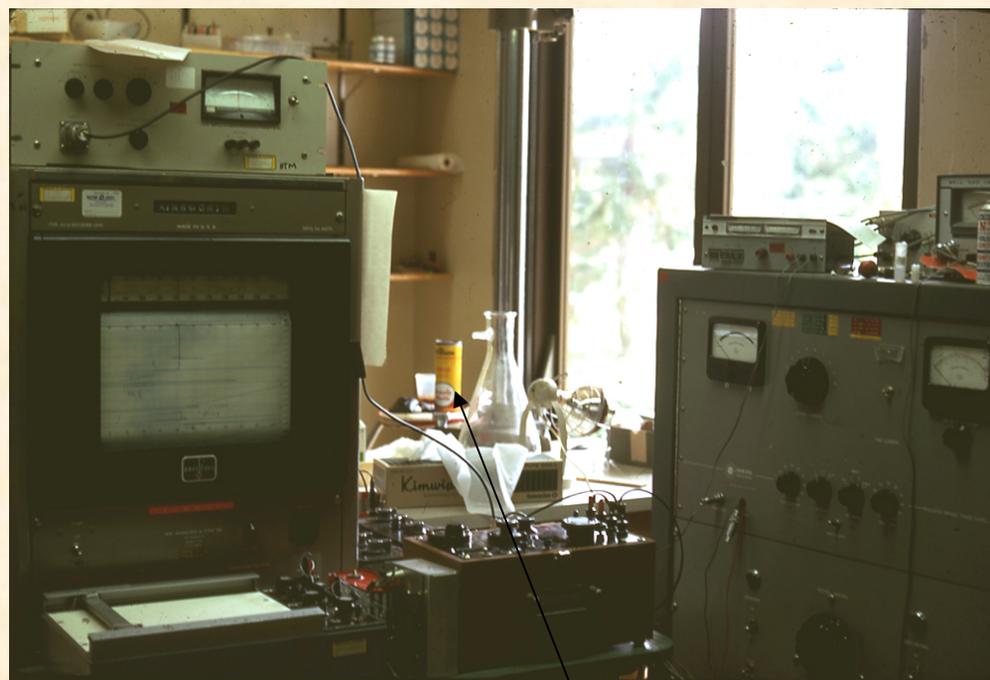
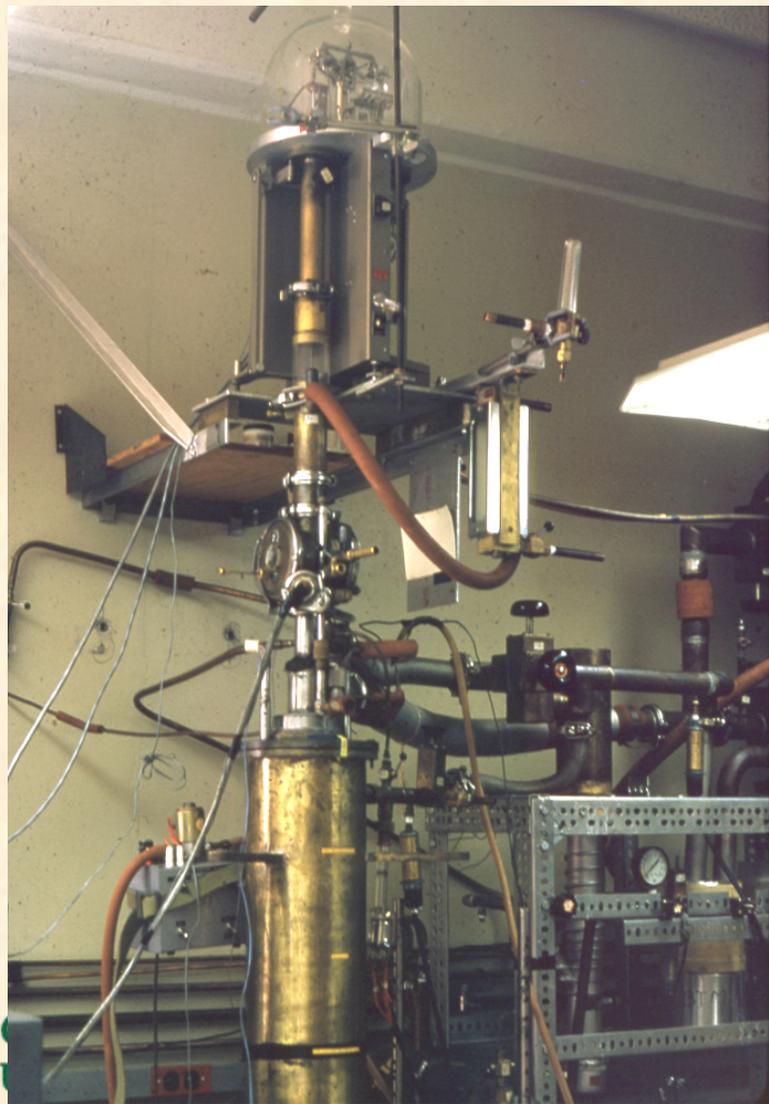


*Surface Science, Tennis and
Softball
"Maplefest 2004"*

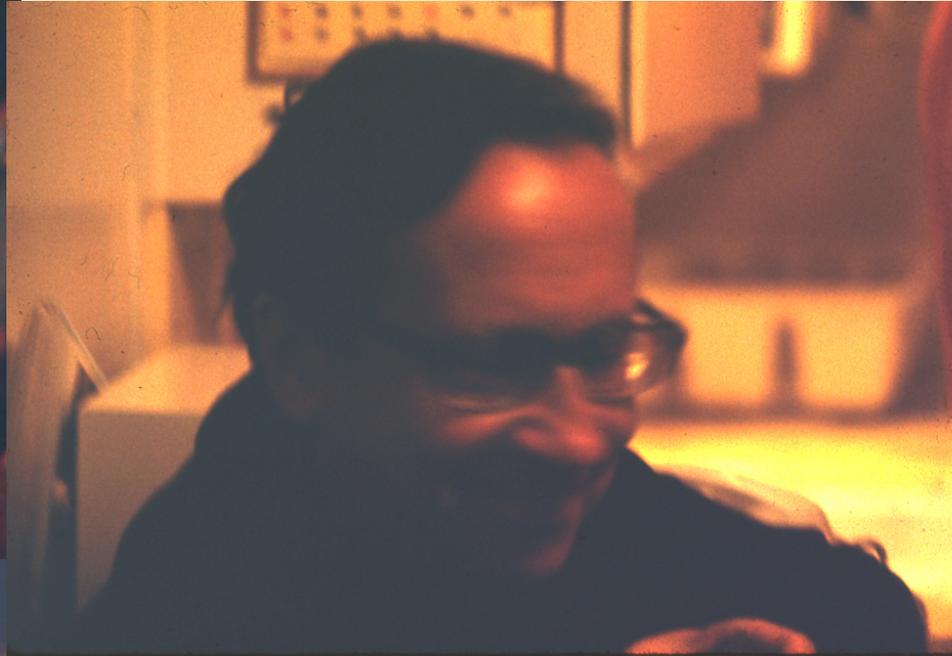
**Brian Sales
Correlated Electron Materials Group
Oak Ridge National Laboratory**

Hermann : A Faraday Magnetometer with a Personality



Tennis Balls

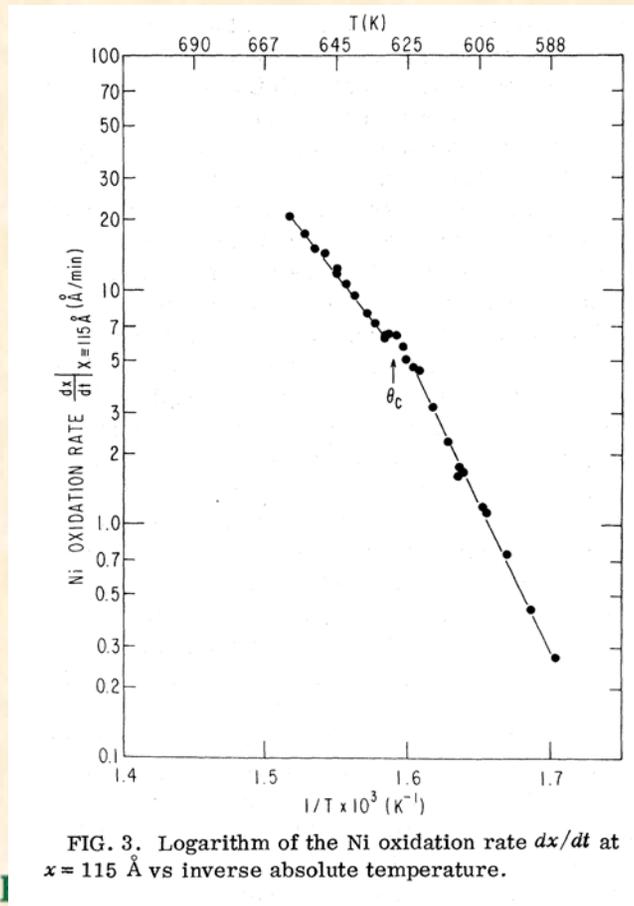
Milieu of Group Augmented by Parties and Sports



One of Many Group Softball Teams: "Einstein's Relatives"



Surface Science Experiments as PostDoc in Brian's Group: Oxidation of Nickel Near Curie Temp



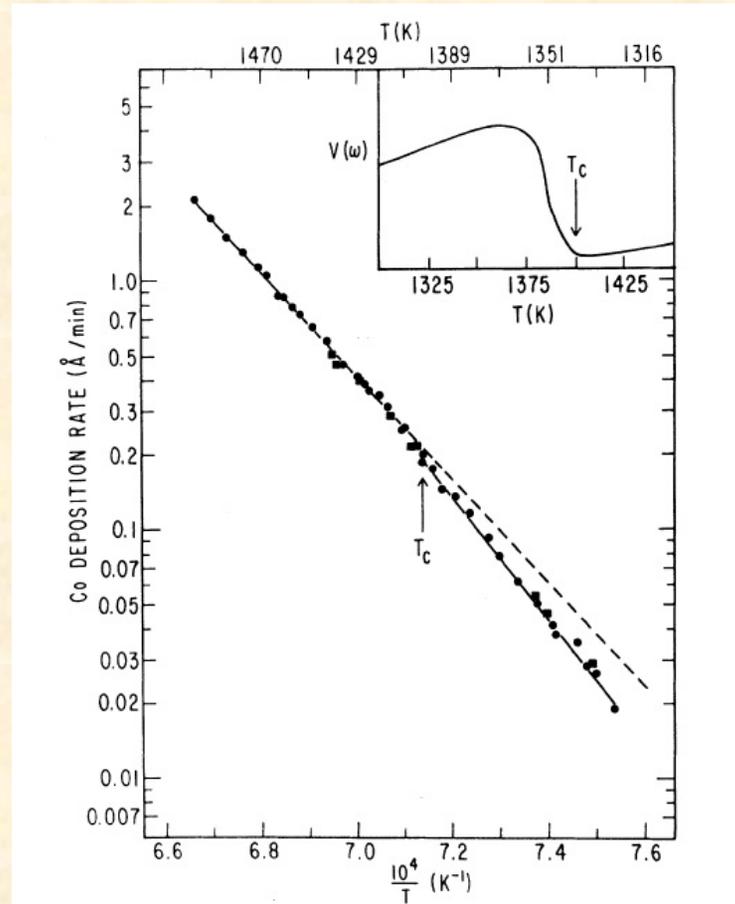
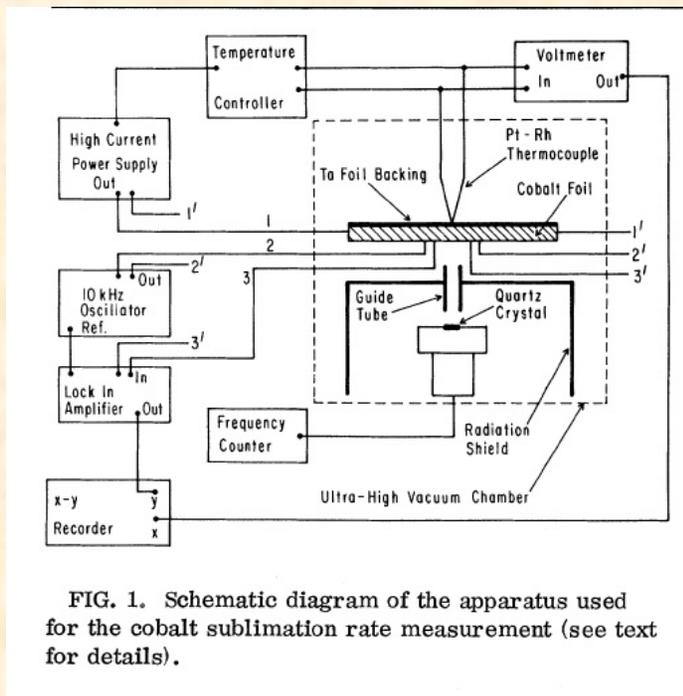
If data above T_c and below T_c
Fit to Arrhenius expression,

$$R \text{ (oxidation rate)} = A e^{-E/kT}$$

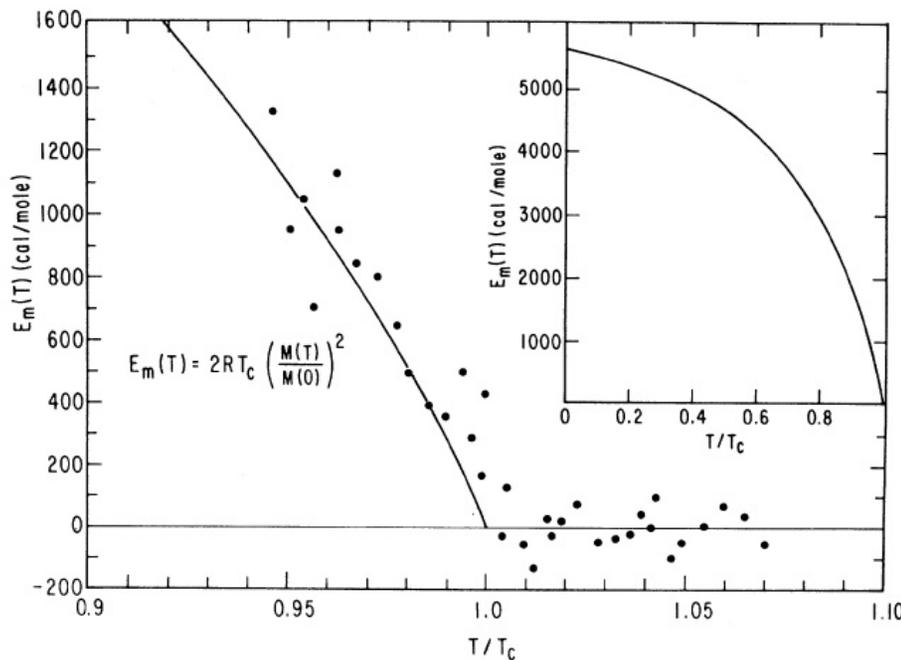
Apparent change in activation
Energy of **1 eV**! Why so large,
Magnetic energy scale $\approx kT_c$

PRL Vol 39, 1636 (1977)

Sublimation rate of Co Metal Near Curie Temperature



If Data Fit to Arrhenius laws Above and Below T_c , Apparent Change in Activation energy of 1eV : Not Physical ! Energy Scale of order $k_B T_c$



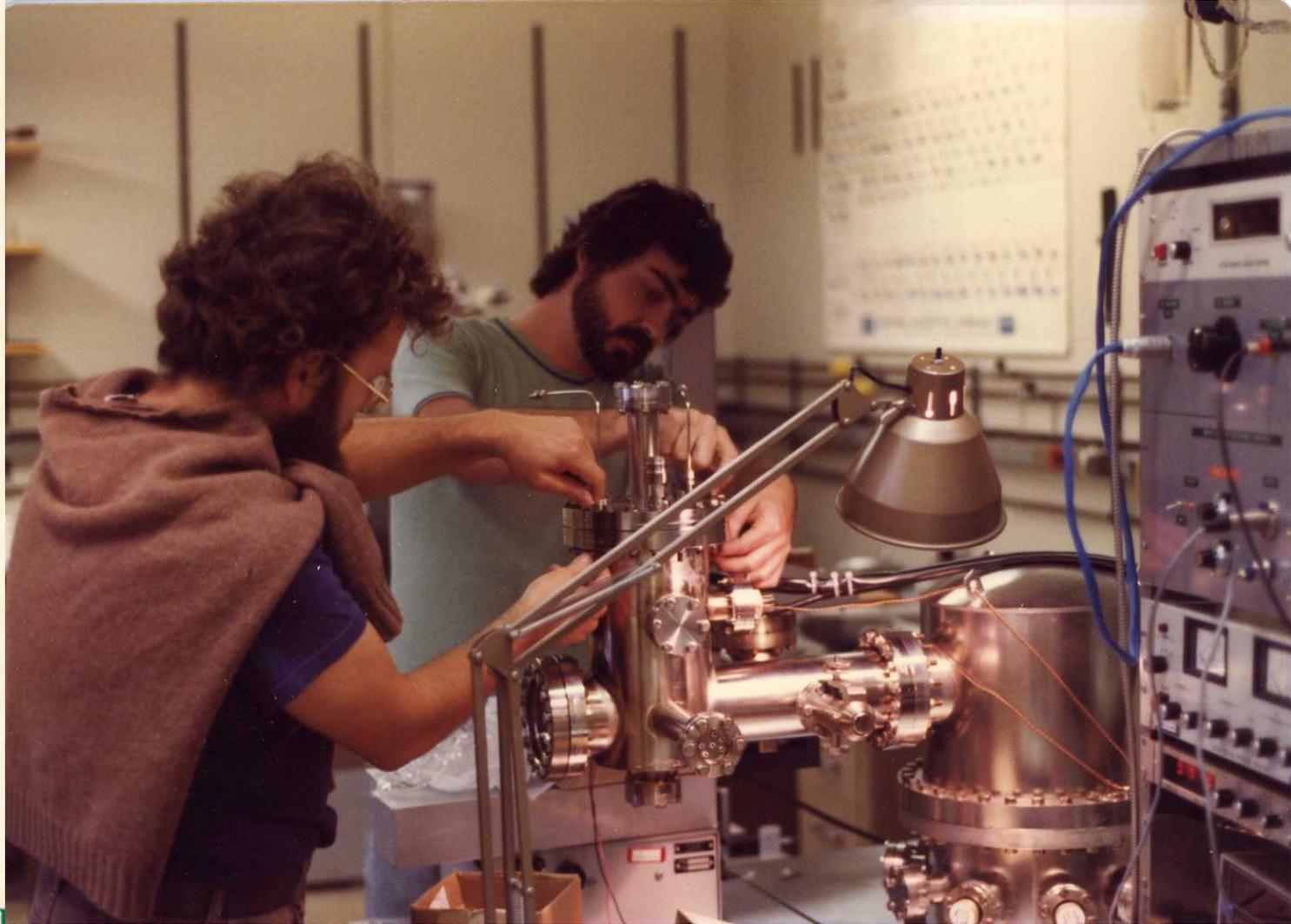
Alternate Hypothesis:
Potential energy well of
of Co atom on surface
becomes deeper below
 T_c as

$$E = E_0 + Ak_B T_c [M(T)/M(0)]^2$$

PRL 44, 586 (1980)

FIG. 3. Magnetic contribution to the activation barrier for Co sublimation $E_m(T)$ vs reduced temperature T/T_c generated from the data shown in Fig. 2 and Eqs. (1) and (2). The solid line for $0 \leq T/T_c \leq 1$ in the figure and its inset represents the best fit of Eq. (3) to the data and corresponds to $A = 2$ (see text for explanation).

Loading yet another Co foil into the UHV System

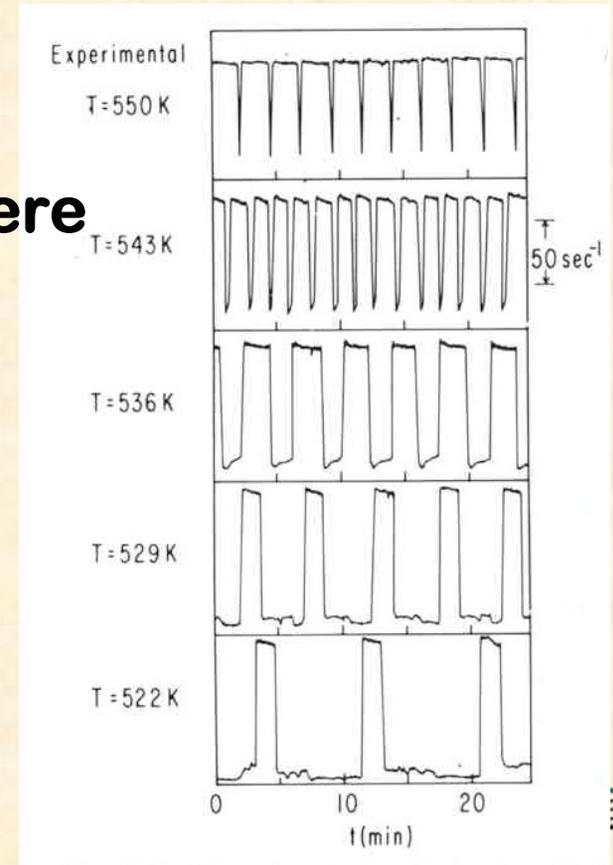


Oscillatory Oxidation of CO Over a Pt, Pd or Ir Catalyst- when and why does it occur?



Experiments done in a flow reactor. A fixed mixture of CO and O₂ gases were flowed over a Pt foil. For a range of temperatures and gas compositions The rate of CO₂ production oscillates in time, **Why?**

Surface Science 114, 381 (1982)



Key Ideas:

1. CO chemisorbed to Pt surface
2. O₂ dissociates and chemisorbs to surface
3. CO and O react on surface to form CO₂
4. Approximate rates of various steps known in great detail
5. These rates indicate millions of monolayers react on Pt surface/sec (Otherwise your catalytic converter wouldn't work)

Why are observed oscillations so slow (minutes)?

Aha Idea:

Metals exposed to oxygen oxidize

Metal oxides exposed to CO are reduced

Time scale for these reactions on Pt consistent with period of oscillations

The kinetics of the oscillatory oxidation of CO can be simulated by considering equations which govern the time evolution of three quantities [11,17], namely, the fractional coverage of chemisorbed oxygen on the catalyst surface (θ_1), the fractional coverage of chemisorbed CO (θ_2), and the fraction of surface sites assumed to be blocked by oxide formation (θ_3):

$$\begin{aligned} d\theta_1/dt = & P_{O_2} k_1(T) (1 - \theta_1 - \theta_2 - \theta_3)^2 \\ & - k_3(T) \theta_1 \theta_2 - k_{ox}(T) \theta_1 (1 - \theta_3), \end{aligned} \quad (1)$$

$$\begin{aligned} d\theta_2/dt = & P_{CO} k_2 (1 - \theta_1 - \theta_2 - \theta_3) - k_{-2}(T) \theta_2 \\ & - k_3(T) \theta_1 \theta_2 - k_{red}(T) \theta_2 \theta_3, \end{aligned} \quad (2)$$

$$d\theta_3/dt = k_{ox}(T) \theta_1 (1 - \theta_3) - k_{red}(T) \theta_2 \theta_3. \quad (3)$$

Each of the terms in this set of coupled differential equations is explained in detail below:

LH reaction on surface is multivalued for a range of temperatures and gas compositions, P_{CO}/P_{O_2}

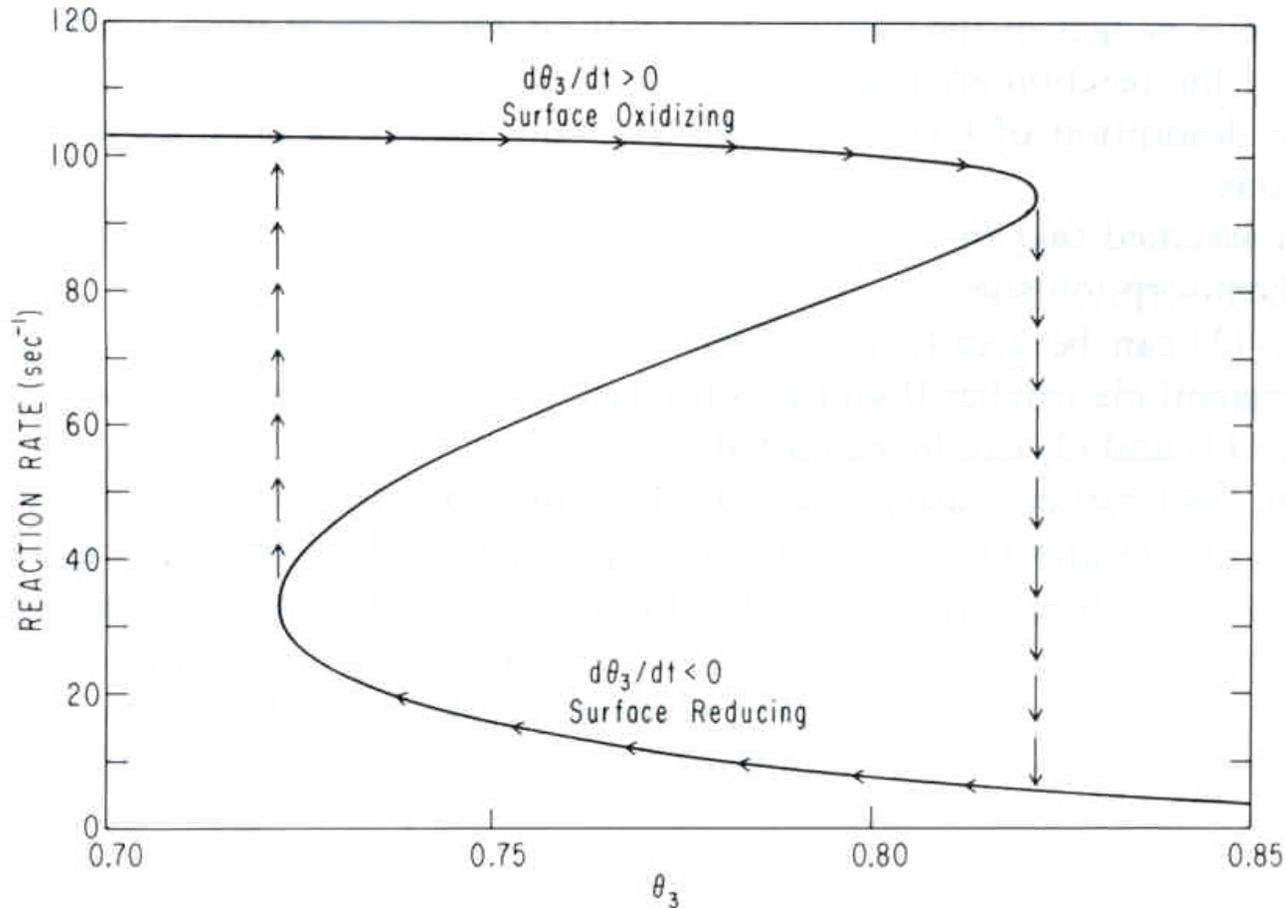


Fig. 1. Rate of CO_2 production versus the amount of subsurface oxygen (θ_3) for $T=523$ K and $P_{CO}^*=0.1$. Other kinetic parameters used are listed in table 1.

Parameter Region Where Oscillations Should Occur

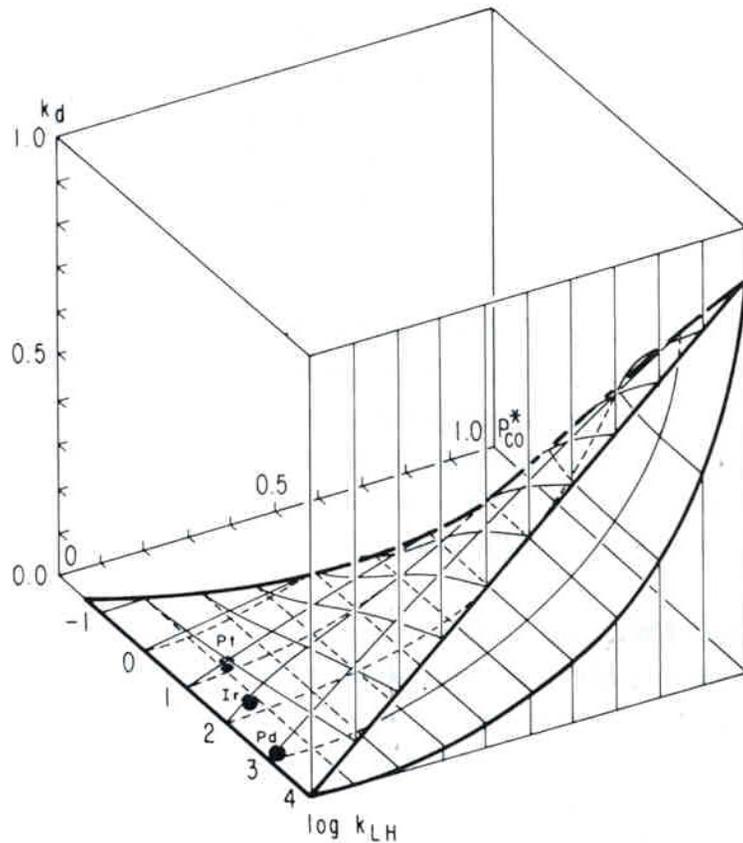


Fig. 2. Three-dimensional representation of oscillatory volume calculated using eqs. (1') and (2'). The bold lines enclose a pocket-shaped volume which extends indefinitely in the $\log(k_{LH})$ direction. Also shown are the approximate locations of three specific experimental oscillatory points for P_t , P_d and I_r .

Comparison of Experimental and Calculated Oscillations

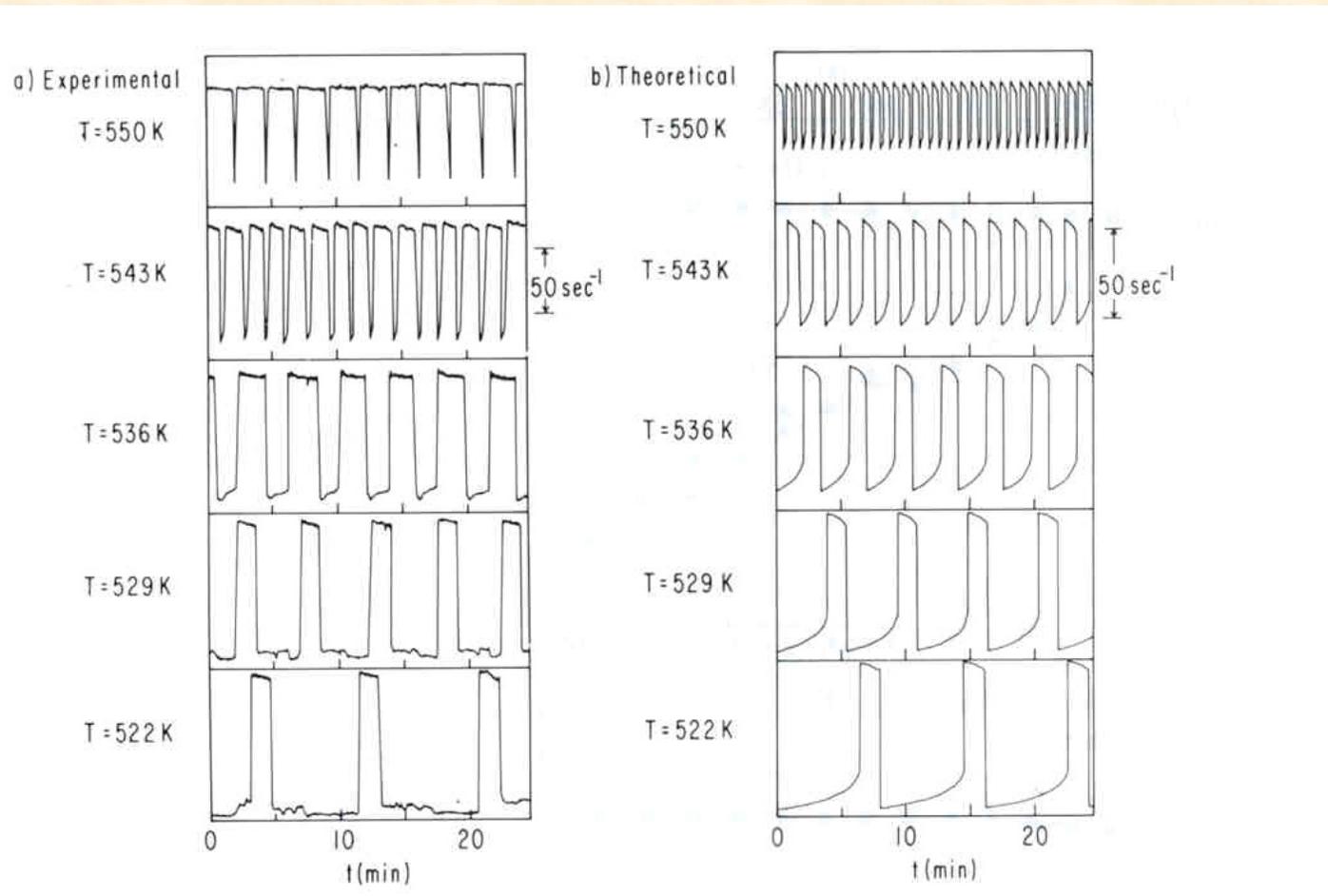


Fig. 4. (a) Experimentally obtained oscillations in the rate of CO_2 production over Pt for various temperatures between 522 and 550 K, with $P_{\text{CO}}/P_{\text{O}_2}=0.01$. (b) Calculated oscillations in the rate of CO_2 production using rate parameters shown in table 1 and $P_{\text{CO}}^*=0.1$

Comparison of Calculated and Experimental Regions (Temperature, Gas Composition) Where Oscillations Occur

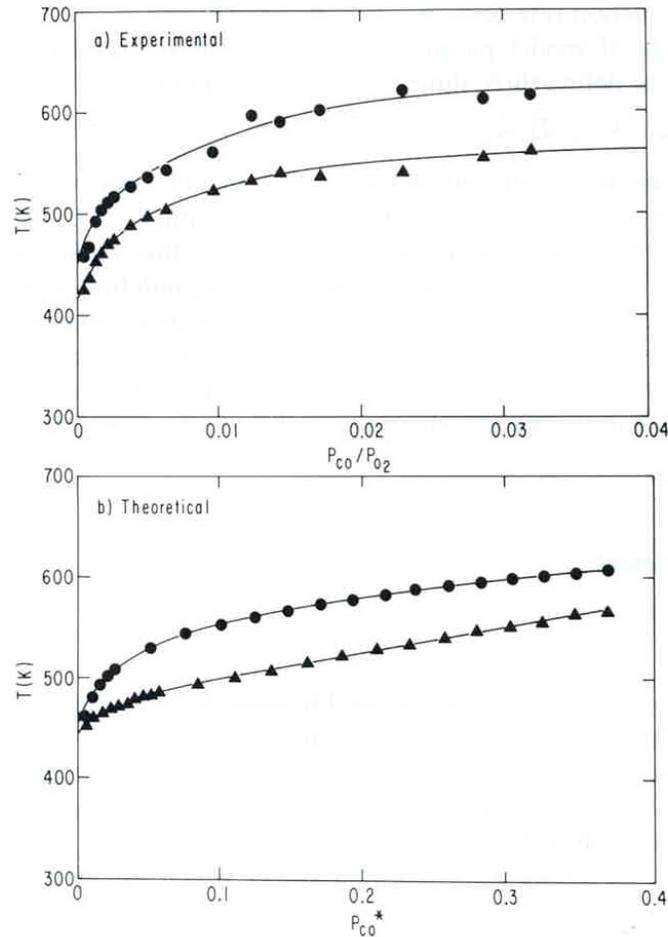


Fig. 3. (a) Experimental upper (●) and lower (▲) temperature bounds for oscillatory behavior versus P_{CO}/P_{O_2} . Reproducible oscillations over Pt were found everywhere within the region defined by these boundaries. (b) Theoretical upper (●) and lower (▲) temperature bounds for oscillatory behavior versus P_{CO}^* . Other kinetic parameters used are shown in table 1.

Changes of shape of oscillations with temperature are well produced by model

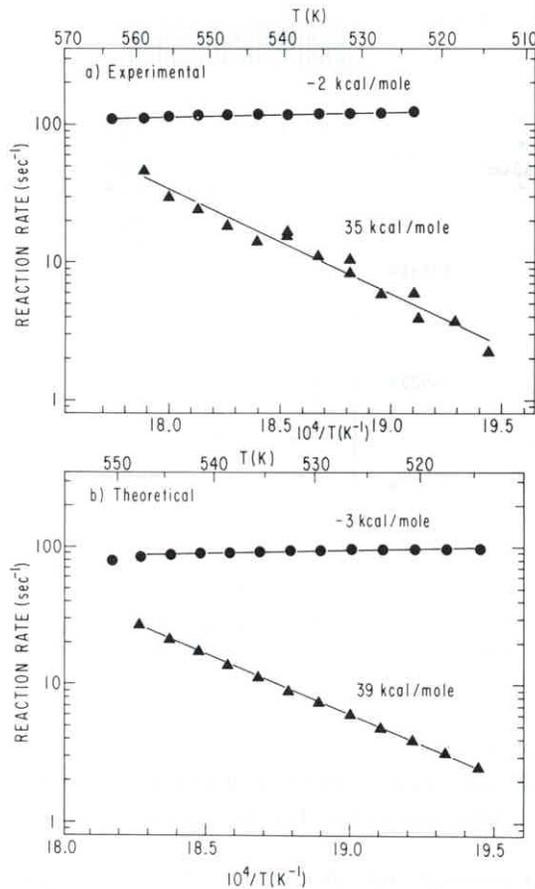


Fig. 5. (a) Experimental-log of the reaction rate versus inverse absolute temperature on the upper branch (●) and lower branch (▲) for $P_{CO}/P_{O_2}=0.01$. (b) Theoretical log of the reaction rate versus inverse absolute temperature on the upper branch (▲) and lower branch (●) for $P_{CO}^*=0.1$. Other kinetic parameters used are shown in table I.

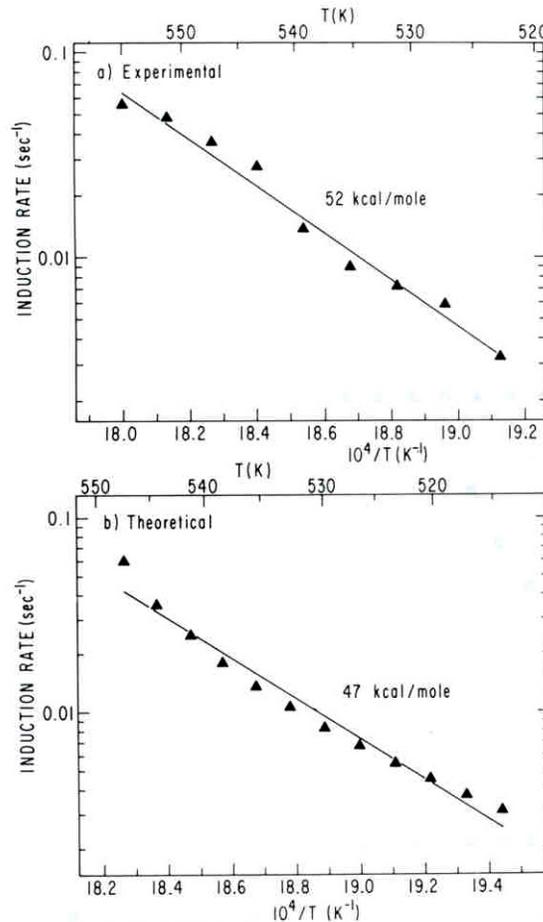


Fig. 6. (a) Experimental log of the induction rate ($1/t_{ip}$) versus inverse absolute temperature for $P_{CO}/P_{O_2}=0.01$. (b) Theoretical log of the induction rate versus inverse absolute temperature for $P_{CO}^*=0.1$. Other kinetic parameters used are shown in table I.

Continued Collaborations



Keystone Colorado
July 2003

Continuing UCSD Tradition of Mixing Science and Softball- "Stonefingers" 2004 Champs



Parameters used to Simulate Oscillations

Table 1

Parameters for theoretical fit to Pt data; all kinetic rate constants are assumed to vary with temperature as $k_i(T) = k_{i_0} \exp(-E_i/RT)$

Rate constant	Value at 550 K (s^{-1})	Activation energy (kcal/mole)	Prefactor (s^{-1})
O ₂ adsorption: $P_{O_2}k_1(T)$	10,000	1	2.5×10^4
CO adsorption: $P_{CO}k_2$	1,000	0	1.0×10^3
CO desorption: $k_{-2}(T)$	300	20	2.7×10^{10}
LH reaction: $k_3(T)$	100,000	10	9.4×10^8
Oxidation: $k_{ox}(T)$	0.11	1	2.8×10^{-1}
Reduction: $k_{red}(T)$	6.5×10^{-3}	10	6.1×10^1