Figure 1 shows the average slope of 2, indicating the composition of the copper complex as 1:2. A study of the same system made by Job's and Slope Ratio methods in a two phase system (2, 3, 7), and the composition of the complex in the solid state (7) indicate this composition is correct.

From Table I, the mean value of log $K_{Cu}$ is found to be $2.521 \times 10^{-4}$. This is in agreement with that arrived at from the intercepts of the straight lines on log $D$ axis in Figure 1.

Similar findings are recorded for nickel also. The value of log $K_{Ni}$ surveyed from Table II and confirmed from the intercepts on log $D$ axis (cf. Figure 2) is $5.446 \times 10^{-11}$.

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# Thermodynamic Properties of HF

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An enthalpy-temperature diagram and an entropy-temperature diagram for anhydrous hydrogen fluoride (HF) were prepared by critical evaluation of published data for temperatures between −40° and 240° C. and absolute pressures between two and 1000 lb. force/in². In the vapor phase HF molecules are strongly associated into polymeric forms; dissociation to the monomeric form is accompanied by large changes in enthalpy. Published information for some regions of the diagrams is inconsistent or discordant, and in places is entirely lacking.

THE THERMODYNAMIC properties of anhydrous hydrogen fluoride (HF), because of molecular association in both the liquid and vapor, cannot be calculated from generalized correlations for ordinary unassociated substances. Experimental data in the literature for some regions of interest are not available, and in other regions are conflicting or not self-consistent. This study was undertaken to make a critical review of the published literature, and to prepare a set of charts summarizing the best values of the thermodynamic properties. This work includes both an enthalpy and an entropy diagram. The pressure range is from 2 to 1000 lb. force/in.² absolute; the temperature range is from −40° to 240° C.

The thermodynamic charts (Figures 1 and 2) were prepared from data in the published literature and have been deposited with the American Documentation Institute. It proved necessary to resolve conflicting data and to convert much information into a different form. This conversion revealed many inconsistencies in the published values. In addition, in a substantial part of the superheated-vapor region there is no published information whatever. Arbitrary techniques of smoothing and interpolation were used in preparing some parts of the diagrams. In all the calculations and in the tabulated data nonsignificant figures were carried to reduce the calculation errors. The final numbers were then rounded off. The sources of information and methods of calculating enthalpy and entropy for the several regions were done with the following procedures.

**Saturated Liquid Line.** Data for $C_p$ of the saturated liquid were taken from Hu, White, and Johnston (7), and for $C_V$ from Franck and Spalthoff (4). The data of Dahmlos and Jung (2) are inconsistent with those of others (4, 7) and were not used. Vapor-pressure data were taken from several sources, among which there was some disagreement. The charts are based on data from Simons (11) for temperatures below 10° C.; from Jarry and Davis (8) for temperatures between 10° and 112° C.; and from Franck and Spalthoff (4) for temperatures above 112° C.

The calculation of enthalpy and entropy from these data is not straightforward, and since the construction of the entire chart depends on the position assigned to the saturated liquid line, the calculation procedure is outlined in detail below.

The specific heat of the saturated liquid is defined by Lewis and Randall [(9), Equation 6-9]:

$$C_s = \lim_{\Delta T \to 0} \left( \frac{\Delta q}{\Delta T} \right)_s = \left( \frac{\partial H}{\partial T} \right)_s - V \left( \frac{\partial p}{\partial T} \right)_s \qquad (1)$$

Since

$$H = \phi(T, p),$$

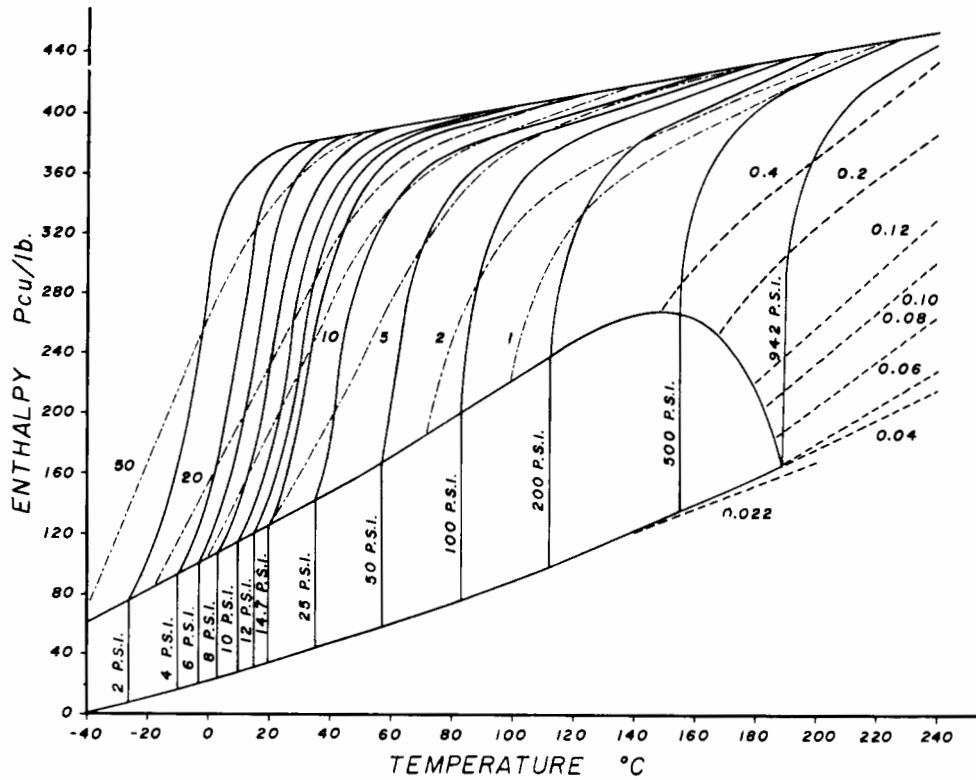$$dH = \left( \frac{\partial H}{\partial T} \right)_p dT + \left( \frac{\partial H}{\partial p} \right)_T dp$$

Figure 1. Enthalpy-temperature diagram for anhydrous HF. (————, constant-pressure lines; ––––––, –·–·–, constant-volume lines. Numbers on constant-volume lines are ft.$^3$/lb.)
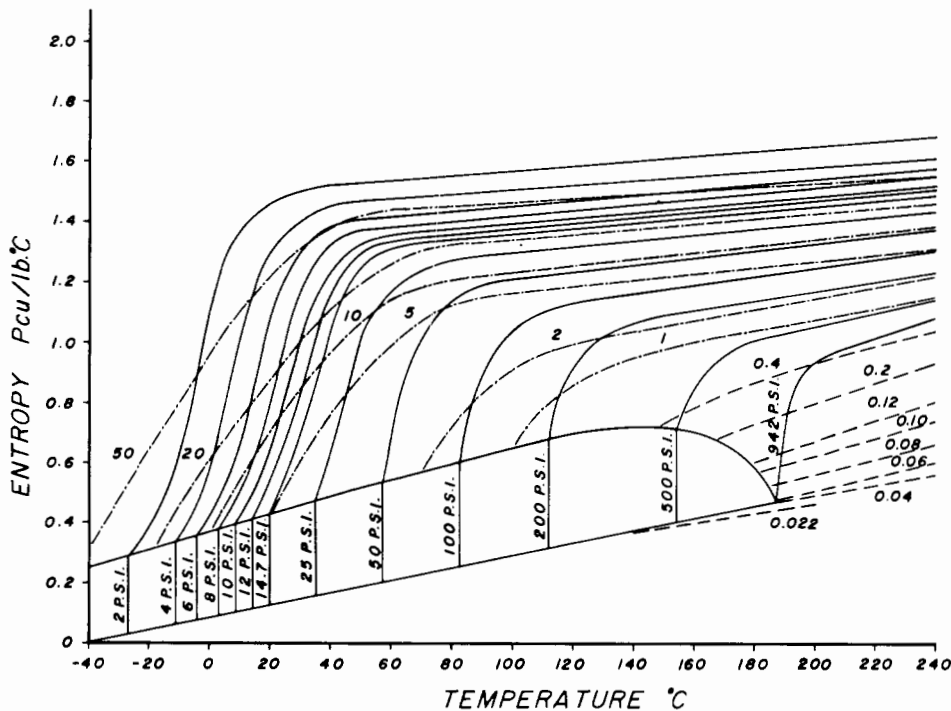


Figure 2. Entropy-temperature diagram for anhydrous HF. (————, constant-pressure lines; ––––––, –·–·–, constant-volume lines. Numbers on constant-volume lines are ft.$^3$/lb.)

and

$$\left( \frac{\partial H}{\partial T} \right)_s = \left( \frac{\partial H}{\partial T} \right)_p + \left( \frac{\partial H}{\partial p} \right)_T \left( \frac{\partial p}{\partial T} \right)_s$$

$$= C_p + \left( \frac{\partial H}{\partial p} \right)_T \left( \frac{\partial p}{\partial T} \right)_s \qquad (2)$$

Combining Equations 1 and 2 gives

$$C_s = C_p + \left[ \left( \frac{\partial H}{\partial p} \right)_T - V \right] \left( \frac{\partial p}{\partial T} \right)_s \qquad (3)$$

Now

$$dH = TdS + Vdp$$

from which

$$T\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial H}{\partial p}\right)_T - V$$

Also, from the Maxwell relation,

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

so that

$$-T\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial H}{\partial p}\right)_T - V \tag{4}$$

Substituting Equation 4 into Equation 3 gives

$$C_s = C_p - T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_s$$

Now, from Equation 10-25 (9):

$$C_p = C_V + T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

Thus

$$C_s = C_V + T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p - T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_s$$

$$= C_V + T\left(\frac{\partial V}{\partial T}\right)_p \left[\left(\frac{\partial p}{\partial T}\right)_V - \left(\frac{\partial p}{\partial T}\right)_s\right] \tag{5}$$

From Equation 1

$$\left(\frac{\partial H}{\partial T}\right)_s = C_s + V\left(\frac{\partial p}{\partial T}\right)_s$$

and

$$\Delta H_s = \int_{T_1}^{T_2}\left[C_s + V\left(\frac{\partial p}{\partial T}\right)_s\right]dT \tag{6}$$

The increment of enthalpy $\Delta H_s$ could be calculated from Equations 5 and 6 if $(\partial V/\partial T)_p$, $(\partial p/\partial T)_V$ and $(\partial p/\partial T)_s$ of the liquid were known. These quantities can be estimated from the published data, but only with considerable uncertainty. It was therefore considered best to assume that $(\partial p/\partial T)_V$ equaled $(\partial p/\partial T)_s$ so that $C_s = C_V$. This is not inconsistent with published data for constant volume. Then

$$\Delta H_s = \int_{T_1}^{T_2}\left[C_V + V\left(\frac{\partial p}{\partial T}\right)_s\right]dT \tag{7}$$

With $(\partial p/\partial T)_s$ estimated from increments of pressure and temperature, Equation 7 becomes

$$\Delta H_s = \int_{T_1}^{T_2} C^* dT \tag{8}$$

where $C^*$ is defined by the equation

$$C^* = V_V + V\frac{\Delta p}{\Delta T}$$

The entropy increment was calculated from

$$\Delta S_s = \int_{T_1}^{T_2} \frac{C^*}{T} dT \tag{9}$$

The enthalpy and entropy of the saturated liquid were calculated by graphical integration of Equations 8 and 9.

At temperatures between $-40°$ C. and $+20°$ C., $C^*$ was taken as equal to $C_p$ since $V(\Delta p/\Delta T)$ closely approximates $C_p - C_V$ in this range of temperatures.

Between $100°$ and $184°$ C. the value of $V(\Delta p/\Delta T)$ is almost constant at 1.72 cal./(20 g.)($°$ C.). At temperatures between $20°$ and $100°$ C. the value of $V(\Delta p/\Delta T)$ was assumed to be a linear function of temperature, with a value of 1.08 at $20°$ C. The value of 1.08 was chosen so that $C^*$ equalled the known value of $C_p$, 12.14 cal./(20 g.) ($°$ C.), at $20°$ C.

**B. Critical Properties.** The critical properties were taken from Franck and Spalthoff (4) as follows:

$T_c = 188°$ C. $\pm 3°$ C.
$p_c = 942$ lb. force/in.$^2$ absolute $\pm 5.0$ lb. force/in.$^2$
$V_c = 0.055$ ft.$^3$/lb. $\pm 0.006$ ft.$^3$/lb.

This critical temperature differs considerably from the value of $230°$ C. reported in 1931 by Bond and Williams (1).

**C. Enthalpy and Entropy of Saturated Vapor.** The enthalpy and entropy of the saturated vapor were found by adding the appropriate values for constant-pressure vaporization to the corresponding values for the saturated liquid at the same temperature. Literature data for the enthalpy of vaporization from three sources (4, 5, 8) were examined. For temperatures above $60°$ C. the values reported by Jarry and Davis (8) are self-consistent and agree with those given by Franck and Spalthoff (4). For temperatures below $60°$ C., however, the values given by Jarry and Davis are appreciably smaller than the calorimetric values given by Fredenhagen (5) and may be in error. In addition other data given by Jarry and Davis are also open to question. Their reported values for specific volume and apparent molecular weight of the vapor agree with those of others for temperatures above $60°$ C. but not at lower temperatures. It was concluded that their reported enthalpies of vaporization are not reliable for temperatures below $60°$ C.

Published data (4, 8) for temperatures between $60°$ C. and $130°$ C. indicate a linear variation of enthalpy of vaporization with temperature. This linear graph was extrapolated from $60°$ C. to lower temperatures, and was found to pass through two of the three calorimetric values reported by Fredenhagen (5) and to come very close to a third one. This extrapolated graph was used in finding enthalpies of vaporization for temperatures between $-40°$ C. and $+60°$ C.

**D. Superheated Vapor-Constant Pressure Lines.** The enthalpy of the superheated vapor at constant pressure was calculated by graphical integration of the equation

$$\Delta H_p = \int_{T_1}^{T_2} C_p dT \tag{10}$$

Values of $C_p$ at several constant pressures between two and 14 lb. force/in.$^2$ absolute are given by Franck and Meyer (3). For temperatures near the saturation temperatures these data are self consistent; at higher temperatures, where the polymeric HF vapor is completely or almost completely dissociated, the data are not self consistent. It was therefore assumed that monomeric HF vapor at these pressures behaves like an ideal gas, with the result that the enthalpy at a given temperature is independent of pressure. The upper parts of the constant-pressure lines on the enthalpy-temperature chart were adjusted to converge to a single line as the temperature increased, the point of convergence depending on the pressure. The limiting line was calculated from the data for a pressure of 8 lb. force/in.$^2$ absolute. The assumption of an ideal gas in these regions is not inconsistent with the generalized compressibility chart (6) nor with the vapor-density data of Seufzer and Katz (10).

Constant-pressure data for pressures above 14 lb. force/ in.$^2$ absolute are not available, except for the single points on the saturated vapor line. In this region the constant-

pressure lines on the enthalpy-temperature chart were drawn parallel with those found for lower pressures, each converging at high temperatures with the limiting line for an ideal gas. A line for 942 lb. force/in.² passing through the critical point was sketched in, but is at best highly approximate.

Constant-pressure lines on the entropy-temperature chart were calculated by graphical integration of the equation

$$\Delta S_p = \int_{T_1}^{T_2} \frac{C_p}{T} \, dT \tag{11}$$

Again, $C_p$ data are available only for subatmospheric pressures, and again they appear inconsistent at elevated temperatures. The inconsistency is less marked, however, than that indicated in the enthalpy chart. At constant temperature the entropy of an ideal gas is not independent of pressure. The variation with pressure was calculated as follows.

Since, in general, entropy is a function of both temperature and pressure,

$$dS = \left( \frac{\partial S}{\partial p} \right)_T dp + \left( \frac{\partial S}{\partial T} \right)_p dT \tag{12}$$

Now

$$\left( \frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T} \tag{13}$$

Also, from a Maxwell relation,

$$\left( \frac{\partial S}{\partial p} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_p \tag{14}$$

For an ideal gas, $V = RT/p$, and

$$\left( \frac{\partial V}{\partial T} \right)_p = \frac{R}{p} \tag{15}$$

Combining Equations 12, 13, 14, and 15,

$$dS = - \frac{R}{p} dp + \frac{C_p}{T} dT$$

At constant temperature, increments of entropy are given by

$$\Delta S_T = - \int_{p_1}^{p_2} \frac{R}{p} dp = -R \ln \frac{p_2}{p_1} \tag{16}$$

Equation 16 was used to smooth the calculated values of entropy at elevated temperatures, and to predict the entropy at higher pressures for which no data are available. For each selected constant pressure, above atmospheric pressure, this procedure gave two points on the constant-pressure line: one on the saturated vapor curve and one at a temperature of 240° C. At this temperature the vapor is probably completely dissociated into monomeric HF except at pressures above 500 lb. force/in.² With the two points available, a curve was sketched in parallel with those indicated by the published data for lower pressures.

**E. Constant-Volume Lines.** Franck and Spalthoff (4) give extensive data for $C_v$ at high pressures. From this the enthalpy and entropy for the constant-volume were computed by graphical integration of the equations

$$\Delta H_V = V\Delta p + \int_{T_1}^{T_2} C_V dT$$

$$\Delta S_V = \int_{T_1}^{T_2} \frac{C_V}{T} dT$$

The results were smoothed and interpolated to give the desired constant-volume lines. Some of these lines are in the region of unsaturated liquid, but are close to and almost parallel with the saturated liquid line. Other lines, for specific volumes between 0.08 and 0.4 ft.³/lb., are in the region of superheated vapor.

Similar data are lacking for lower temperatures and pressures. In this region use was made of the vapor-density measurements and apparent molecular weights reported by Strohmeier and Briegleb (12) and Seufzer and Katz (10). For a selected constant vapor volume, corresponding values of temperature and pressure were found by trial from the published data. Use of the previously established constant-pressure lines on the enthalpy and entropy charts then permitted construction of the constant-volume lines. Thus, the position of the constant-volume lines depends on the accuracy not only of the vapor-density measurements, and of their interpretation, but also on the accuracy of the constant-pressure lines. The constant-volume lines are therefore subject to the greatest uncertainty of any of the indicated quantities.

## ACCURACY OF THE CHARTS

The estimated accuracy of the charts varies widely from region to region. The following quantities, found from self-consistent published data, from several investigators, are believed highly reliable and probably accurate to within 1 per cent: vapor pressure; enthalpy of saturated liquid; enthalpy of saturated vapor at pressures above atmospheric; constant-volume lines at high pressures (specific volumes of 0.4 ft.³/lb. and less); constant-pressure lines at subatmospheric pressures and temperatures below 40° C. Somewhat less certain are the saturated vapor curves at pressures below atmospheric; the constant-pressure lines at low pressures and temperatures above 40° C.; and the constant-pressure lines for pressures above atmospheric. Moderately uncertain are the constant-volume lines at pressures below 500 lb. force/in.² absolute.

In many regions it is impossible to make a quantitative estimate of the accuracy of the charts, especially in regions where experimental data are lacking. New measurements and information in these regions are highly desirable.

## NOMENCLATURE

$C$ = specific heat, P.c.u./lb.-° C. or cal./20g.-° C.; $C_p$, at constant pressure; $C_s$, of saturated liquid; $C_V$, at constant volume

$C^*$ = approximate specific heat used in calculating enthalpy of saturated liquid

$H$ = enthalpy, P.c.u./lb.

$p$ = pressure, lb. force/in.² or lb. force/ft.²

$q$ = quantity of heat, P.c.u.(pound-centigrade unit. 1 P.c.u. = 1.8 B.t.u.; 1 P.c.u./lb. = 1 cal./g.)

$R$ = gas constant, 1.9864 P.c.u./lb. mole-° C.

$S$ = entropy, P.c.u./lb.-° C.

$T$ = absolute temperature, ° K.

$V$ = specific volume, ft.³/lb.

**Greek Letters**

$\Delta$ = increment of

$\phi$ = function of

**Subscripts**

$c$ = critical value

$p$ = at constant pressure

$s$ = of saturated liquid

$T$ = at constant temperature

$V$ = at constant volume

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# Thermodynamic Properties of Inorganic Substances VII.

## The High Temperature Heat Content of Zirconium Diboride

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The high temperature heat content of a high-purity sample of $ZrB_2$ has been measured in a copper-block drop calorimeter over the range 410° to 1125° K., and the results correlated with low temperature heat capacity data on a similar sample. Derived thermodynamic properties over the range 0° to 2000° K. are presented based on experimental data up to 1200° K. and on extrapolations of computer-selected fits of the experimental points.

FIVE SETS OF HIGH TEMPERATURE thermodynamic data (1, 2, 7, 8, 10) and a single low temperature study (11) have previously been available for $ZrB_2$ samples of 95-99% purity but large positive and negative discrepancies (10-20% or more) have been observed even though all the calorimeters have been calibrated in standard ways. In a cross-check of data, Pears and coworkers (9) made runs on the same $ZrB_2$ used by Barnes and coworkers (1) and reproduced the results of Barnes within a few per cent, which indicates that the reported large differences between samples are real and not measurement errors. The AVCO results are pulse-type heat capacity measurements (2) over the temperature range 2000° to 2500° K. and seem to differ drastically from conventional extrapolations of the lower temperature results, as do the results of Prophet (10).

This report presents high temperature measurements on a sample of $ZrB_2$ prepared by Feick (3) which is from the same batch as the sample used by Westrum and Feick (11) for their low-temperature studies.

## EXPERIMENTAL

The calorimeter used in this work has been described previously (4) and the samples were contained in platinum or platinum-rhodium capsules under an argon atmosphere. Temperature measurements were made with a Pt vs. Pt-10% Rh thermocouple calibrated against a reference which had been recently calibrated at the National Bureau of Standards. The reliability of the calorimeter was checked by rerunning a standard sample of synthetic sapphire. The heat content for the empty Pt capsules was measured at several temperatures and found to check well with the equation of Kelley (6) while the heat content of the Pt-10% Rh capsule was calculated from Kelley's data on the elements.

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According to Feick (3), the samples used (Bar No. 80) had been zone-refined and had the stoichiometry $ZrB_{1.97}$. Representative impurities in such bars are: 0, 52 p.p.m.; C, 215 p.p.m.; N, 134 p.p.m.; Si, 100-1000 p.p.m.; Hf and Fe, 10-1000 p.p.m.; Mg, 10-100 p.p.m.; and Ag, Ca, Cu, Ti, V, Cr, and Mn, 10 p.p.m. There is also some possibility of ZrB being present originally (11), although it probably annealed out during the heating cycles.

## RESULTS

Two sets of data were obtained. The first set, covering the range 410-773° K., was terminated when the capsule sprang a leak and allowed oxidation of the $ZrB_2$ as detected by a large, sudden weight gain in the next run attempted after 773° K. The second series covered the range 450-1126° K. and no weight changes were observed. The results were processed on a CDC-1604 high-speed computer to yield the data in Table I. These data were then used for

Table I. Experimental Heat Contents of $ZrB_2$

| $T$, ° K. | $T_{cal.}$, ° K. | $H_T - H_{T_{cal.}}$ Cal. Mole$^{-1}$ |
|---|---|---|
| 410.46 | 298.60 | 1510 |
| 463.46 | 298.69 | 2204 |
| 553.76 | 298.93 | 3564 |
| 598.66 | 298.81 | 4288 |
| 711.06 | 298.89 | 5926 |
| 773.06 | 298.97 | 7114 |
| 450.02 | 297.88 | 1998 |
| 514.25 | 298.92 | 3017 |
| 724.16 | 299.44 | 6031 |
| 888.46 | 299.26 | 8782 |
| 986.46 | 299.02 | 10626 |
| 1123.46 | 299.17 | 12781 |
| 1125.62 | 299.17 | 13000 |