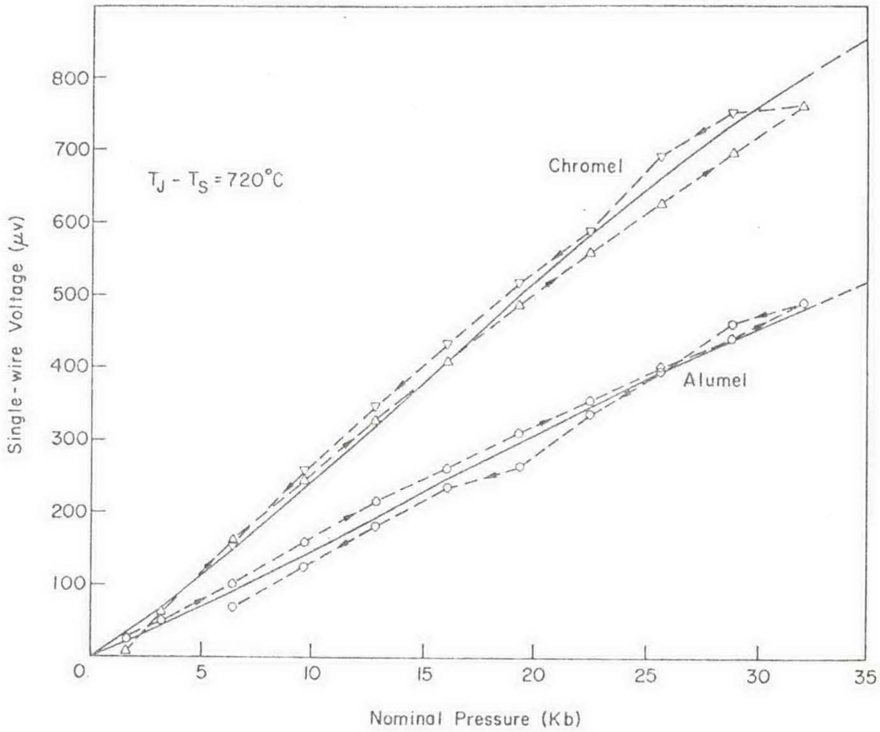

FIG. 10. Isothermal data for Chromel and Alumel.

least-squares analysis with polynomial surfaces of the form

$$E = a_1\Delta TP + a_2\Delta TP^2 + a_3\Delta T^2P + a_4\Delta TP^3 + a_5\Delta T^2P^2 + a_6\Delta T^3P,$$

where P is the pressure as determined above and $\Delta T = T_J - T_S$ is the pressurized temperature interval. This permits smoothing over both independent variables simultaneously as well as appropriately weighted consideration of the data from both types of excursions. The surface represented above is a general polynomial surface with only the cross-product terms retained. This constrains the surface to pass through the ΔT and P axis assuring compliance with the boundary conditions that the single-wire voltage be zero whenever the pressure cell is isothermal or whenever the pressure is zero. Ultimately it is the differences in single-wire voltages which appear as the thermocouple corrections. These differences were calculated point by point from the data for individual thermoelements and also fit with surfaces. Table I shows the standard deviation associated with each fit.

These data include implicitly the specific relation between the two seal temperatures T_J and T_S which occurred in this particular experimental setup. In order to generalize the results, this relation must be determined explicitly and taken into account. For each of the original data points, both T_J and T_S were recorded. For conductive heat transfer to the cold seal from the hot seal region, the relation between the two seal temperatures should be linear at equilibrium. The fit by least-squares analysis was

$$T_S - 20 = 0.0909(T_J - T_S),$$

with a standard deviation of ±12°C. The standard deviation was essentially unchanged for polynomials of higher degree. Thus the rise above ambient of the cold seal was 9% of the pressurized temperature interval.

We would like to determine the single-wire voltages, and hence the thermocouple corrections, for the case in which the cold seal temperature remained fixed at ambient, 20°C. The single-wire voltages, like thermocouple voltages, are additive over adjacent temperature intervals. Thus, for example, the voltage generated between 1000° and 20°C is equal to that generated between 1000° and 110°C plus that between 110° and 20°C. This principle was applied to our data in a one step iteration to calculate generalized single-wire voltages and subsequent thermocouple corrections. This process increases the temperature uncertainty slightly to ±6%.

We have also extrapolated the data from 35 kbar and 1000°C to 50 kbar and 2000°C for Pt–Pt10Rh and 50 kbar and 1200°C for Chromel–Alumel. Smooth graphical extrapolations on evenly spaced isobaric and isothermal profiles were made to the surface fits. No additional experimental data is included in these extrapolations, however.

The final results are shown in Figs. 11 and 12. Here the thermocouple corrections (the differences in single-wire voltages) are plotted versus a generalized temperature scale at various pressures. The voltages shown are