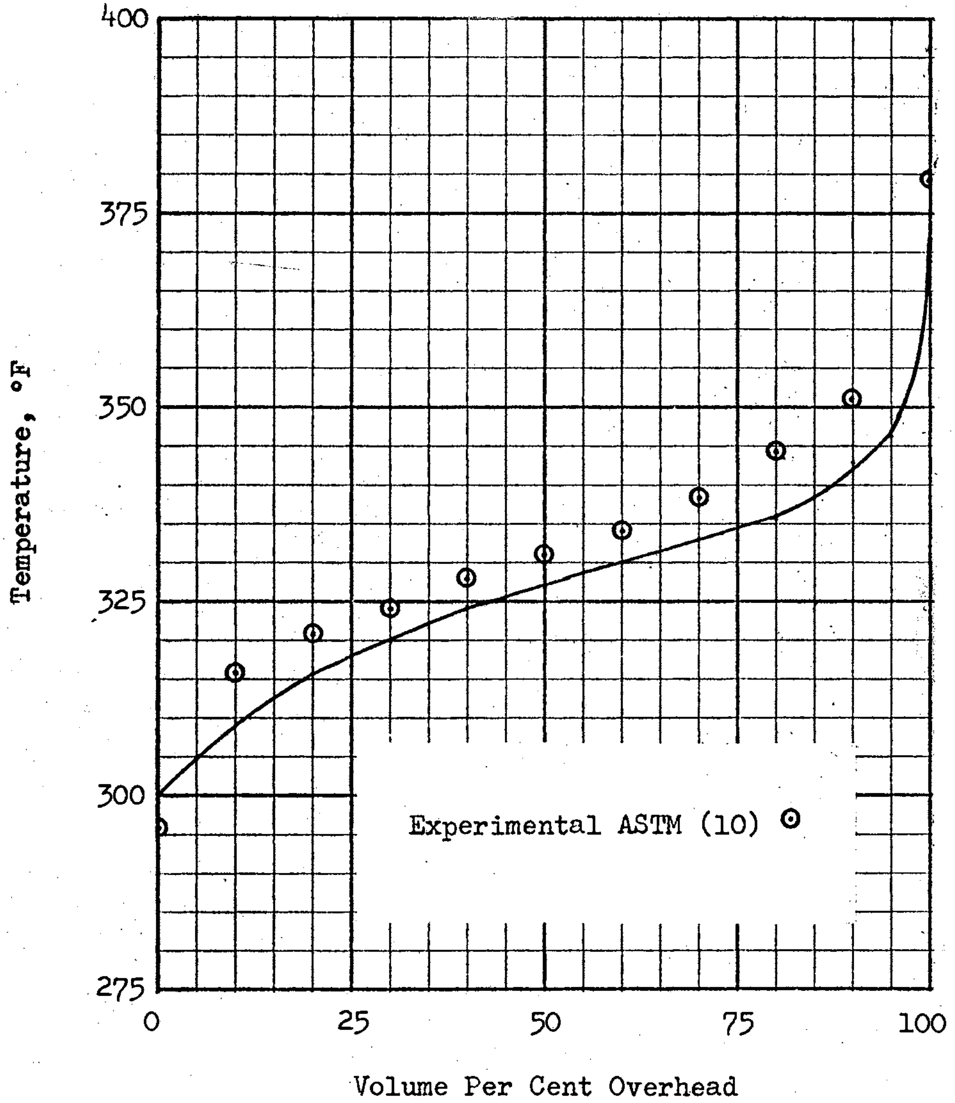


Figure 35. Experimental Points and Calculated ASTM Curve for Sample No. 22

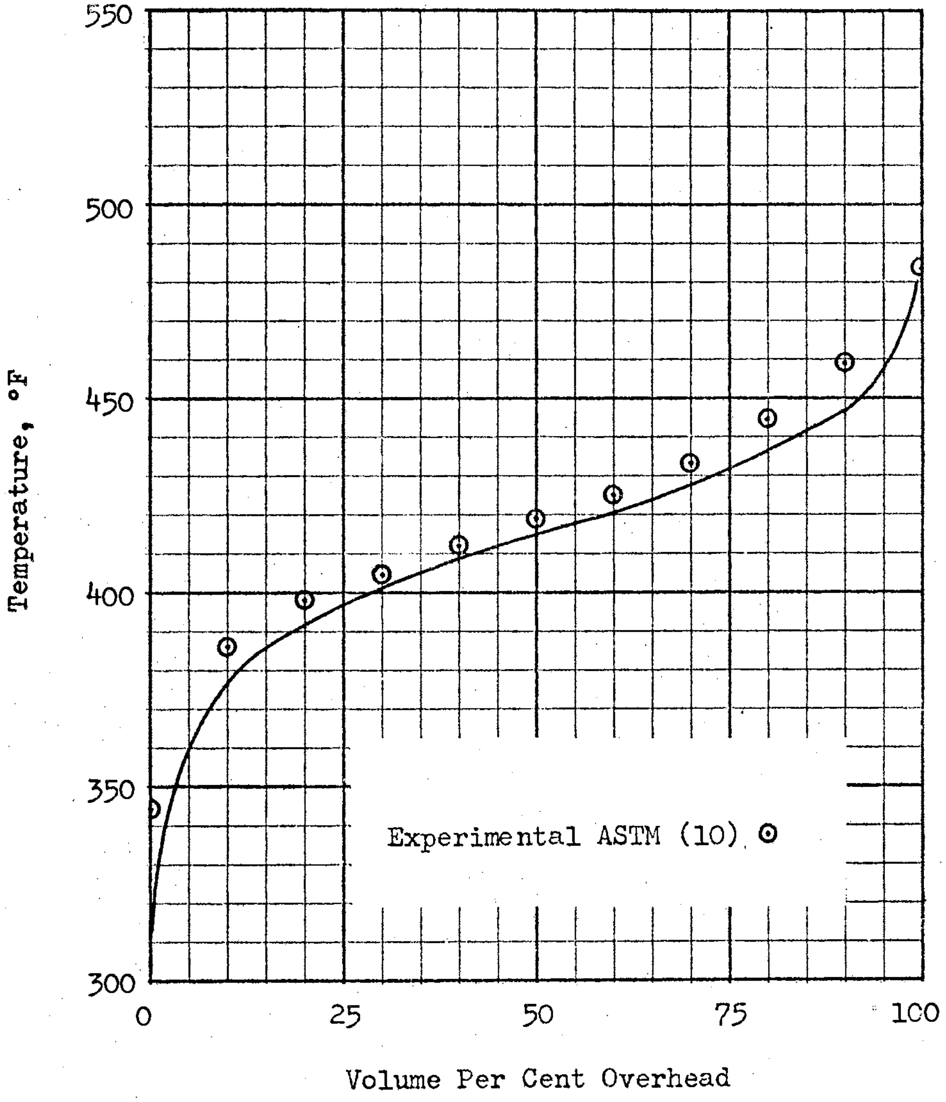


Figure 36. Experimental Points and Calculated ASTM Curve for Sample No. 23

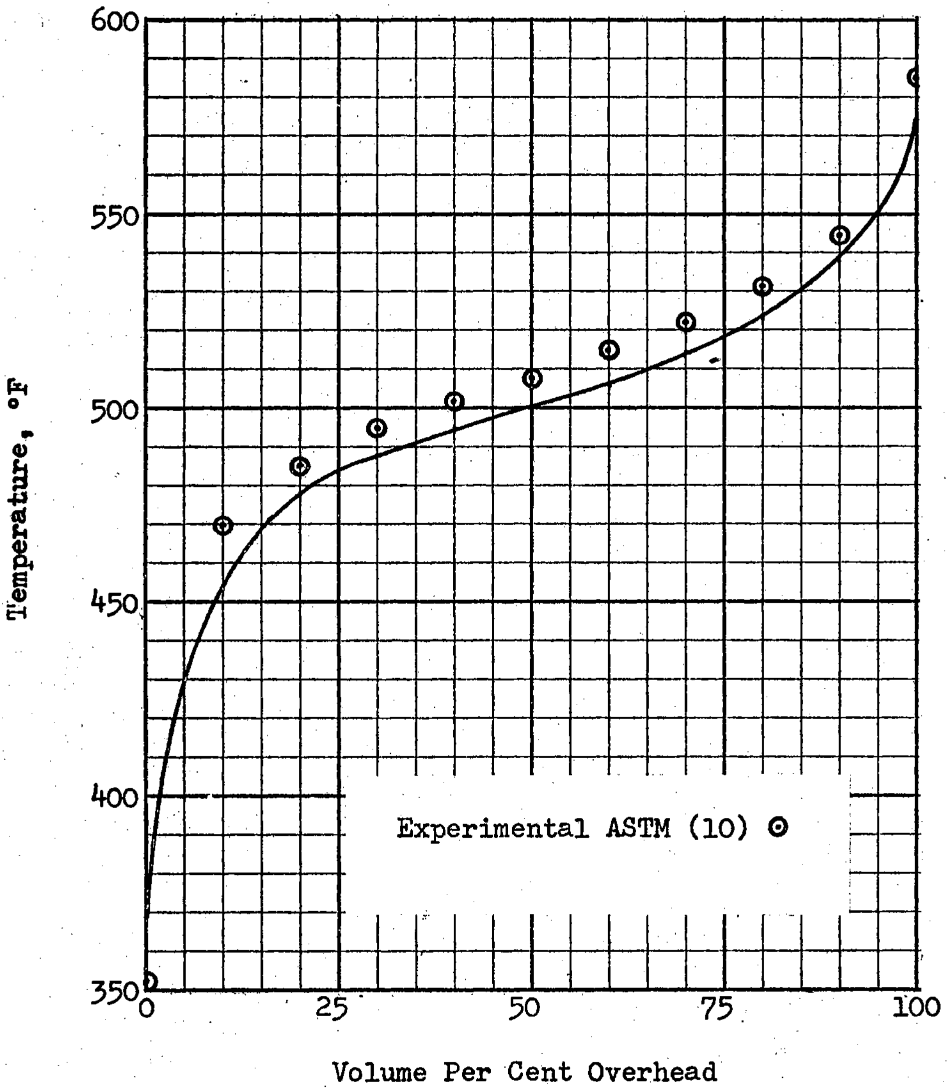


Figure 37. Experimental Points and Calculated ASTM Curve for Sample No. 24

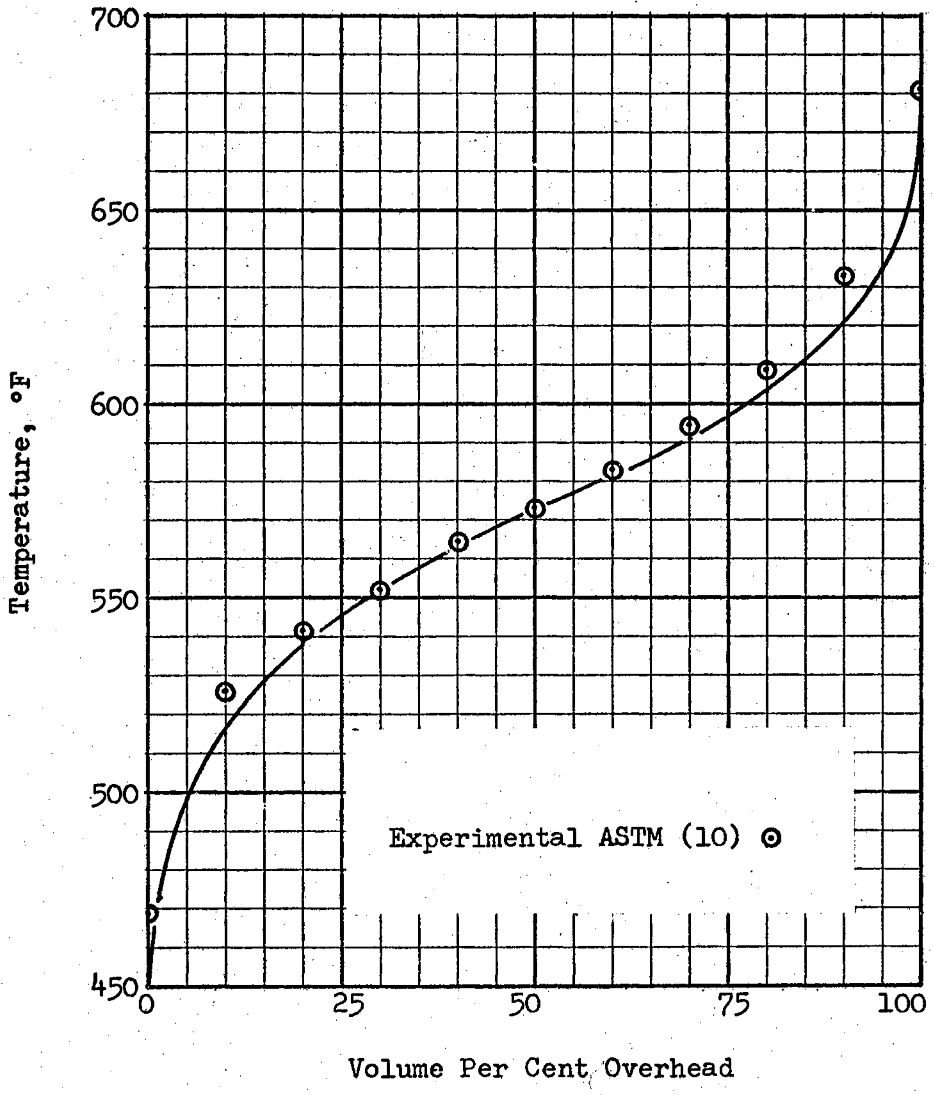


Figure 38. Experimental Points and Calculated ASTM Curve for Sample No. 25

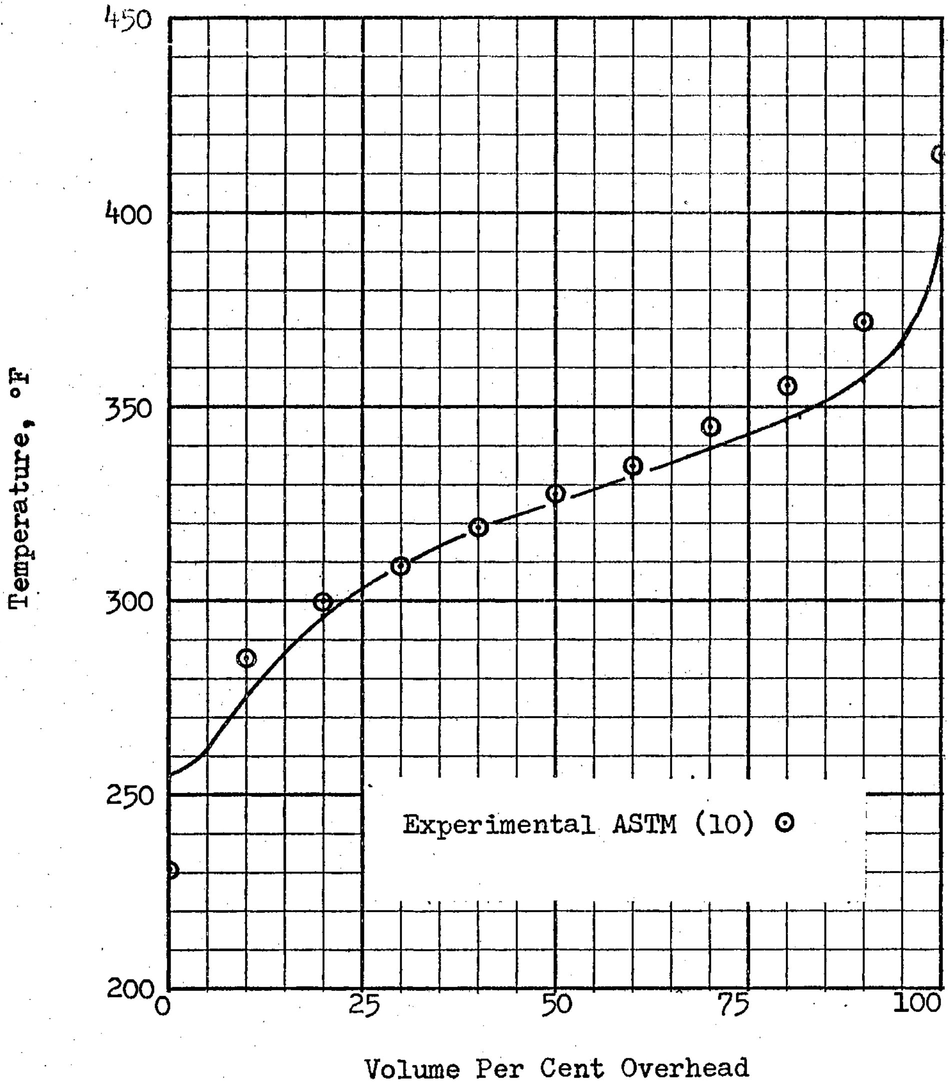


Figure 39. Experimental Points and Calculated ASTM Curve for Sample No. 27

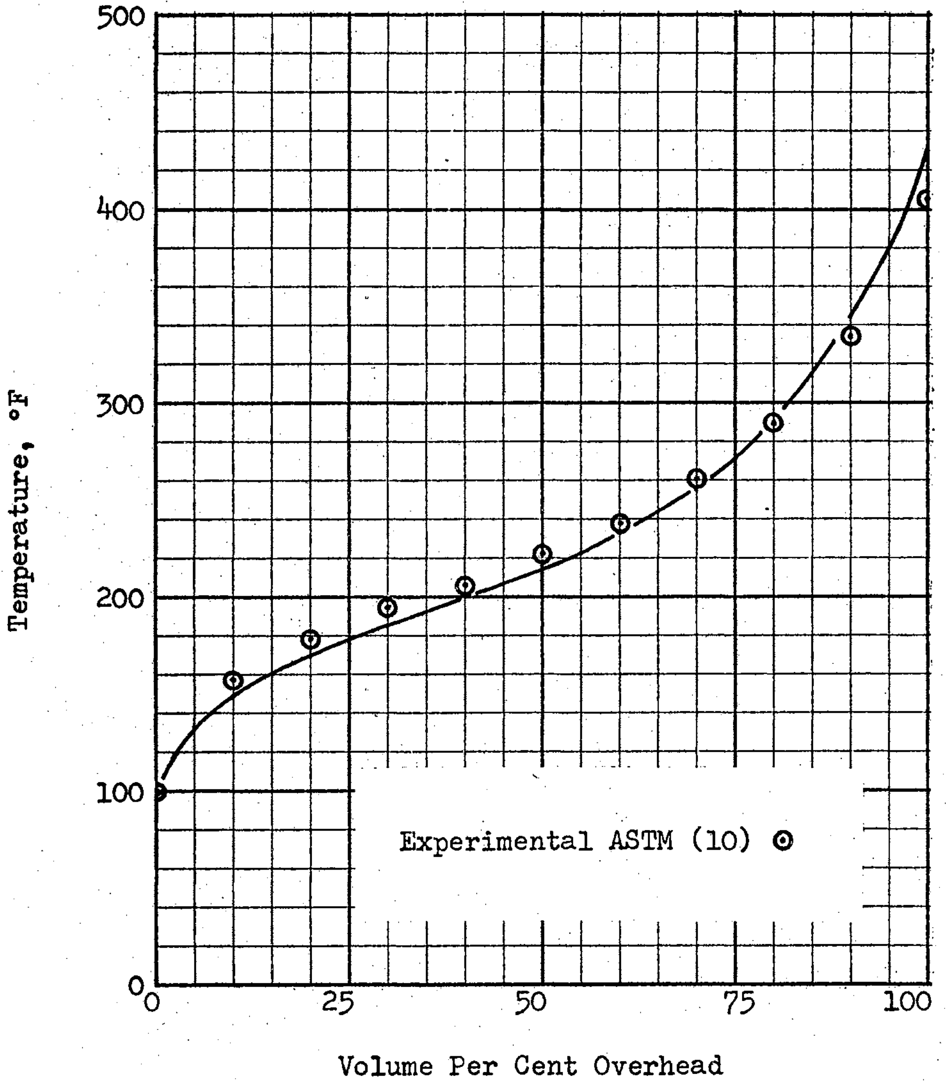


Figure 40. Experimental Points and Calculated ASTM Curve for Sample No. 30

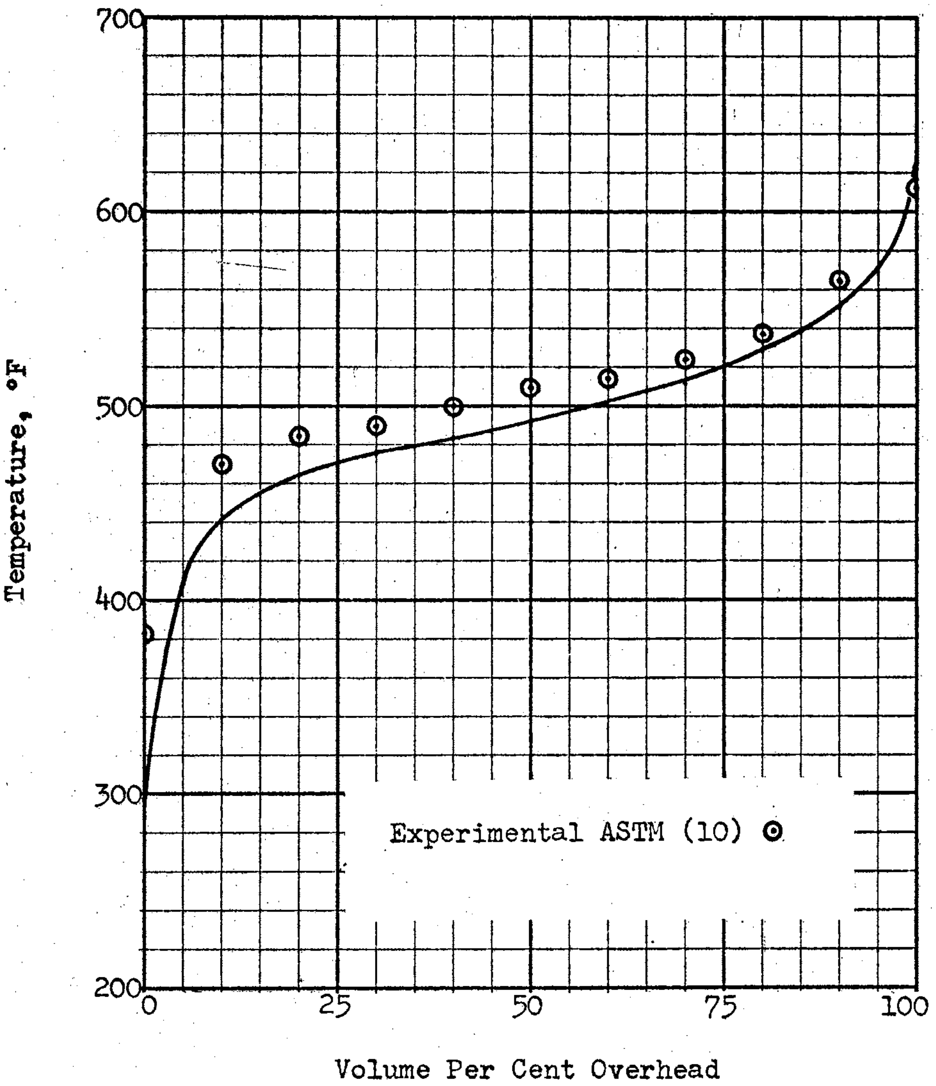


Figure 41. Experimental Points and Calculated ASTM Curve for Sample No. 58

TABLE IV

DEVIATION OF CALCULATED ASTM TEMPERATURES FROM ACTUAL ASTM TEMPERATURES FOR CONTINUOUS TBP DATA

Sample	Deviation, °F										
Number	IBP	10%*	20%	30%	40%	50%	60%	70%	80%	90%	EP
1	-15	-1	+3	+4	+5	+6	+8	+9	+9	+8	0
2	-3	-12	-6	-5	-3	0	0	+1	+1	-3	-7
3	+4	-6	-3	-4	-3	-5	-5	-5	-6	-6	+2
4	-7	-8	-4	-5	-5	-6	-7	-8	-9	-10	-8
5	+14	+2	0	0	+1	+2	0	0	0	-1	+21
6	-2	-6	-4	-4	-4	-4	-5	-5	-6	-7	+11
7	-4	-6	-5	-4	-5	-6	-6	-7	-10	-14	0
8	+2	-3	0	0	0	+1	0	-2	-2	-2	+8
9	+25	+2	0	+3	+4	+6	+5	+4	+4	+1	+4
10	+50	0	+8	+12	+16	+16	+16	+11	+6	+1	+16
11	+76	-18	+9	+12	+16	+19	+13	+10	+4	+4	+8
12	-1	+1	+5	+7	+6	+5	+5	+3	+2	-3	+12
13	-1	+3	+9	+11	+11	+9	+8	+6	+3	0	+11
14	-2	+7	+10	+12	+11	+10	+8	+6	+5	+1	+6
15	+12	+7	+9	+13	+13	+11	+8	+5	+2	0	+9
16	+3	+1	+5	+6	+9	+9	+9	+10	+9	+4	+14
17	+11	+1	+7	+8	+7	+7	+5	+4	+1	-2	+6
18	+7	-3	-2	-1	0	+1	+2	+3	+4	+3	+22

*Volume per cent overhead

TABLE IV (Continued)

Sample Number	Deviation, °F										
	IBP	10%*	20%	30%	40%	50%	60%	70%	80%	90%	EP
19	-8	+1	+5	+7	+8	+7	+6	+5	+3	0	+19
20	+2	-13	-3	0	-2	-3	-3	-4	-6	-3	+12
21	-21	-24	-17	-15	-12	-9	-4	-2	-3	-11	-26
22	+4	-7	-5	-4	-4	-4	-4	-5	-8	-8	-7
23	-32	-10	-5	-2	-3	-4	-4	-5	-8	-12	-1
24	+17	-17	-7	-7	-7	-8	-9	-8	-8	-7	-11
25	-18	-11	-3	+1	0	0	-1	-4	-6	-13	-7
27	+25	-10	-4	0	-1	-3	-3	-7	-8	-15	-21
30	-1	-9	-9	-10	-6	-6	-4	-5	-3	+9	+27
58	-84	-28	-20	-15	-15	-15	-14	-11	-10	-14	+11

*Volume per cent overhead

first is 2.7 °F, and the standard deviation is 4.8°F. Thus, the new method reproduced the experimental ASTM curves with about the same accuracy as the ASTM distillation data. Where two distillation curves were available, temperatures were averaged for developing this correlation and checking its accuracy. A summary of average deviations, standard deviations and maximum deviations of the new method from experimental data is given in Table V.

For the continuous TBP curves of Geddes, the average deviation of the ASTM curve calculated by the new method from the experimental curves is 7.4 °F for all points calculated. The standard deviation of all points calculated is 15.6 °F. If the initial and end points are omitted, average deviation is 6.1 °F and standard deviation is 7.7 °F.

The data of Geddes were taken from routine laboratory analyses. Geddes stated "a critical survey of the many distillations showed that the most common apparent inaccuracy in the data occurred in errors of temperature levels due to shifts, between analyses, in the calibrations of the thermocouples and thermometers used in the TBP and ASTM distillations, respectively." Such a shift would cause errors in the absolute temperature reading, but would not change the shape of the distillation curve. In order to determine how well the new method reproduced the shape of the distillation curve, the calculated ASTM curves were shifted up or down to give a zero algebraic average deviation for the calculated curve between the ten and ninety per cent points. The average absolute deviation of the shifted curves from the actual curves between the ten and ninety per cent points is 2.8°F, and the standard deviation is 4.0°F. Thus the new method reproduced the shape of the distillation curve about as well for the continuous

TABLE V

DEVIATION OF CALCULATED ASTM TEMPERATURES FROM ACTUAL TEMPERATURES

Step Input	Deviation, °F										
	IBP	10%*	20%	30%	40%	50%	60%	70%	80%	90%	EP
Average Deviation	3.2	2.8	2.5	2.5	3.8	2.8	2.5	3.2	2.7	2.3	2.8
Standard Deviation	3.8	3.6	3.5	3.8	5.3	3.8	3.4	4.1	3.1	2.7	3.5
Maximum Deviation	7	9	10	11	14	11	8	10	6	5	7
Continuous Curve											
Average Deviation	16.1	7.8	6.0	6.1	6.3	6.5	5.8	5.5	5.2	5.8	11.0
Standard Deviation	26.4	10.4	7.5	7.7	7.9	8.0	7.0	6.2	6.0	7.5	13.2
Maximum Deviation	84	28	20	15	16	19	16	11	10	15	27

*Volume per cent overhead

data of Geddes as it reproduced the pure component blend data. Deviations of calculated ASTM temperatures from the shifted curves are given in Table VI.

The reproducibility of an ASTM curve is a function of the slope of the ASTM distillation curve. The reproducibility of curves with slopes from 0.5 to 3 degrees F per per cent evaporated is 5 to 8 degrees for the initial boiling point, 6 to 7 degrees for the end point and 4 to 7 degrees for intermediate points (1). The above reproducibilities are for pressure corrected distillations. It is probable that the ASTM data published by Geddes were not corrected for variations in barometric pressure.

The calculated end points for the continuous curves are less accurate than intermediate points. One of the reasons for decreased accuracy at the end points is that the end points of the TBP curve were not given. The TBP end points were estimated by linear extrapolation from the last two points given, usually the 90 and 95 per cent points.

The average deviation of the calculated initial boiling points from experimental data is 16.1°F, considerably higher than the deviation for the remainder of the curve. The higher deviations are caused by large deviations for curves with sharp temperature rises for the initial part of the TBP curve. All deviations larger than 15°F are for samples with a temperature difference of 150°F or more between the initial boiling point and 20 per cent point of the TBP curve. The average deviation of calculated ASTM IBP from actual IBP is 5.1 degrees for all samples with less than a 150°F temperature difference between the IBP and 20 per cent points on the TBP curve.

TABLE VI

DEVIATION OF SHIFTED** ASTM TEMPERATURES FROM ACTUAL ASTM TEMPERATURES

Sample	Deviation, °F										
Number	IBP	10%*	20%	30%	40%	50%	60%	70%	80%	90%	EP
1	-21	-7	-3	-2	-1	0	+2	+3	+3	+2	-6
2	0	-9	-3	-2	0	+3	+3	+4	+4	0	-4
3	+9	-1	+2	+1	+2	0	0	0	-1	-1	+7
4	0	-1	+3	+2	+2	+1	0	-1	-2	-3	-1
5	+14	+2	0	0	+1	+2	0	0	0	-1	+21
6	+3	-1	+1	+1	+1	+1	0	0	-1	-2	+16
7	+3	+1	+2	+3	+2	+1	+1	0	-3	-7	+7
8	+3	-2	+1	+1	+1	+2	+1	-1	-1	-1	+9
9	+23	-1	-3	0	+1	+3	+2	+1	+1	-2	+1
10	+40	-10	-2	+2	+6	+6	+6	+1	-4	-9	+6
11	+68	-26	+1	+4	+8	+11	+5	+2	-4	-4	0
12	-5	-3	+1	+3	+2	+1	+1	-1	-2	-7	+8
13	-8	-4	+2	+4	+4	+2	+1	-1	-4	-7	+4
14	-10	-1	+2	+4	+3	+2	0	-2	-3	-7	-2
15	+4	-1	+1	+5	+5	+3	0	-3	-6	-8	+1
16	-4	-6	-2	-1	+2	+2	+2	+3	+2	-3	+7

*Volume per cent overhead

**Calculated curves were shifted up or down to give an average deviation of zero for calculated points between 10% and 90% on each curve. The deviation of the shifted curves from the actual curves indicates how well the shape of the ASTM curve is duplicated.

TABLE VI (Continued)

Sample Number	IBP	10%*	20%	30%	40%	50%	60%	70%	80%	90%	EP
17	+7	-3	+3	+4	+3	+3	+1	0	-3	-6	+2
18	+6	-4	-3	-2	-1	0	+1	+2	+3	+2	+21
19	-13	-4	0	+2	+3	+2	+1	0	-2	-5	+14
20	+6	-11	+1	+4	+2	+1	+1	0	-2	+1	+16
21	-10	-13	-6	-4	-1	+2	+7	+9	+8	0	-15
22	+9	-2	0	+1	+1	+1	+1	0	-3	-3	-2
23	-26	-4	+1	+4	+3	+2	+2	+1	-2	-4	+5
24	+26	-8	+2	+2	+2	+1	0	+1	+1	+2	-2
25	-14	-7	+1	+5	+4	+4	+3	0	-2	-9	-3
27	+31	-4	+2	+6	+5	+3	+3	-1	-2	-9	-15
30	+6	-3	-3	-4	+1	+1	+3	+2	+4	+16	+34
58	-68	-12	-4	+1	+1	+1	+2	+5	+6	+2	+27

*Volume per cent overhead

Comparison of New Method with the Methods of Geddes and Edmister

A comparison of the new method with the methods of Geddes (10) and Edmister (5) was made. ASTM distillation curves were estimated from the TBP data in Table II using both methods. The correlations were extrapolated where necessary. Deviations for the method of Geddes are given in Table VII. Deviations for the method of Edmister are given in Table VIII. A summary of Geddes' method is given in Appendix B. A summary of Edmister's method is given in Appendix C.

A comparison of the deviations of the three methods is given in Table IX. For the continuous TBP data of Table II, the new method is about equivalent to the method of Geddes and gives considerably better results than the method of Edmister. The overall average deviation for all points calculated was 7.4°F for the new method, and 7.4°F and 15.1°F for the methods of Geddes and Edmister, respectively.

It should be pointed out that the correlation of Geddes was based, in part, on the above data while the method of Edmister and the correlation presented in this thesis were developed from independent data. A quantitative comparison of the three methods based on these data should be done with caution; the method of Geddes might not reproduce independent data as well.

TABLE VII

DEVIATION OF CALCULATED ASTM TEMPERATURES FROM ACTUAL ASTM TEMPERATURES FOR THE METHOD OF GEDDES

Sample	Deviation, °F						
Number	IBP	10%*	20%	50%	80%	90%	EP
1	-12	-5	0	+1	+7	+16	-2
2	-5	-11	-4	+1	+6	+9	0
3	+3	+2	+1	-1	0	+8	+9
4	-4	-1	-1	-2	+1	-1	-5
5	-13	-7	-7	-3	-2	-6	+12
6	0	-3	-3	-3	-2	-8	-6
7	-2	-1	-1	-2	+5	+6	+11
8	+6	-3	+4	-1	+5	-3	-5
9	-28	-6	-7	-2	+2	+6	-3
10	-48	-6	-7	-1	+2	-1	-1
11	-38	+9	+5	-2	-3	-5	-7
12	+10	+4	+8	+4	+6	-7	-4
13	+15	0	+5	+6	+2	-1	-3
14	+15	+15	+18	+14	+11	+7	+3
15	+2	+6	+6	+1	-5	+6	+4
16	+5	+1	+5	+3	+6	+14	+14
17	+13	+11	+11	+2	0	+6	+7
18	+5	+4	+3	-2	+11	+14	+20
19	+38	+14	+12	+8	+11	+4	+10
20	+54	+4	+2	-4	-1	-4	-1
21	-12	-22	-23	-21	+3	-6	-28
22	0	+1	-1	-2	+2	-2	-4
23	+4	+2	-1	0	+2	-3	-1
24	+61	+2	-2	-8	+2	0	-17
25	+11	-3	0	+2	+3	-13	-21
27	+18	0	-1	0	-2	-6	-23
30	+5	-21	-17	-19	-21	-17	+11
58	+23	-5	-11	-11	-3	-17	-2

*Volume per cent overhead

TABLE VIII

DEVIATIONS OF CALCULATED ASTM TEMPERATURES FROM ACTUAL ASTM TEMPERATURES FOR THE METHOD OF EDMISTER

Sample Number	Deviation, °F						
	IBP	10%*	30%	50%	70%	90%	EP
1	-25	-9	+1	0	+4	+4	-29
2	-11	-13	+2	0	+1	-1	-13
3	-27	-10	-3	-2	-6	+2	-12
4	-35	-12	-12	-7	-8	-7	-22
5	-57	-14	-4	-4	-1	-8	-22
6	-19	-10	-7	-6	-4	-4	-4
7	-27	-17	-12	-12	-10	-17	-27
8	-31	-13	-12	-15	-18	-17	-31
9	-64	-12	-4	-4	-4	-16	-35
10	-76	-15	-10	-5	-5	-7	-10
11	-9	-26	-22	-9	-13	-14	-5
12	-27	-10	-8	-8	-15	-19	-4
13	-38	-10	-4	-7	-11	-16	-5
14	-37	-1	+5	+6	-1	-2	-2
15	-20	+3	+3	-1	-9	-5	-5
16	-16	-2	+3	+3	+6	0	+7
17	-35	-2	+6	-2	+2	-5	-6
18	-40	-6	-4	-2	+3	+4	+19
19	-54	+1	+2	-1	0	-3	+13
20	-26	-12	-13	-17	-18	-16	-1
21	-52	-34	-42	-36	-24	-23	-39
22	-74	-6	-2	-3	-2	-2	-9
23	-98	-6	-9	-9	-8	-13	-7
24	0	-12	-18	-21	-16	-8	-23
25	-56	-23	-13	-13	-16	-25	-19
27	-40	-8	0	-4	-9	-10	-30
30	-26	-20	-16	-19	-25	-21	+7
58	-157	-24	-33	-24	-24	-26	+3

*Volume per cent overhead

TABLE IX

A COMPARISON OF DEVIATIONS OF THE NEW METHOD WITH THE METHODS OF EDMISTER AND GEDDES FOR CONTINUOUS TBP DATA

	Deviation, °F										
	IBP	10%*	20%	30%	40%	50%	60%	70%	80%	90%	EP
Average Deviation											
New Method	16.1	7.8	6.0	6.1	6.3	6.5	5.8	5.5	5.2	5.8	11.0
Geddes	16.1	6.9	6.4			4.9			4.6	7.6	9.2
Edmister	42.0	11.8		9.7		8.6		10.7		10.5	14.6
Standard Deviation											
New Method	26.4	10.4	7.5	7.7	7.9	8.0	7.0	6.2	6.0	7.5	13.2
Geddes	23.1	9.7	8.8			7.6			6.4	10.1	12.9
Edmister	51.6	14.2		13.5		11.9		12.0		13.1	18.3
Maximum Deviation											
New Method	84	28	20	15	16	19	16	11	10	15	27
Geddes	61	22	23			21			21	17	28
Edmister	157	34		42		36		25		26	39

*Volume per cent overhead

CHAPTER VI

SUMMARY AND CONCLUSIONS

A method was developed for calculating ASTM distillation curves from TBP curves. The method is applicable to both pure component blend data and continuous TBP curves. Batch distillation calculations are made using the Rayleigh equation. Bubble point temperatures are calculated for the liquid and for the vapor in equilibrium with the liquid. ASTM temperatures are then calculated as a weighted average of the bubble point temperature of the residual liquid and the bubble point temperature of the vapor in equilibrium with the residual liquid. All physical properties required for calculations are estimated from normal boiling points of the components or pseudocomponents.

The method presented in this thesis works well for both pure component blend data and continuous TBP data. The calculated results for pure component blends have an average deviation slightly greater than the average deviation of a carefully determined second ASTM distillation on the same samples. The shape of the ASTM distillation curve between the 10 and 90 per cent points is reproduced as well for continuous TBP data as for the pure component blends. A comparison of the new method with the methods of Edmister and Geddes shows that the new method gives better results than Edmister's method, and results equivalent to the method of Geddes on continuous TBP data presented by Geddes.

Caution is indicated for the initial boiling point of stocks having a temperature difference of 150°F or greater between the IBP and the 20 per cent point on the TBP curve. For the eleven stocks in this category, the new method had an average deviation of 32°F for the IBP. For the same stocks the average deviations for Geddes' and Edmister's methods were 28°F and 58°F, respectively.

Caution is also indicated for the initial boiling point of feedstocks having a TBP initial boiling point below 0°F. The four stocks in this category had calculated initial boiling points with an average deviation of 41°F from actual values. These stocks also had temperature differences greater than 200°F between the IBP and 20 per cent point on the TBP curve. In the absence of further data, a tentative lower temperature limit of 0°F for the TBP initial boiling point is suggested. This limitation applies to the estimated ASTM IBP only.

The new method gives satisfactory results on all types of feedstocks tested, including cracked gasoline, gasoline, kerosene, stoddard solvent, rubber solvent, stripped and unstripped gas oil, stripped and unstripped naphtha, and blends, including blends of from two to twelve pure components. It has not been tested on crudes.

The new method was developed and tested for hydrocarbons only. It is believed that it will be valid for other compounds if good physical properties can be supplied. The physical properties estimation methods used in this study apply to hydrocarbons only.

It should be possible to use the new method for estimation of vacuum ASTM distillation curves. This has not been tested, however.

The new method should be particularly useful in gasoline blending calculations and in evaluation of the results of theoretical fractionation calculations for petroleum fractions.

LIST OF NOMENCLATURE

A, B, C, D - mols of individual components in Rayleigh equation

A_m, B_m, C_m - molal density curve fit constants

C1 - Antoine vapor pressure equation constants

C2 - Antonine vapor pressure equation constants

Frn - fraction of key component overhead

K - equilibrium vaporization constant, y/x

P - pressure, any units

P_V - vapor pressure, atmospheres

R - gas-law constant

T - temperature, °F

T_{ASTM} - ASTM distillation temperature, °F

T_b - normal boiling point, °F

T_{bk} - normal boiling point, °K

T_{BL} - bubble point temperature of liquid, °F

T_{BV} - bubble point temperature of vapor in equilibrium with liquid, °F

T_c - critical temperature, °F

T_r - reduced temperature

T_S - stem correction, °F

V - volume per cent overhead

d - differential

e - base of natural logarithms

f(V) - weighting factor for calculating T_{ASTM}

ln - natural logarithm

log - common logarithm

v - molal volume of liquid

x - mole fraction of component in vapor

y - mole fraction of component in liquid

Greek Letters

α - relative volatility

γ - liquid activity coefficient

δ - solubility parameter

$\bar{\delta}$ - volumetric average solubility parameter

ΔE - energy of vaporization of liquid to infinite attenuation

λ - latent heat of vaporization

λ_b - latent heat of vaporization at the normal boiling point

ρ_m - molal density, mols/gal

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APPENDIX A

ESTIMATION OF PHYSICAL PROPERTIES

The estimation of the ASTM distillation curve of a mixture by the method presented in this thesis requires a knowledge of the molal densities and equilibrium vaporization constants for the components or pseudocomponents in the mixture. These properties were estimated from normal boiling point by the methods described below for petroleum hydrocarbons.

Molal densities at 60°F were calculated from curves presented by Maxwell (15) of API gravity and molecular weight as functions of normal boiling point. The calculated molal densities were then curve fitted to an equation of the following form:

$$\rho_m = A_m e^{(B_m + C_m T_b)} \qquad (7)$$

where ρ_m is molal density in mols per gallon, T_b is normal boiling point in degrees F, and A_m, B_m and C_m are constants. Values of the constants are as follows:

Crude Type (15)	Temperature of Curve Fit, °F	A_m	B_m	C_m
n-Paraffins	200-1000	0.01	2.1069	-0.001875
I	200-900	0.01	2.1411	-0.001898
II	300-900	0.01	2.1808	-0.001832
III	300-900	0.01	2.2138	-0.001791

These equations reproduce the molal density data calculated from Maxwell's charts with an average deviation of 2 per cent for n-paraffins and less than 1 per cent for the three crude types. The curves extrapolated reasonably well; the calculated molal density for propane, with a normal boiling point of -43.7 °F, was 6.7 per cent low for the n-paraffin curve, and 3.3 per cent low, 0.3 per cent high and 3.5 per cent high for the type I, type III and type V crude curves, respectively.

Vapor-liquid equilibrium ratios were estimated by the relationship

$$K_i = \gamma_i P_{vi}/P \tag{8}$$

where γ_i = liquid activity coefficient of component i

P_{vi} = vapor pressure of component i

P = total pressure

This equation is theoretically valid if Raoults law is valid for the pure components, and if the vapor activity coefficient is equal to one. These two qualifications are sometimes good assumptions at low pressures (5). Vapor pressures and liquid activity coefficients for use in the above expression were estimated by the methods discussed in the following paragraphs.

Vapor pressures are estimated from equations of the Antoine form

$$\ln (P_v) = C1 + C2/(T + 350) \tag{9}$$

where C1 and C2 are constants. The constants are calculated for each component from the normal boiling point of the component and the infinite point or convergence point as suggested by Dreisbach (4). The infinite point is 2264 °F and 1711 atmospheres (1240 °C and 1.300×10^6 mm) for aliphatic saturated hydrocarbons.

Liquid activity coefficients are estimated from the Scatchard-Hildebrand (12) equation

$$\ln \gamma_i = \frac{v_i}{RT} (\bar{\delta} - \delta_i)^2 \tag{10}$$

where γ = liquid activity coefficient

v = molal volume of the liquid

$\delta = \left(\frac{\Delta E}{v}\right)^{1/2}$ = solubility parameter

ΔE = energy of vaporization of liquid to infinite attenuation

$\bar{\delta}$ = volumetric average solubility parameter of liquid

Chao and Seader (2) found that it is permissible to evaluate v and δ at any convenient reference temperature. Since molal densities of the components were estimated earlier at a temperature of 60°F, this temperature was chosen as the reference temperature. The energy of vaporization is calculated from the relationship

$$\Delta E = \lambda - RT \tag{11}$$

where λ is the latent heat of vaporization at the reference temperature T and R is the gas-law constant. The latent heat of vaporization is estimated at the normal boiling point by the Kistyakovskii (13) equation

$$\lambda_b = T_{bk}(8.75 + 4.571 \log T_{bk}) \tag{12}$$

and corrected to the reference temperature by the Watson (36) equation

$$\lambda = \lambda_b((1-T_r)/(1-T_{br}))^{0.38} \tag{13}$$

where T_{br} is the reduced normal boiling point temperature of the component or pseudocomponent and T_r is the reduced temperature. The critical temperature is estimated from the following expression:

$$T_c = T_b + 300 \tag{14}$$

The maximum error of the above expression is 18°F for normal hydrocarbons between 100°F and 650°F. In comparison, the relation of Guldberg (11),

$$T_c = 1.5\,T_b \tag{15}$$

has a maximum error of about 270°F for normal hydrocarbons over the same temperature range.

APPENDIX B

ESTIMATION OF ASTM CURVES BY THE METHOD OF GEDDES

Geddes' correlation for estimation of ASTM curves from TBP curves is given in Figures 42 through 48. The estimation of the ASTM distillation curve by this method involves seven steps, using the graphical correlations as indicated:

TBP Temp.	ASTM Temp.	Figure No.
50%	50%	42
50-20%	50-20%	43
80-50%	80-20%	44
20-10%	20-10%	45
10-1%	10-IBP	46
98-50%	EP-50%	47
98-90%	EP-90%	48

The use of the correlation will be illustrated by an example. Taking the TBP curve of sample No. 15 of Table I, the estimated ASTM curve is derived as follows:

TBP Curve		Estd. ASTM Curve		Figure No.
50% Temp.	267°F	50% Temp.	266°F	42
Slope, (80-20%)/60	2.72			
50-20%	88°F	50-20%	56°F	43
80-50%	75°F	80-50%	58°F	44
20-10%	37°F	20-10%	23°F	45
10-1%	90°F	10%-IBP	57°F	46
98-50%	136°F	EP-50%	123°F	47
98-90%	29°F	EP-90%	31°F	48

The resulting estimated ASTM curve is:

IBP	10%	20%	50%	80%	90%	EP
130	185	208	266	324	358	389

The experimental data are:

IBP	10%	20%	50%	80%	90%	EP
128	179	202	265	329	352	385

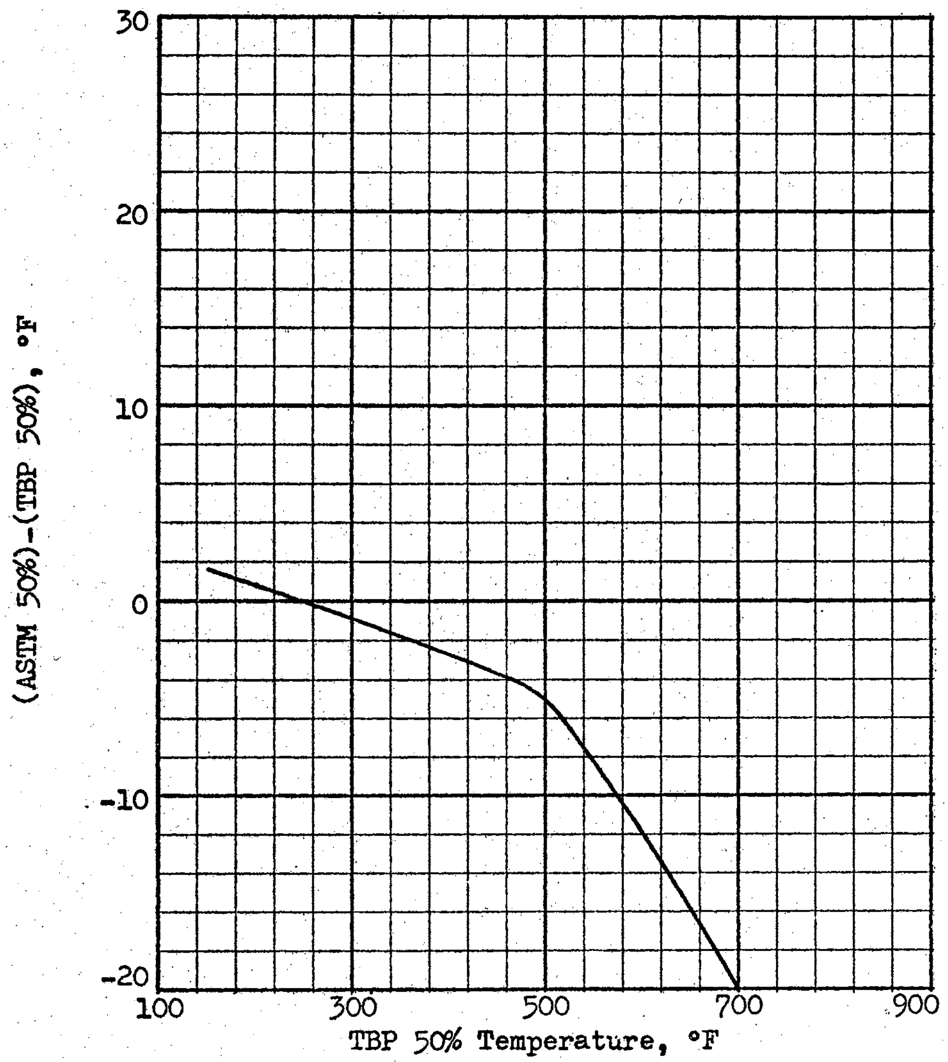


Figure 42. TBP 50 Per Cent Temperature Versus ASTM 50 Per Cent Temperature (Geddes)

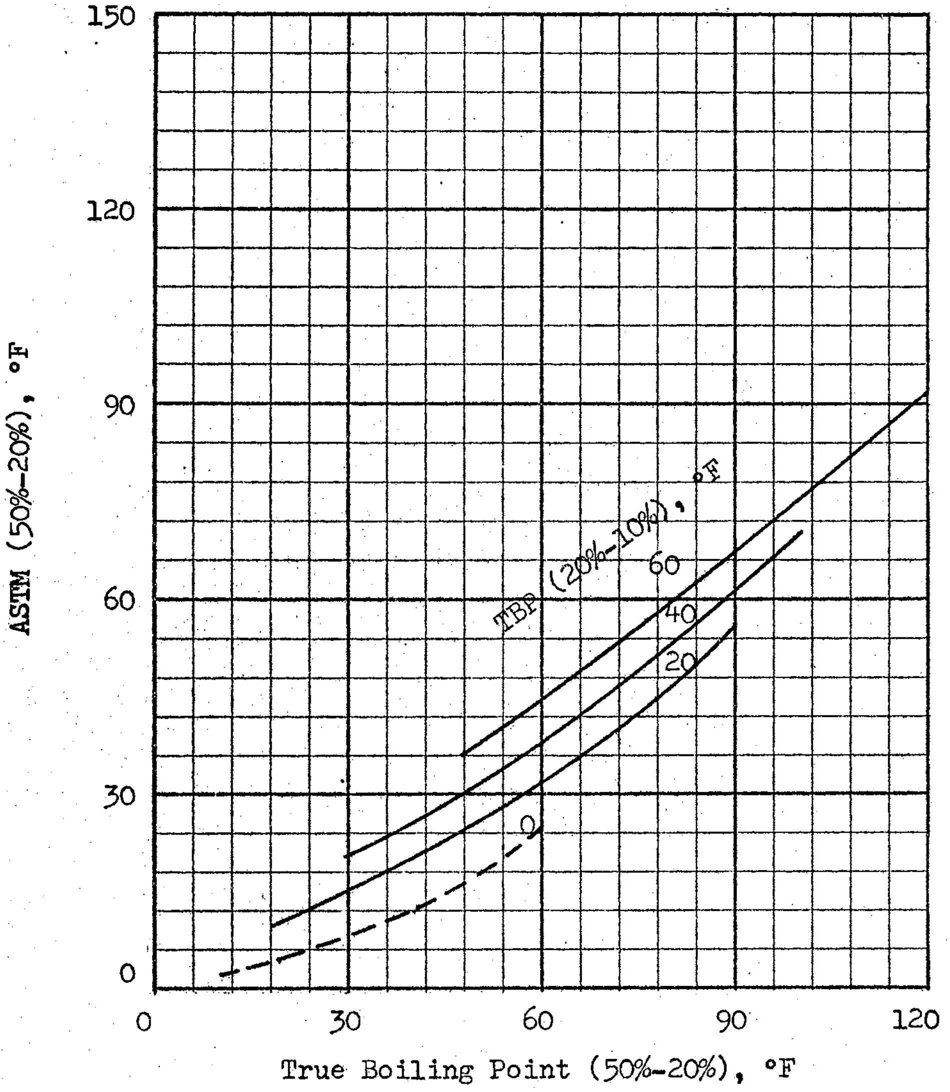


Figure 43. TBP (50-20 Per Cent) Temperature Difference Versus (50-20 Per Cent) Temperature Difference (Geddes)

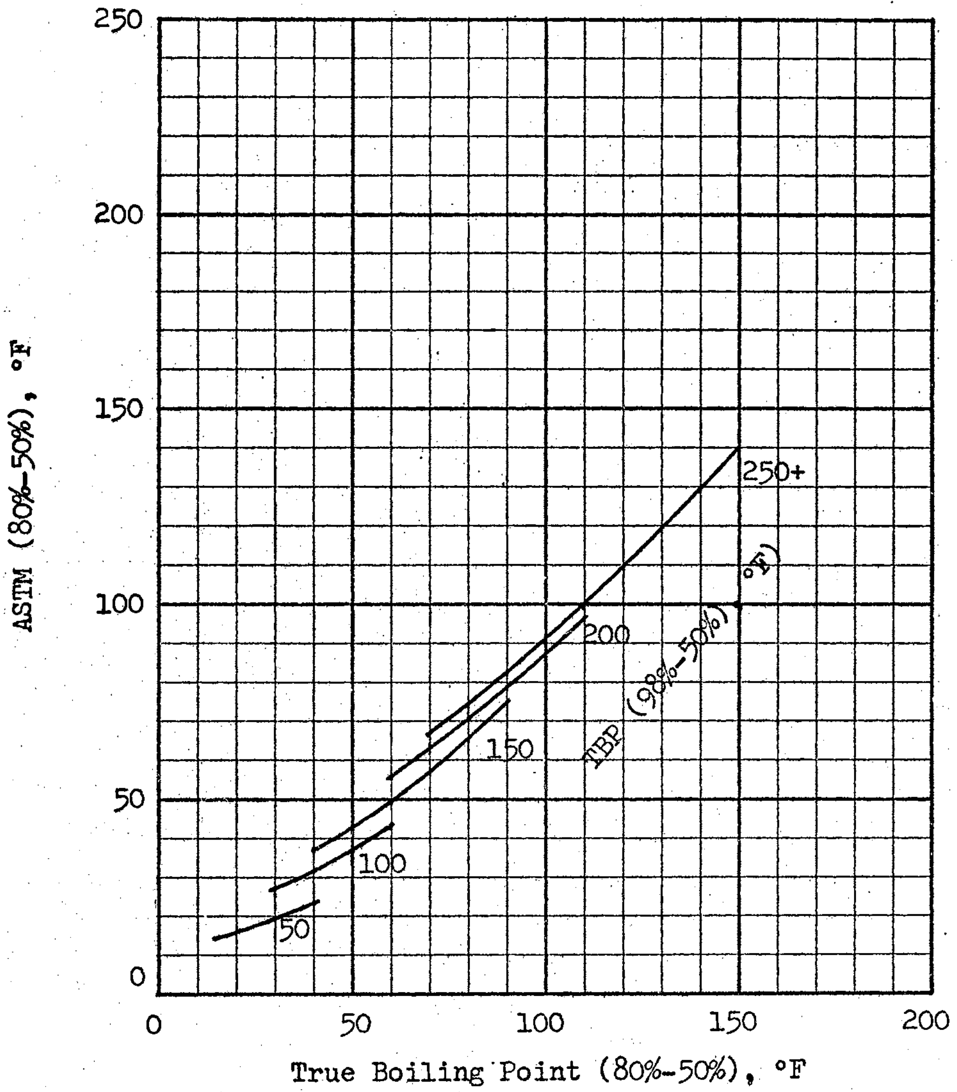


Figure 44. TBP (80-50 Per Cent) Temperature Difference Versus ASTM (80-50 Per Cent) Temperature Difference (Geddes)

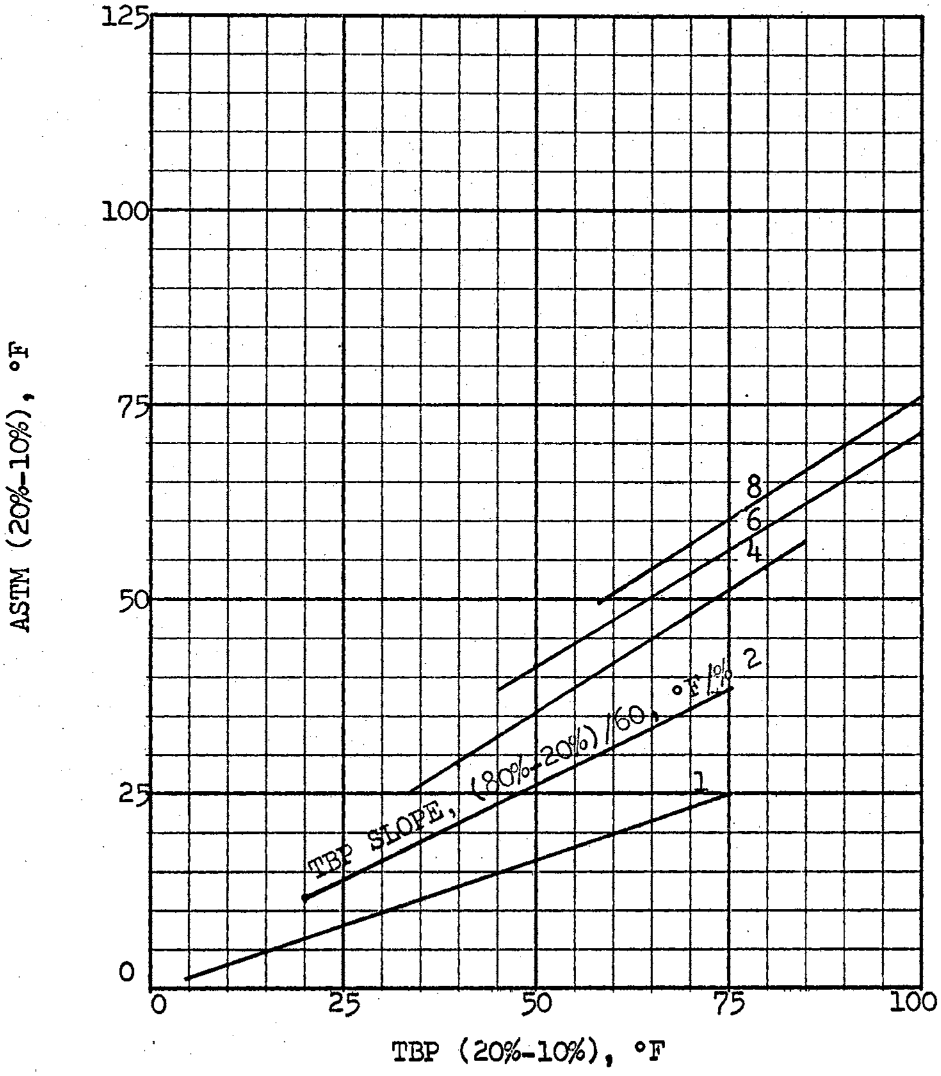


Figure 45. TBP (20-10 Per Cent) Temperature Difference Versus ASTM (20-10 Per Cent) Temperature Difference (Geddes)

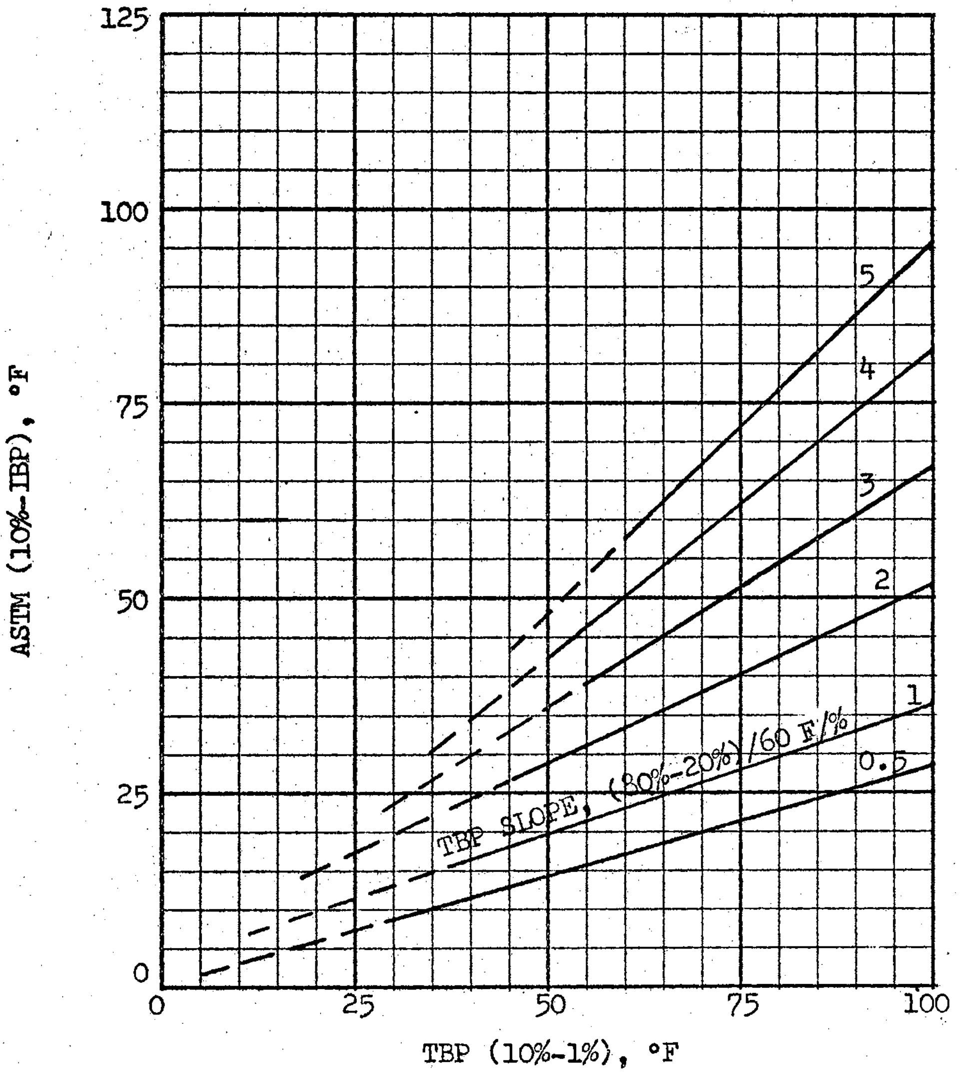


Figure 46. TBP (10-1 Per Cent) Temperature Difference Versus ASTM (10 Per Cent-IBP) Temperature Difference (Geddes)

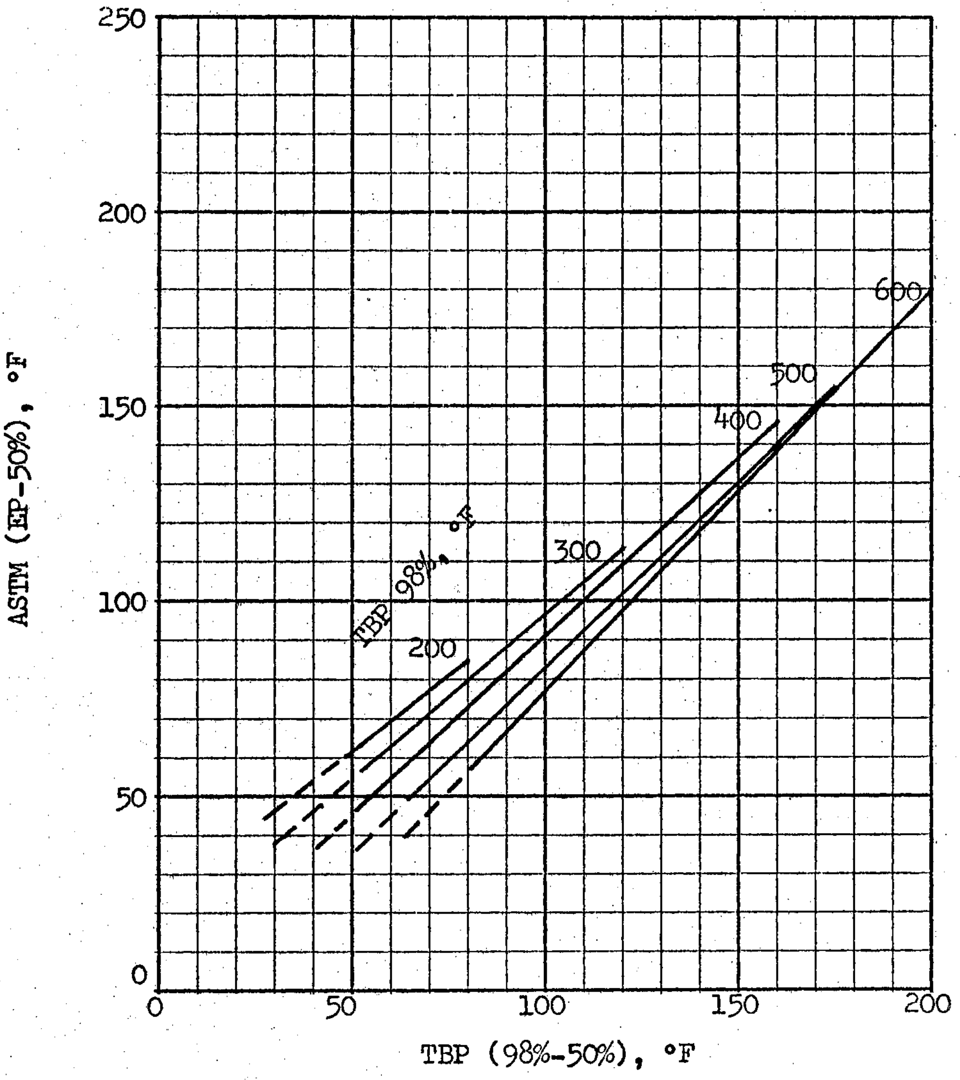


Figure 47. TBP (98-50 Per Cent) Temperature Difference Versus ASTM (End Point-50 Per Cent) Temperature Difference (Geddes)

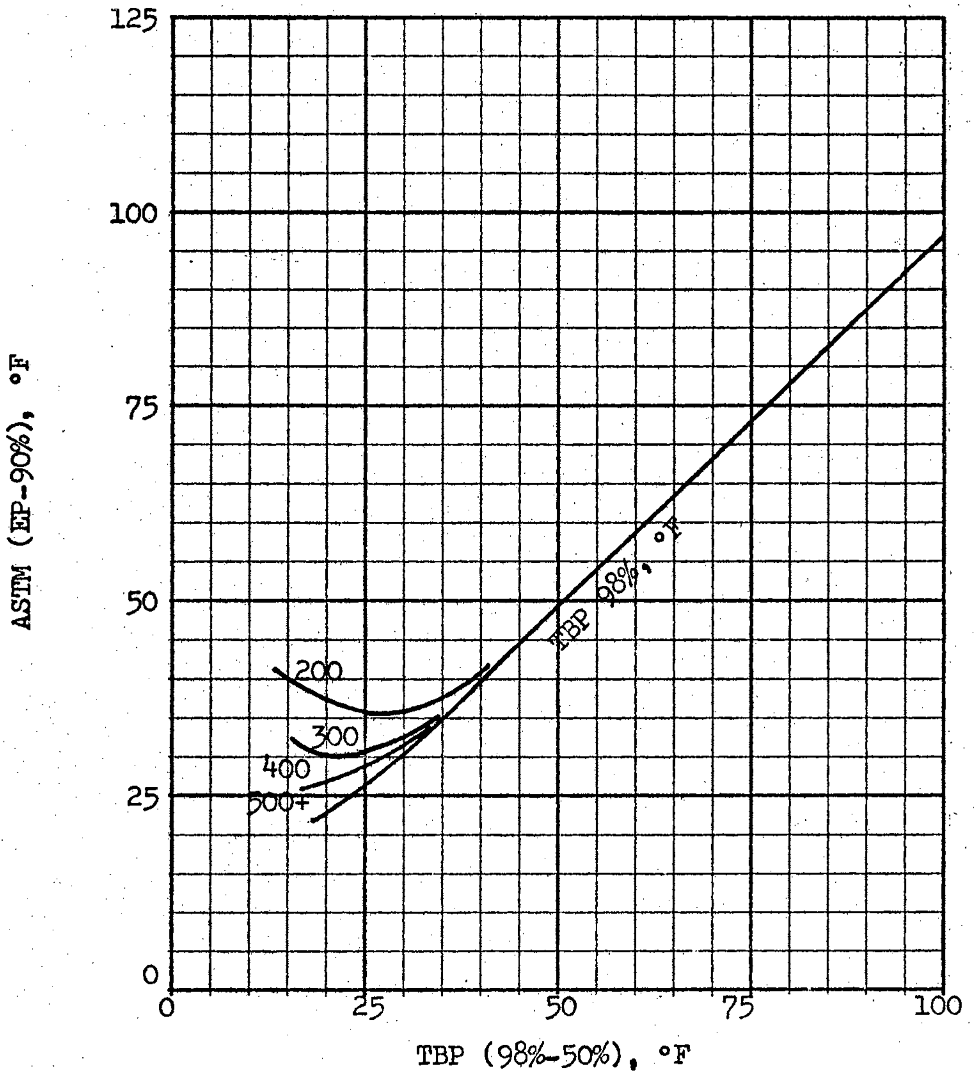


Figure 48. TBP (98-90 Per Cent) Temperature Difference Versus ASTM (End Point-90 Per Cent) Temperature Difference (Geddes)

APPENDIX C

ESTIMATION OF ASTM CURVES BY THE METHOD OF EDMISTER

The correlation of Edmister is given in Figures 49 and 50. Estimation of ASTM curves by this method involves seven steps, using the graphical correlations as indicated:

TBP Temp.	ASTM Temp.	Figure No.
50%	50%	49
50-30%	50-30%	50
70-50%	70-50%	50
30-10%	30-10%	50
10-IBP	10-IBP	50
90-70%	90-70%	50
EP-90%	EP-90%	50

The 50 per cent temperature correlation is presented for ease in calculating TBP curves from ASTM curves. Trial and error will quickly give ASTM 50 per cent temperature from IBP 50 per cent temperatures.

As an example, the ASTM curve will be estimated for sample No. 15 of Table I. The ASTM 50 per cent temperature is estimated from Figure 49 by trial and error. An ASTM temperature of 264°F corresponds to a temperature difference of 3°F, giving the actual TBP temperature of 267°F. The temperature difference between various parts of the ASTM curve is then obtained from Figure 50 as tabulated below.

TBP Curve		Estd. ASTM Curve		Figure No.
50% Temp.	267°F	50% Temp.	264°F	49
50-30%	56°F	50-30%	38°F	50
70-50%	49°F	70-50%	35°F	50
30-10%	69°F	30-10%	44°F	50
10-IBP	110°F	10-IBP	74°F	50
90-70%	58°F	90-70%	48°F	50

TBP Curve		Estd. ASTM Curve		Figure No.
EP-90%*	37°F	EP-90%	33°F	50

*The end point of the TBP curve was estimated by linear extrapolation

The resulting estimated ASTM curve is as follows:

IBP	10%	30%	50%	70%	90%	EP
108	182	226	264	299	347	380

The experimental data are:

IBP	10%	30%	50%	70%	90%	EP
128	179	223	265	308	352	385

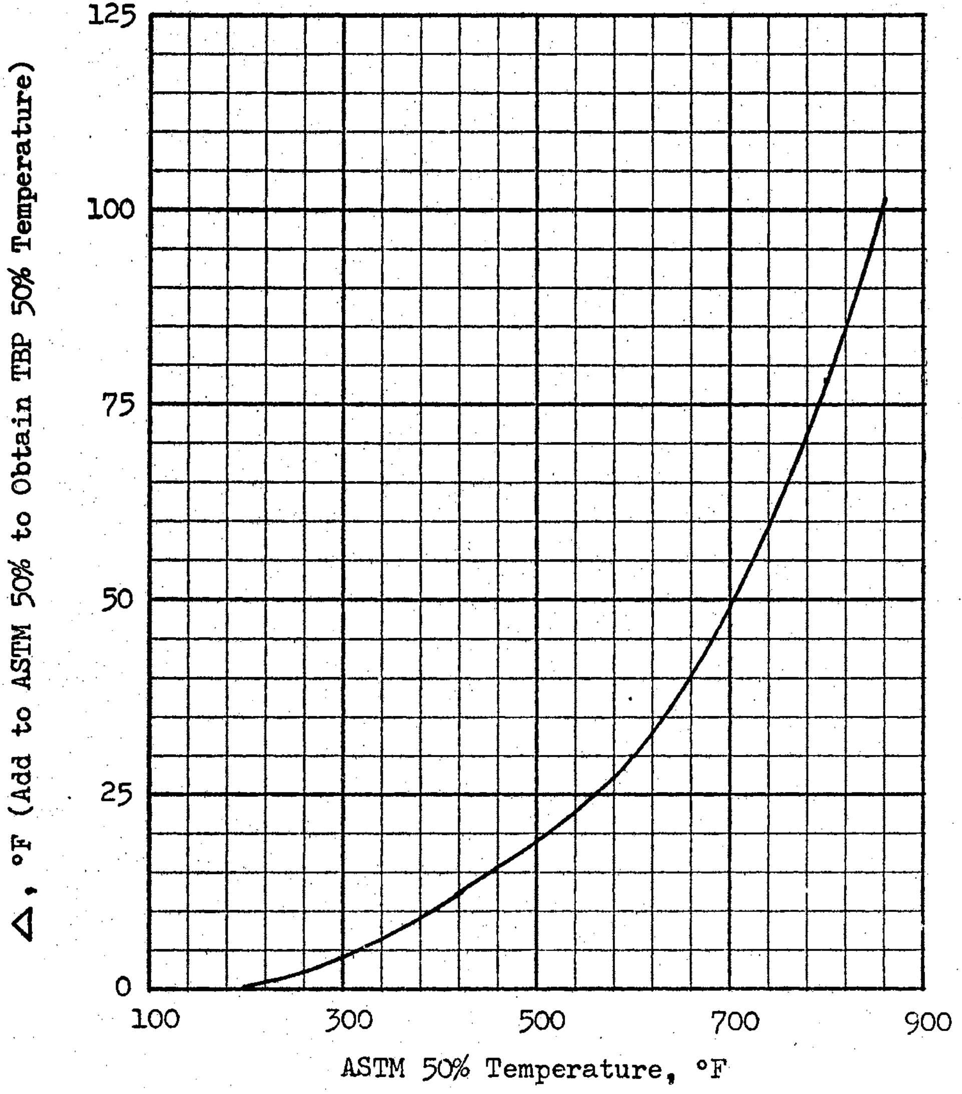


Figure 49. ASTM 50 Per Cent Temperature Versus TBP 50 Per Cent Temperature (Edmister)

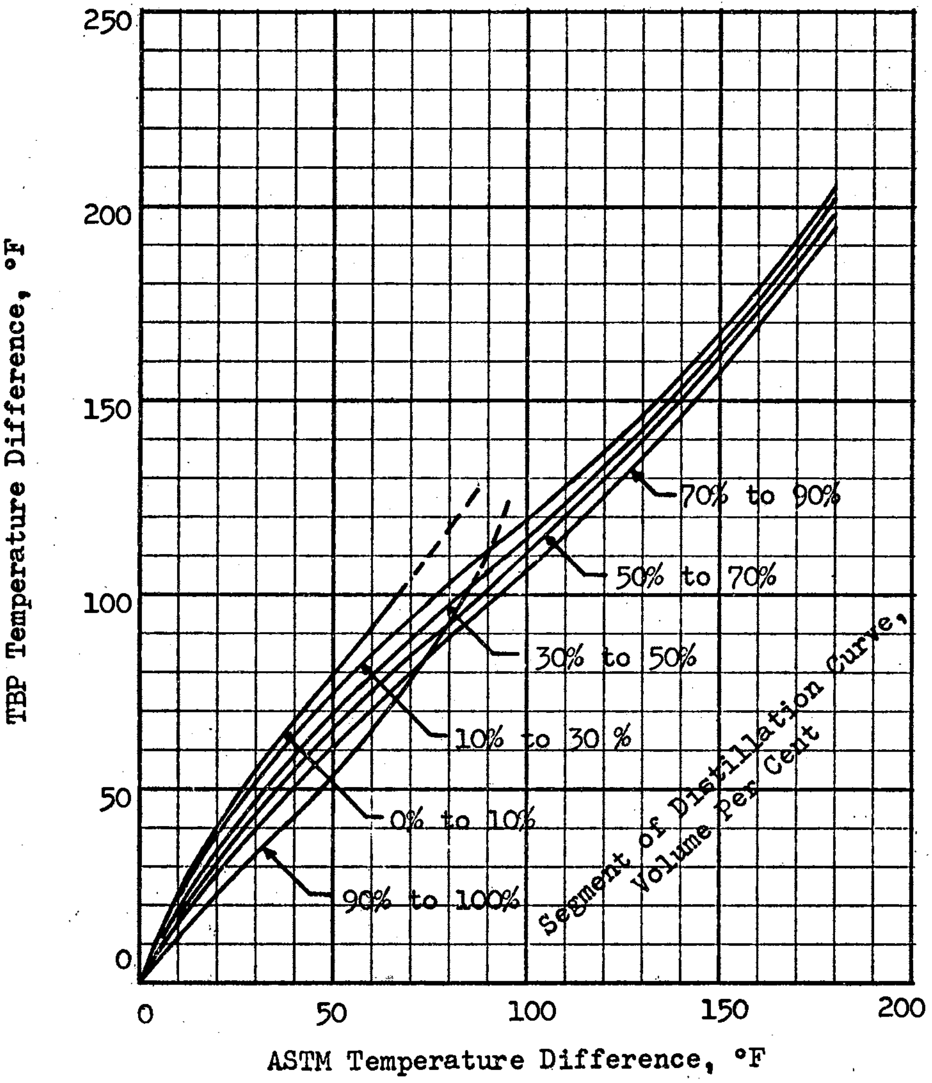
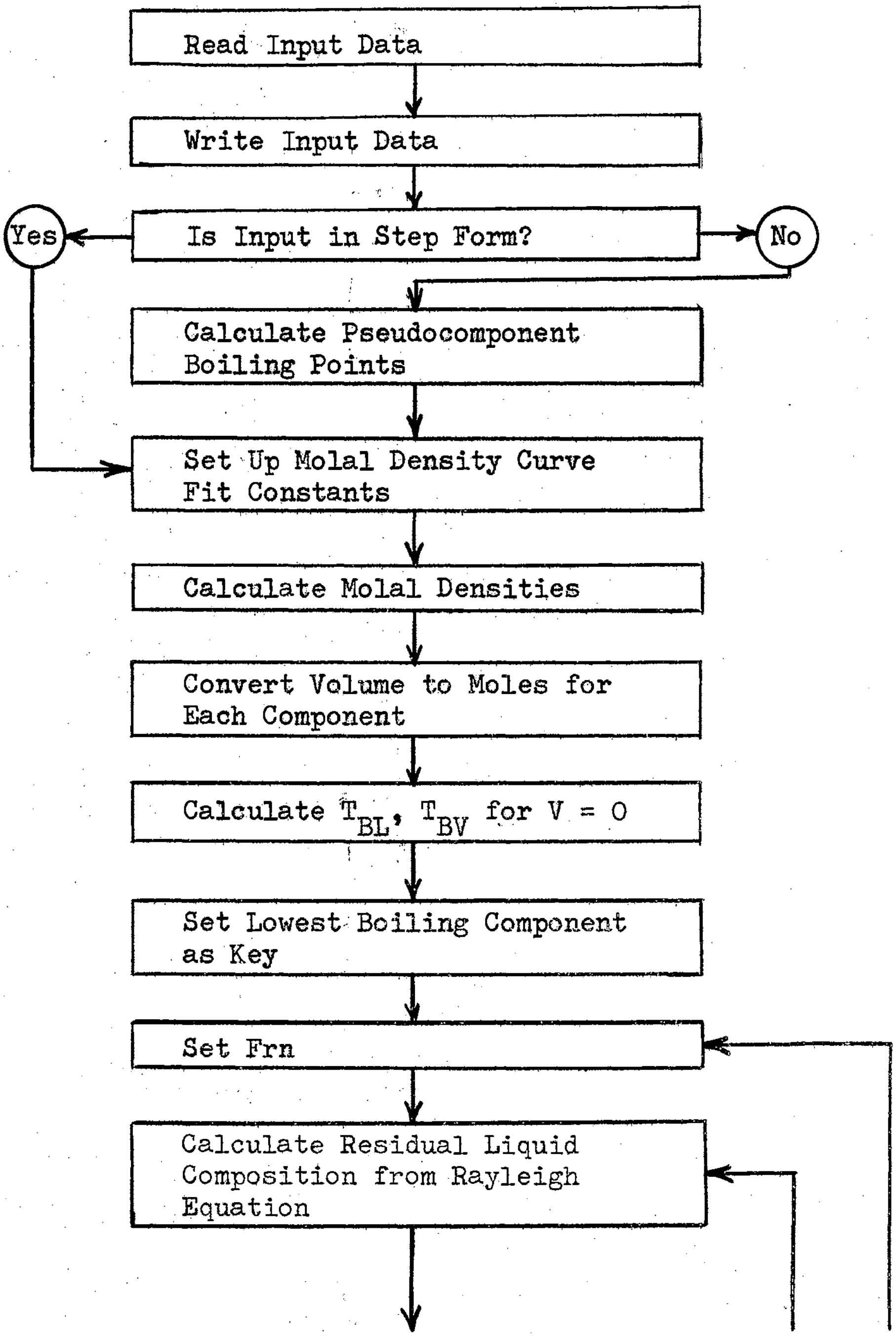
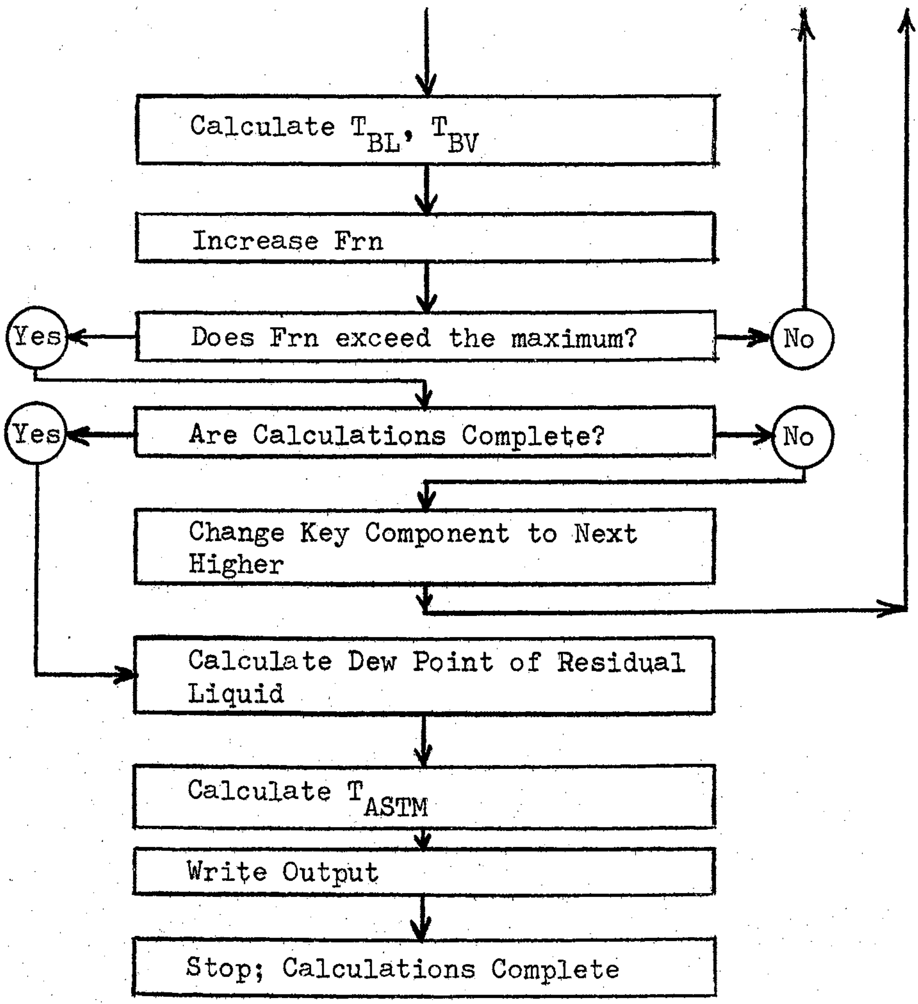


Figure 50. ASTM Temperature Difference Versus TBP Temperature Difference (Edmister)

APPENDIX D

BLOCK DIAGRAM FOR NEW METHOD




Calculate T_{BL}, T_{BV}
Increase Frn
Does Frn exceed the maximum?
Yes
No
Are Calculations Complete?
Yes
No
Change Key Component to Next Higher
Calculate Dew Point of Residual Liquid
Calculate T_{ASTM}
Write Output
Stop; Calculations Complete

APPENDIX E

DATA SHEETS FOR COMPUTER PROGRAM

The data sheets for the computer program are attached. One Form 1 and as many Form 2's as necessary are used for each data case. The maximum number of components or data points is 100. The data sheets are self-explanatory.

It is suggested that the fraction of key component overhead per iteration be specified as 0.5 for continuous input and 0.1 for step input, and the fraction of key component overhead after which the key component is changed be specified as 0.5 for continuous input and 0.9 for step input.

If intermediate temperature printout is desired, the bubble point temperature of the kettle liquid, the bubble point temperature of the vapor in equilibrium with the kettle liquid, and the calculated ASTM temperature for each point in the distillation will be printed out. These intermediate temperatures do not have the reverse stem correction applied.

CALCULATION OF ASTM CURVES FROM TRUE BOILING POINT CURVES

Form 1

	Card Columns	
Problem Number	1 - 5	_ _ _ _ _
Date	6 - 11	_ _/_ _/_ _
Type Feedstock for Densities 0 = n-paraffins 1 = Crude Type I 2 = Crude Type III 3 = Crude Type V	12	_
Pressure, Atmospheres	13 - 20	_ _ _ _._ _ _ _
Fraction of Key Component Overhead after which Key Component is Changed	21 - 23	_ _._
Fraction of Key Component To be taken Overhead Per Interation	24 - 26	_ _._
Number of Components if TBP Data are in Step Form	27 - 29	_ _ _
Number of Points if TBP Data are in Continuous Form	30 - 33	_ _ _
Are Intermediate Temperatures To be Printed? 0 = Yes 1 = No	34	_
Card Number	78 - 82	_ _ _ _ _

Figure 51. Data Sheet (Form 1) for Computer Program

CALCULATION OF ASTM CURVES FROM TRUE BOILING POINT CURVES

Form 2

	Volume Per Cent	Temperature, °F	Card No.
Card Columns	1 to 7	8 to 14	78 to 82
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NOTE: For step input data, the volume per cent column should contain the volume per cent of the component in the mixture and the temperature column should contain the normal boiling point of the component. Volume per cent must total 100, and number of components must match the number of components specified on Form 1.

For continuous TBP data, the volume per cent column should contain the volume per cent distilled and the temperature column should contain the corresponding distillation overhead temperature. The first point must be zero (the initial boiling point) and the number of points supplied must match the number of points specified on Form 1.

Figure 52. Data Sheet (Form 2) for Computer Program

VITA

Gary Duane Gooch

Candidate for the Degree of

Master of Science

Thesis: CALCULATION OF ASTM DISTILLATION CURVES FROM TRUE BOILING POINT CURVES

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Biographical:

Personal Data: Born near Stroud, Oklahoma, March 28, 1936, the son of George Francis and Ruby Viola Gooch.

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