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(U) CHICAGO UNIV IL JAMES FRANCK INST R GOMER
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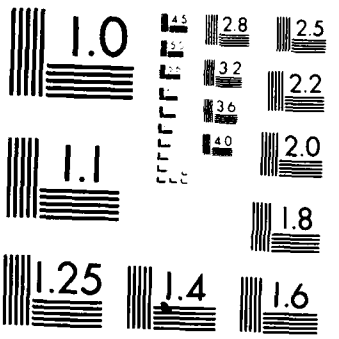

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This annual summary report describes work function, sticking coefficient, isothermal and temperature programmed desorption, Leed, and equilibrium measurements for CO adsorption on $W(110)/Cu_n$ surfaces, with emphasis on n = 1 and to a lesser extent n = 6.

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ANNUAL SUMMARY REPORT ON ONR CONTRACT N00014-~~80-K-0047~~

December 1, 1985 - July 1, 1986

Work carried out during this period has consisted of a detailed study of the adsorption, desorption and thermodynamics properties of CO on W(110) covered with one or more Cu monolayers. The most detailed measurements were made for $W(110)/Cu_1$. Preliminary equilibrium measurements were also made for $W(110)/Cu_6$. Some work function measurements for CO adsorption were also carried out on intermediate layer thicknesses. The principal tools in this phase of the work were thermal desorption, using a quadrupole mass spectrometer as detector for isothermal and temperature ramped measurements, and work function measurements using the newly constructed and higly accurate, reproducible (< 1 meV) and fast (< 0.1 sec response time) Kelvin probe for work function measurements[1]. The latter were used to determine sticking coefficients, coverage vs. temperature rise (i.e. ramped desorption giving not the rate but the remaining coverage) and adsorption isobars, i.e. coverage as function of surface temperature for a series of constant CO pressures.

CO ADSORPTION ON $W(110)/Cu_n$
(M. Chelvayohan and R. Gomer)

Work Function Changes for CO Adsorption

For one Cu layer $\Delta\phi$ rises monotonically and almost linearly to ~400 meV with CO coverage. For 2 or more Cu layers work function at first decreases and then increases; this has also been seen on bulk Cu surfaces[2,3] and is probably associated with changes in π^* orbital filling. Significant differences were found for annealed (800 K) and unannealed Cu multilayers. For annealed layers $\Delta\phi$ becomes positive at saturation coverage, while remaining negative for unannealed ones.

Sticking Coefficients and Absolute Coverage

Sticking coefficients for $W(110)/Cu_1$ were determined by comparing $\Delta\phi$ vs. exposure time curves with the crystal at 25 K (where s is unity to very high coverage) with similar curves at higher crystal temperature, T_s. For $T_s \leq 220$ K s is initially ≥ 0.75 and shows the plateau associated with precursor models[4]; for higher T_s s is lower initially and decreases almost linearly with coverage. Absolute coverages could be determined by calibrating against clean W(110) for which maximum coverage is known from previous work in this laboratory[5]. For $W(110)/Cu_1$ this turned out to be CO/Cu = 0.72, at 25 K. Long exposure at $T_s \geq 80$ K increases the uptake (with very low sticking coefficient) to 0.75. At 25 K incorporation of this last increment apparently cannot take place; CO in excess of 10^{15} molecules/cm^2 is simply held as physisorbed CO in a second layer. A similar phenomenon was seen for $W(110)/Cu_6$.

Thermal Desorption

Temperature programmed desorption results confirmed those carried out earlier by Hamadeh and the writer[6]; there are 3 peaks for $W(110)/Cu_1/CO$ at 192, 226 and 261 K (depending slightly on heating rate) and a small peak near 383 K corresponding to tungsten-like adsorption, probably in defect sites or where Cu has been pushed aside at Cu domain boundaries. Isothermal desorption experiments were also carried out and show that desorption obeys no simple rate law except at very low coverage where good first order kinetics were seen, corresponding to $\nu \sim 10^{14}$ sec^{-1} and E_{des} = 18 Kcal/mole. The reason for the complicated desorption behavior can be found in terms of the thermodynamic properties of the layer, which will be described later.

LEED Results

Three structures were seen. For CO/Cu < 0.24 no new order was seen but the Cu p(1x1) structure seen for $W(110)/Cu_1$ remained intact. For $0.24 \leq CO/Cu \leq 0.5$

a structure describable by the real space matrix $\begin{pmatrix} 2\sqrt{2} & 0 \\ -\sqrt{2} & 2 \end{pmatrix}$ was seen. For $0.5 < CO/Cu \leqslant 0.72$ a new structure appeared $\begin{pmatrix} 2\sqrt{2} & 0 \\ -\sqrt{2} & n \end{pmatrix}$ where n is continuously variable; this is indicated by the fact that the corresponding spot separation changes continuously but the spots remain sharp. At CO/Cu > 0.72 this structure goes over into p(4x1). All the structures are incommensurate; since the CO/Cu = 0.5 structure is seen at CO/Cu as low as 0.25 this suggests attractive CO-CO interactions.

Equilibrium Measurements

It was possible to obtain isobars, i.e. coverage vs. T_s curves at constant CO pressure by means of the Kelvin probe, using the previously determined $\Delta\phi$ vs. coverage curve. A set of isobars is shown in Fig. 1. It is then possible to obtain H_a the isosteric heats of adsorption from ln p vs. $1/T_s$ plots at constant coverage. Corrections for the fact that the gas temperature T_g = 300 K rather than T_s can be made, assuming only that the ratio of sticking coefficients $s(T_s, T_g=T_s)/s(T_s, T_g = 300)$, varies only slightly with T_s, which is highly probable[4], particularly over the small ranges of T_s used in a given ln p vs. $1/T_s$ plot. Since the (corrected) gas pressures are equilibrium values

$$-H_a/T = \Delta H/T = \Delta S = S_g - S_s \qquad (1)$$

where ΔH and ΔS refer to desorption. The entropy of gaseous CO is given by

$$S_g = S_g^o - R\ln p/p_o \qquad (2)$$

p_o = 1 atm referring to the standard state, with S_g^o = 47.3 cal/^{o}K/mole. Thus the differential surface entropy per mole (at given coverage) S_s can be found. Figure 2 shows H_a and S_s as function of coverage. The striking feature of these curves is the decrease in H_a and the near divergence of S_s at CO/Cu $\sim$ 0.5. This coverage also corresponds to the plateaus in the isobars.

To the best of our knowledge such plateaus and divergences have not previously been seen. The meaning of the plateaus and the divergence is fairly clear: The system has completed an adsorption state at CO/Cu $\sim$ 0.5 and further uptake can occur (at least at the moderate pressures available here, $p_{max} \sim 10^{-6}$ torr) only when T_s is lowered. Thus H_a approaches zero and the differential surface entropy becomes very high, corresponding roughly to the fact that at very low θ (for the new state)

$$S_s = R \ln (1-\theta)/\theta \qquad (3)$$

which diverges as $\theta \to 0$. Here θ is relative coverage. This explanation is also supported by the Leed results, since there is a change in structures at CO/Cu = 0.5 i.e. after the surface is fully covered by the $\begin{pmatrix} 2\sqrt{2} & 0 \\ -\sqrt{2} & 2 \end{pmatrix}$ structure. It is not all clear, however, why such divergences do not occur at the other phase transition near saturation coverage. It is equally unclear why such divergences have not been seen previously in other systems. Possibly they have simply not been looked for since very few equilibrium measurements on chemisorption systems seem to have been carried out.

The entropy values seen on the low coverage side of the divergence seem reasonable for low frequency vibrational degrees of freedom and some configurational entropy. At the conditions of the lowest measurable values there is still some order, as indicated by Leed results so that CO cannot be regarded as a 2 dimensional gas, which would increase S_s to 12-14 cal/mole/^{o}K. Perhaps more surprising are the large negative values at high coverage. They suggest participation of Cu in adsorption, most likely by reconstruction which decreases the entropy per Cu atom. Similar, if not as dramatic effects have been seen by Estrup and coworkers for H adsorption on W(110)[7] and more recently on W(100)[8].

The present results also indicate that the heat of adsorption essentially has two values, 15 Kcal/mole for CO/Cu > 0.5 and 20 Kcal/mole for Cu/CO < 0.5 and

drops to very low values, as already explained at CO/Cu = 0.5.

Relation of H_a and S_s to Desorption Kinetics

Even if the detailed reasons why surface entropy behaves as it does are not fully understood its variation with coverage helps to explain why desorption kinetics are complex and why a three peak TPD spectrum is observed. The basis of these considerations, which have also been used by other workers[7] is that the rate of desorption at equilibrium equals that of adsorption and that the absence of ambient gas does not affect desorption in first approximation. Thus we can write (even at zero ambient pressure)

$$-\dot{n} = s\, p/(2\pi mkT)^{\frac{1}{2}} \tag{4}$$

where p is the equilibrium CO pressure and $-\dot{n}$ the rate of desorption in molecules cm^{-2} sec^{-1}. It follows from standard thermodynamics that $-\dot{n}$ can be written

$$-\dot{n} = \frac{sp_o}{(2\pi nkT)^{\frac{1}{2}}}\, e^{-\bar{\Delta}H^o/RT}\, e^{(\bar{S}_g^o - \bar{S}_s)/R} \tag{5}$$

It is now easy to see that desorption cannot obey first order kinetics unless $\bar{S}_s$ contains a term -Rln n. This condition is met for a lattice gas (see Eq. 3) and for a 2-d translational gas, but clearly not for $W(110)/Cu_1/CO$ (except possibly at very low θ where CO may be mobile enough to be a 2-d gas), as indicated by Fig. 2.

If ΔH is constant and $\bar{S}_s$ decreases linearly with coverage n for instance

$$\bar{S}_s/R = \bar{S}_s(n = 0)/R - \gamma n \tag{6}$$

it is clear from Eq. 5 that

$$\dot{n}(t) = \dot{n}_o\, s(n)\, e^{\gamma n(t)} \tag{7}$$

where $\dot{n}_o$ means the rate at n = 0 i.e. when $\bar{S}_g = \bar{S}_s$ (n = 0). Since n decreases as desorption proceeds, it is obvious even from Eq. 7 why the rate of desorption

slows below the values appropriate for first order kinetics after a very short time. If the sticking coefficients s(n) could be taken as constant, Eq. 7 would lead to a rate law

$$-\dot{n}(t) = \left[\gamma t + \frac{1}{s\dot{n}_o \, e^{\gamma n(t=0)}} \right]^{-1} \tag{8}$$

which bears little resemblance to

$$-\dot{n}(t) = -\dot{n}(0) \; [n(t)/n(0)] \tag{9}$$

which is the first order rate law, $-\dot{n} = k\, n$ written in analogous fashion to Eq. 8.

The variation of s with coverage makes Eq. 8 invalid, but there is a way of showing the general validity of the present approach: It is possible to determine experimentally $\Delta\phi$ vs. T by measuring $\Delta\phi$ with the Kelvin probe as temperature is ramped linearly. When such a plot is superimposed on the isobars its intersection with a given isobar corresponds to the equilibrium pressure p(T) at that particular coverage and temperature and is thus by Eq. 5 proportional to the rate of desorption. If the variation in sticking coefficient is neglected it is then possible to construct a simulated TPD spectrum. The latter correctly gives the 3 peaks observed experimentally in the right positions but does not give their correct relative intensities. The reason for this is the neglect of the variation of s with T and n. To date we have not determined s over a sufficient range of coverages and temperatures to include this effect. Further measurements of s are planned in order to include its effect.

Work on W(110)/Cu_6/CO

Heats of adsorption and surface entropies have been determined for this system. There are no plateaus in the isobars and H_a decreases monotonically from 14.5 Kcal at low to 9 Kcal at high coverage. $\bar{S}_s$ shows no divergences but

is extremely high, 25 cal/mole/^{o}K at low coverage $\sim$11 cal/mole/^{o}K at high coverage. There is some evidence from work function measurements that CO adsorption leads to some surface roughening and it is possible that this accounts for the high entropy values. Comparable entropy values can be calculated by analyzing Tracy's data for CO on Cu(100)[2].

The work reported here is nearing completion and will be written up for publication after some additional sticking coefficient measurements and probably some Leed experiments for W(110)/Cu_6/CO have been carried out.

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[8] J. A. Prybila, P. J. Estrup and Y. J. Chabal, to be published.

Title of Report
Annual Summary ONR Contract N00014-77-C-0018
Per Dr. Bobby R. Junker, ONR/Code 1112

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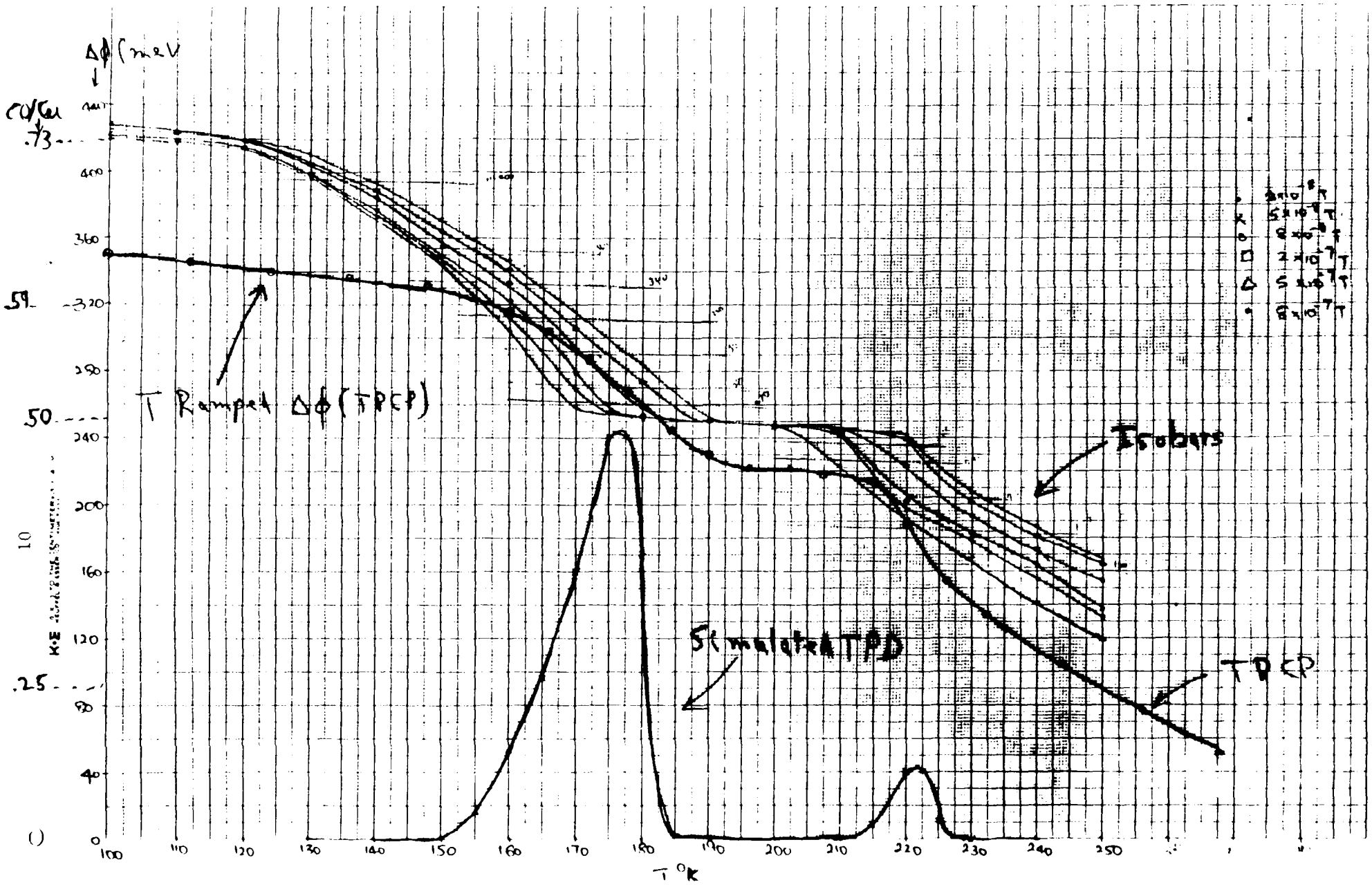
Figure Captions

1. Isobars ($\Delta\phi$ vs. T at constant pressures) for W(110)/Cu_1/CO. Also shown are coverages in units of CO/Cu. CO/Cu = 1 corresponds to 1.4×10^{15} molecules/cm^2. A temperature programmed work function vs. T (TPCP for temperature programmed contact potential) plot is superimposed on the isobars and a calculated temperature programmed desorption spectrum (TPD) obtained from this superposition as discussed in the text is also shown. The calculated TPD ignores the changes in sticking coefficient with T and coverage. In this set of runs temperatures were not taken high enough to show the third peak in the spectrum because of irreversibilities. A previous set of measurements which went to high enough T does show the third peak. Note in particular the plateaus in the isobars, which are discussed in the text.

2. Plots of differential surface entropy $\bar{S}_s$ and heat of adsorption $\bar{H}$ vs. work function increment and (also coverage in units of CO/Cu). Also shown are Leed structures corresponding to the various coverage regimes. Note the sharp increase in $\bar{S}_s$ and the concomitant sharp decrease in $\bar{H}$ near CO/Cu = 0.5, corresponding to the change in Leed patterns and also to the plateaus in the isobars shown in Fig. 1.


ΔΦ (mV
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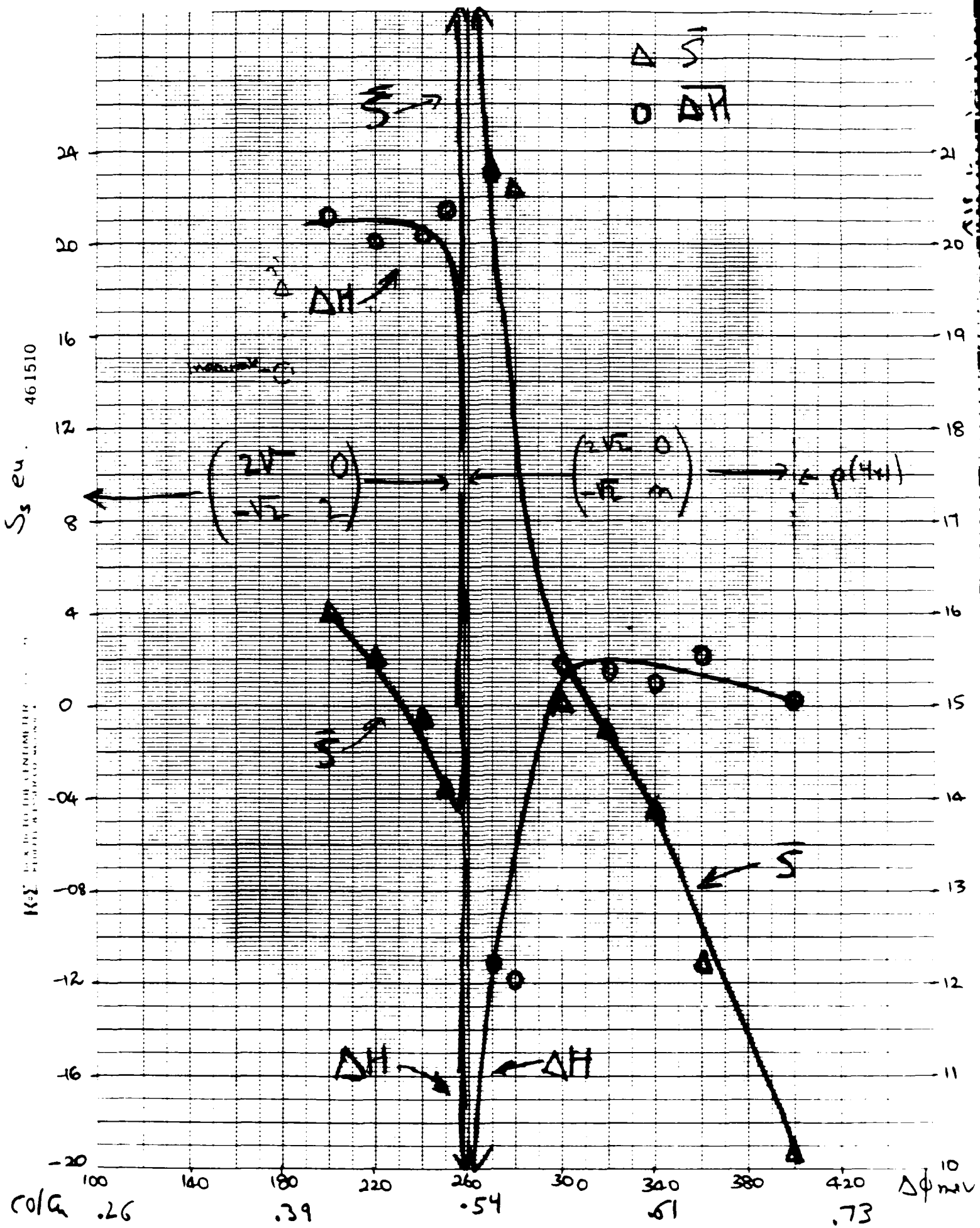
.59
.50
.25
T Ramped ΔΦ (TPCP)
Isobars
Simulated TPD
TPCP
T °K

Fig 1



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STATUS REPORT ON ONR CONTRACT N00014-~~86-K-0047~~ 77-C-0018

December 1, 1985 - July 1, 1986

1) Personnel: J. C. Lin, graduate student
M. Chelvayohan, research associate

2) Other Government Sponsored Research

The research of the Principal Investigator is also supported by the National Science Foundation at an annual rate of $110,000 by grant CHE83-16647 and its successor grant CHE86-03230. He also benefits from the Materials Research Laboratory of the National Science Foundation at the University of Chicago.

3) Current Status on Contract Funds

It is expected that there will be unexpended funds in the current contract at its expiration, November 30, 1986.

4) No permanent equipment was purchased during the current contract period.

END

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