A THEORY OF PLASMA CHEMICAL TRANSPORT

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ABSTRACT

Existing theories are combined and extended to interpret the plasma chemical transport, or etching and deposition, of gold in a chlorine plasma. The subtractive aspect of this transport process is often referred to as Plasma Etching (PE) or Reactive Ion Etching (RIE). A transport equation results, relating heterogeneous reaction thermochemistry to surface reaction and diffusion rates, which provides a framework for the effects of reactor geometry, electrical plasma excitation, reactant flow, and pressure in the reactor. The temperature dependence of the etch rate is shown to give information about the plasma modified thermochemistry of the transport reaction.

1. INTRODUCTION

The transport of materials, at temperatures where their vapor pressures are negligible, by chemical reactions leading to volatile product(s), was first systematically investigated by Schaefer (1956) (1)(2). In 1961, Mandel (3) clarified the theory of such processes and expanded upon Schaefer's earlier work. According to Vepřek (4), Hauptmann proposed such chemical transport in a plasma in 1965, and subsequently, Vepřek and others (5)(6)(7) investigated this phenomenon theoretically and experimentally. In 1969 Manes (8) provided a foundation for the consideration of chemical equilibria in the conditions found in low pressure plasmas. This was extended by Vepřek in 1972 (5) to account for modified chemical equilibria in plasmas, and, in this paper, applying the concept of plasma shifted chemical equilibria to surface reactions, we explain how the different conditions of particle bombardment, occuring at the two electrodes, provides the potential for driving the chemical transport.

We shall extend an existing theory (3) of the temperature dependence of the transport of a non-volatile solid in a gas yielding a volatile product, by accounting for the effect of the plasma upon the non-equilibrium heterogeneous chemical transport reaction, to interpret our experimental results for the transport of gold in a chlorine plasma. The data from these experiments in a 40 mTorr chlorine plasma, exhibits a peak at about 180 °C when plotted as the etch rate vs temperature (Fig 1a,b). This and other data (9) were obtained in the process of characterizing the Plasma Etching (PE) or Reactive Ion Etching (RIE) of gold in a chlorine plasma. The similarity of the temperature dependence of this plasma transport and the purely thermal transport observed (10) at 760 Torr with a peak rate at 250 °C, in the absence of a plasma (Fig 2a,b), suggested that these two processes were related.

Persuasive evidence of the essentially chemical nature of PE comes from the temperature dependence of the etch rate, the negligible rare gas sputter etch rates found under otherwise identical conditions, and, in contrast with rare gas sputter etching, the strong (chemical) selectivity frequently exhibited by this process, e.g., in chlorine, gold etches more than ten times faster than iron and nickel. Furthermore, this is supported by the absence of known volatile heterogeneous reaction products which generally accompany negligible PE rates.

Experimental verification of some of the theoretical predictions were performed in an RF driven chlorine plasma at 13.56 MHz, with a diode electrode configuration (Fig 3), the details of which are described in (9).

The predictions from theory, which were confirmed experimentally, are:

a- that the temperature dependence of the etch rate exhibits a peak for such endothermic reactions.

b- that the temperature direction of transport is from hot to cold, as required for this effectively endothermic transport reaction in this temperature range.

c- that the chemical reactivity of the counter electrode markedly effects the etch rate, i.e., negligible etch rate when this electrode is stainless steel, but approaching the rates shown here as the stainless steel is coated with gold.

d- that the negative slope of the logarithm of the etch rate vs 1/T, at sufficiently small T, is decreased by the plasma, indicating a decreased effective transport reaction free energy.

e- that the etch rate depends on both the difference in the particle bombardment from the plasma of the reactants and products on the surface of the two electrodes, and the temperature difference between these electrodes. Furthermore, these are in the same direction when the etched film is on the hotter, more (DC) negatively biased electrode, for effectively endothermic reactions.

f- that the flow rate of the reactant weakly effects the etch rate for this endothermic transport reaction, and, in contrast, this is expected to more strongly affect the etch rate of exothermic transport reactions.

2. *The Thermally Driven Chemical Transport Reaction for Gold in One Atmosphere of Chlorine*

In a study of the chemical transport of gold in 760 Torr of chlorine across a temperature gradient, as indicated above, Biltz et al (10) found that the transport rate exhibited a fairly sharp maximum at about 250 °C (Fig 2a,b). The etch rates reported here exhibit remarkably similar thermal behavior with the peak at 180 °C in a 40 mTorr chlorine plasma (Fig 1a,b). Since only one reaction product, the dimer of auric chloride $(AuCl_3)_2$, is sufficiently volatile below 500 °C to permit such transport, the applicable transport reaction in both cases is very likely to be:

$$Au(s) + 3/2\ Cl_2(g) \rightleftarrows AuCl_3(s)$$

where the the molecularity of the chlorine is not necessarily as shown and intermediate steps, such as the prior formation of monochlorides, are possible. The subsequent desorption (sublimation) would then be:

$$AuCl_3(s) \rightleftarrows 1/2\ Au_2Cl_6(g),$$

so that the overall transport reaction is:

$$Au(s) + 3/2\ Cl_2(g) \rightleftarrows 1/2\ Au_2Cl_6(g).$$

Biltz, et al (10) found that the dimer of auric chloride was dominant in the vapor from thermochemical considerations. The temperature at which the peak transport rate occurs will be later shown to depend upon the apparent effective free energy change of the transport reaction and the departure from chemical equilibrium at which the surface reaction occurs.

Alternatively, with plasma bombardment, modifications of these transport reactions may occur (see references (4) and (5)). One such alternative, due to bombardment from the plasma, is the dissociation of the chlorine molecule. While our attempts at observing the likely transport reaction product (Au_2Cl_6) using the mass spectrometer have been without result to this writing, the substantial increase in monatomic chlorine and the consequent decrease of diatomic chlorine, were clearly observed in the presence of the plasma.

3. *The Nature of Chemical Transport*

In these chemical transport reactions five steps are identifiable: 1- the diffusion of the reactant to the surface and 2- its adsorption thereon, 3- the forward reaction, resulting in an adsorbed reaction product, which, 4- is subsequently desorbed and 5- diffuses away from the surface. In the back reaction these steps are reversed, so that, *at equilibrium,* both proceed at the same rate and the rate of arrival of the reactant at the surface and departure of the product are equal to the ratio of their molecularity, which for simplicity, we take here as unity (see Fig 4). When the process is taken to occur *out of chemical equilibrium,* so that the reactant above the surface is richer than its equilibrium concentration, and the reaction product poorer, etching occurs. Alternatively, when the concentration of the reaction product is greater than the equilibrium value, deposition occurs. If, as shown in Fig 4, two surface reactions at different equilibria (different temperatures, T, and/or plasma surface bombardment energy parameter, U) are connected so that the flow of the product away from one surface results in etching while its arrival at the other surface results in deposition, we have the conditions for plasma promoted chemical transport.

We collect the adsorption, reaction and desorption rates as *the surface reaction transport rate,* I_r, and the rate of diffusion to and from the surface as *the diffusion transport rate,* I_d. If the surface reaction rate is much greater than the transport diffusion rate, the partial pressures of the reactants and products, near the solid surface, approach that determined by the reaction equilibrium constant. But, if the reaction product diffuses away from the surface at rates comparable to that at which it is generated, its local pressure will begin to significantly depart from its equilibrium value. *The extent to which the reactant and product pressures depart from their equilibrium values, is therefore determined by the equality of the diffusion and reaction rates, at steady state.* It will be shown that this model predicts a maximum in the transport rate with temperature (see Fig 5), similar to that found experimentally with the plasma, (Fig 1a,b), and without the plasma, (Fig 2a,b), so that, from the observed apparent effective transport reaction free energy change, and the temperature at which this transport maximum occurs, the effective thermochemistry of the transport reaction can be deduced.

Finally, this leads to a transport equation relating a chemical transport driving potential difference, $\Delta\Phi$, to the the chemical transport rate, I_t, in terms of the surface reaction and diffusion rates. This transport driving potential difference consist of two terms: one which is proportional to the temperature difference between which the transport occurs, and the other, on the difference in surface bombardment from the plasma. Also, reactant flow through the reactor produces a driving potential. An analogy with an electric circuit containing a storage battery can be made, where the chemical transport driving potential difference is shown to be equivalent to the open circuit battery voltage, a surface reaction resistance, R_s, is equivalent to the internal resistance of the battery and a diffusion resistance, R_d, is the equivalent of the load resistance. Since the surface resistance of each surface is consecutive, or in series, their "resistances" are additive: $R_s = R_{s1} + R_{s2}$. These resistances are defined as the transport driving potential difference divided by the chemical transport rate or "current" (see Fig 6). In this electrical equivalent circuit, reactant flow is analogous to the introduction of a current generator across the surface reaction resistance, R_s. By noting the dependence of the forward reaction rate coefficient on the exposed area of the transported solid (surface reactivity), we will obtain the dependence of the transport process on geometry (e.g., "loading" effects, which is similar to that obtained from somewhat more phenomenological considerations and verified experimentally elsewhere (11)).

4. Theory of Plasma Chemical Transport

To permit interpretation of the experimental results, we outline, in somewhat modified, extended and simplified form, a theory of (non-equilibrium) heterogeneous chemical transport, following that given by Mandel (3) in the absence of a plasma, and incorporate the effects of the plasma bombardment of the surface, by extending the ideas of Vepřek (5) to heterogeneous reactions modified by such bombardment.

We consider a generic heterogeneous chemical transport reaction described by:

$$S(s) + A(g) \underset{k_b}{\overset{k_f}{\rightleftarrows}} B(g) \qquad (1)$$

where S is some solid, well below its melting point, of exposed area A_s, A is a gaseous reactant and B is a gaseous product of the reaction. As shown in Fig(4), the reaction is assumed to occur on two surfaces at different temperatures, T_1 and T_2, and different plasma energy bombardment parameters, U_1 and U_2, connected by a region of crossectional area, C, and length, L. The ratio of the forward reaction coefficient, $k_f = \kappa_f A_s$, on each surface, and the back reaction coefficient, k_b, is the equilibrium constant K. κ_f is the forward reaction rate coefficient per unit exposed area of the transported solid. K is given by:

$$K = \exp(-\Phi) \qquad (2)$$

where $\Phi = (\Delta F - U)/RT$, is the normalized effective (plasma modified) transport reaction free energy. $\Delta F = \Delta H - T\Delta S$, is the change in the Gibbs free energy of the transport reaction and ΔH, R, T and ΔS are respectively, the enthalpy change, the gas constant, the temperature and the entropy change of the reaction. Further, the quantity U, following Vepřek(5), takes account of the effect of the plasma in changing the chemical equilibrium constant, here, in a surface reaction.

This modification of the reaction free energy from ΔF to $\Delta F - U$, is due to the modification of any or all of the three steps lumped above as the surface reaction (steps 2,3 and 4 of Section III), since the free energy modification of these consecutive steps is additive by Hess's law (14). For example, the plasma bombardment of the surface adsorbed reactant or product (steps 2 and 4) promotes their desorption from the surface by a "sputtering" process, thereby providing translational energy to the adsorbed species and modifying the free energy of desorption. Similarly, we cannot exclude the modification of free energy of the reaction on the surface (step 3) by production of adsorbed reactant and product in some state of internal excitation under such bombardment, which may modify this step's free energy. The overall surface reaction free energy modification by bombardment is then $\Delta F - U = (\Delta F_A - U_A) + (\Delta F_r - U_r) + (\Delta F_B - U_B)$. In the simplest case, U_r has the following interpretation: if excited states of the reactant and product (mostly electronic and/or dissociative), are populated to that given by Boltzmann statistics at the equilibrium temperature of the system, U_r is the difference in the energy changes between the reactant and product excited states and their ground states (see Fig 7). To the extent that the bombardment radiation is in equilibrium at its own (higher) temperature, U_r is expected to approach the above defined value as an upper limit. Thus, $U_r/RT = (\Delta F_A - \Delta F_B)/RT_b$, where ΔF_A and ΔF_B are the energy differences between the excited and ground states of the adsorbed reactant and product, respectively, and RT_b is the mean energy of the bombarding radiation from the plasma per mole (greater than or equal to the atomic or molecular temperature).

Letting P be the initial pressure of the reactant A, before the reaction proceeds, the pressure of the product $p_b = P - p_a$, or $b = 1 - a$, where a and b are the mole fractions of A and B, respectively. At chemical equilibrium, $a = a_o$ and $b = b_o$ and $K = b_o/a_o = b_o/1 - b_o$, and there is no steady state net rate of conversion of S into the product, B. *It should noted that no steady state transport reaction can occur unless there is some local departure from chemical equilibrium, as we will see more clearly below.*

Three processes operate consecutively, the surface reaction at one surface (product generation or etching), and at the other (product consumption or deposition), and the diffusive flow between them, and, if there is reactant flow through the reactor, removal or pumping out of the system of both the reactant and product. The first two can be lumped together as the surface reaction. Since the rate of production or consumption of the product is zero unless some mean departure from chemical equilibrium exists, we assume such a departure and then determine its value from the equality of the two processes (the surface reaction and the diffusive transport) at steady state. We do this by first calculating the chemical transport rate due to the surface reaction, then the transport rate due to diffusive flow across the temperature and plasma bombardment difference induced pressure difference and, finally, equating these, obtain a relation for the departure from chemical equilibrium and a chemical transport equation, for which an equivalent electrical circuit can be constructed, and where the transport rate (say, in moles/sec) is analogous to an electrical current.

a) The Chemical Transport Rate Due to the Surface Reaction

Following the usual methods of kinetics, the mole fraction rate of generation of B, $\mathring{b}$, is obtained as follows:

$$\mathring{b} = k_f a - k_b b = r(1 - k_b b/k_f a) = r(1 - Q/K) \qquad (3)$$

The quantity $r = k_f a$ will be referred to as the surface reactivity, and $Q = b/a = b/1 - b$, is the mole fraction ratio different from that at chemical equilibrium. It can be seen that the generation of B (etching), requires that Q be less than K, while the consumption of B (deposition), requires that Q be greater than K. Alternatively, the product is undersaturated at the surface where etching occurs and oversaturated where deposition occurs.

At steady state, the transport of the reaction product between the surfaces, $\mathring{b}_t$, where each surface is at a different temperature and bombardment parameter, is equal to the generation of B (or etching of S) at T_2 and U_2 (say), and the consumption of B (or deposition of S) at T_1 and U_1, plus the product that is carried away before its deposition, due to any flow of the reactant through the space between these surfaces (see Fig 4):

$$\mathring{b}_t = \mathring{b}_2 = -\mathring{b}_1 + \mathring{b}_p,$$

where $\mathring{b}_p$ is the mole fraction rate of removal of the product by flow of the reactant through the reactor. For constant pressure, the reactant mole fraction rate of flow into the reactor, $\mathring{a}_i$, less its rate of removal, $\dot{a}_p$, must be equal to the rate of removal of the reactant converted to the product by the transport reaction, $\dot{b}_p$, or, $\dot{b}_p = \dot{a}_i - \dot{a}_p$. Consequently,

$$\dot{b}_t = r_2(1-Q_2/K_2) = r_1(Q_1/K_1-1) + \dot{b}_p,$$

which *we take as greater than zero for transport from* T_2 *and* U_2 *to* T_1 *and* U_1. We thus obtain:

$$\dot{b}_t = ((K_2Q_1/K_1Q_2)-1+\dot{b}_p/r_1)/((1/r_2)(K_2Q_1/K_1Q_2)+ (1/r_1))$$

The equilibrium constant, K, is obtained from Eq(2), while Q is defined in terms of K as:

$$Q=K^{\beta}=\exp(-\beta\Phi) \qquad (4)$$

thus,

$$Q/K\doteq K^{\beta-1}=\exp(1-\beta)\Phi \qquad (5)$$

which is slightly greater or smaller than unity, depending on whether β is greater or smaller than unity (deposition or etching, respectively, for endothermic reactions). The quantity, $1-\beta$, is a measure of the departure from chemical equilibrium at each surface. This "departure" is negative where etching occurs and positive where deposition occurs, for $\Delta\Phi>0$. Thus $K_2Q_1/K_1Q_2 = \exp((1-\bar{\beta})\Delta\Phi$ where $\Delta\Phi = \Phi_1-\Phi_2 = ((\Delta F-U_1)(T_2-T_1)/RT_1T_2) + (U_2-U_1)/RT_2$, and $\bar{\beta}= (\beta_1\Phi_1-\beta_2\Phi_2) /(\Phi_1-\Phi_2)$, is a "mean" of the values of β at each surface, so that, $1-\bar{\beta}$ is the departure from equilibrium of the transport system, whose value lies between zero and unity (equilibrium). With the definition of *the surface reaction transport rate* as, $I_r = \dot{\mu}_B = (PV/RT)(\dot{b}_t)$, we obtain:

$$I_r=(PV/RT)(\exp((1-\bar{\beta})\Delta\Phi)-1 +\dot{b}_p/r_1/((1/r_2)(\exp((1-\bar{\beta})\Delta\Phi))+(1/r_1)) \quad (6a)$$

which, for small changes, or $\Delta\Phi<<1$, reduces to:

$$I_r=G_s(1-\bar{\beta})\Delta\Phi + I_p \qquad (6b),$$

where $I_p=(r_m/r_1)(PV/RT)\dot{b}_p=G_s\dot{b}_p/r_1$, is the contribution to the "current" of the product due to flow of the reactant, which "sweeps" some of the product out of the reactor. We may thus interpret $G_s=r_mPV/RT=k_{fm}aPV/RT$ as a (mean) surface reaction conductance and $\Delta\Phi= ((\Delta F-U)/RT)(\Delta T/T) + (\Delta U/RT)$ as a chemical transport driving potential difference. Thus, the "current", I_r, flows thru the "conductance", G_s, due to the applied reaction "potential difference", $(1-\bar{\beta})\Delta\Phi$. Note that, for $I_p=0$, when $\bar{\beta}$ is equal to unity, the reaction transport rate, $I_r=0$, as required. The surface reaction conductance, G_s, is the mean of that at surfaces 1 and 2. Because these processes are consecutive or in series, we may express the mean conductance, G_s, as follows: $1/G_s = 1/G_{s1} + 1/G_{s2}$, or $R_s = R_{s1} + R_{s2}$, where $R_{sj} = 1/G_{sj}$, is the surface reaction resistance on the surface at temperature, T_j, and plasma bombardment energy parameter, U_j. Consequently, this mean rate is the reciprocal of the sum of the reciprocals of the rates at each surface, or: $k_{fm} = ((k_{f1}k_{f2})/ (k_{f1}+k_{f2}))$, where it should be remembered that the exposed area of the transported solid, at both surfaces, is incorporated into $k_f(=\kappa_fA_s)$.

b) The Chemical Transport Rate Due to Diffusive Flow

To obtain the transport rate due to diffusion, we employ Fick's law, $J_d= D(\text{grad } n_B)/N_o = (DP/R)(\text{grad } (b/T))$, which states that the number of moles of B transported per unit area is proportional to the gradient of transported mole fraction of B divided by the temperature, grad(b/T). D is the diffusion coefficient and N_o is Avogadro's number. Thus, the diffusion transport rate of B is,

$$I_d=CJ_d=(DCP/RL)((b_2/T_2)-(b_1/T_1)) \qquad (7)$$

where L, C and P where defined earlier, as the separation between the electrode surfaces, the crossectional area of the region between them, and the total pressure in the reactor, respectively. D is the coefficient applicable to the diffusion of the product B through a mixture of A and B. In this case, the gas is primarily the reactant A and changes in composition with temperature can be ignored.

To obtain the difference, $(b_2/T_2)-(b_1/T_1)$, induced by the differences in temperatures and/or plasma bombardment energy parameters on the two surfaces, we employ the definition of $Q=b/a=b/(1-b)$ to obtain: $b=Q/1+Q$, so that,

$$(b_2/T_2)-(b_1/T_1) = (Q_2/T_2(1+Q_2))-(Q_1/T_1(1+Q_1)) \qquad (8)$$

Introduction of Eq(8) into Eq(7), and taking $Q<<1$, as for an endothermic reaction, yields *the diffusion transport rate:*

$$I_d=(DCP/LRT_1)\ Q_1((Q_2T_1/Q_1T_2)-1)$$

$$=G_dQ_1((T_1/T_2)\ \exp(-(\beta_1\Phi_1-\beta_2\Phi_2))-1)$$

$$=G_dQ_1((\gamma\Phi_2/\Phi_1)\exp\ (\bar{\beta}\Phi_1(1-\Phi_2/\Phi_1))-1) \qquad (9a)$$

where $G_d=DCP/LRT_1$, will be referred to as the diffusive conductance, and $\gamma = (\Delta F-U_1)/(\Delta F-U_2)$ We have treated G_d as essentially temperature independent, since D/T is proportional to $T^{1/2}$, which varies slowly with the applicable gas temperature, and furthermore, which is the mean of T_1 and T_2. Taking Φ_1 as fixed, and Φ_2 $(=(\Delta F-U_2)/RT_2)$ as variable, i.e., the temperature of the lower surface of Fig (4) is varied so that we obtain the temperature dependence of the transport rate. Fig(5) shows a plot of the diffusion transport rate vs $\Phi_2/\Phi_1=T_1/\gamma T_2$, given by Eq (9a). This diffusion transport rate will be equated to the surface reaction rate and to the system transport rate, at steady state, in the next section to obtain the departure from equilibrium parameter and the transport equation; but from these considerations, it can be seen that the transport rate would be expected to follow the same temperature dependence as the diffusion transport rate. Thus, from Eq (9a), we may also obtain the 1/T dependence of the logarithm of the transport rate. Letting $y=(I_d/G_dQ_1)+ 1$,

$$\ln y = \ln(\gamma/\Phi_1) + \ln \Phi_2 + \bar{\beta}(\Phi_1-\Phi_2) \qquad (10)$$

Thus, $d(\ln y)/d(1/T_2)=(d(\ln y)/d\Phi_2))(d\Phi_2)/d(1/T_2)= \bar{\beta}(1/\bar{\beta}\Phi_2)-1)(d\Phi_2/d(1/T_2))$,

which, for $\bar{\beta}\Phi_2>>1$ or $T_2<<\bar{\beta}(\Delta F-U_2)/R$, reduces to $\bar{\beta}(d\Phi_2/d(1/T_2))$.

But,

$$d\Phi_2/d(1/T_2)=(\Delta F-U_2)/R, \qquad (12)$$

so that, in this approximation,

$$d(\ln y)/d(1/T_2)=-\bar{\beta}(\Delta F-U_2)/R \qquad (13)$$

which states that the slope of the logarithm of the transport rate vs 1/T is expected to be proportional to the negative of the apparent ($\bar{\beta}$) effective (plasma modified) transport reaction free energy, $\bar{\beta}(\Delta F-U_2)$.

c) Departure From Chemical Equilibrium and the Transport Equation for Steady State

Since the transport reaction and the diffusion transport processes are consecutive, at steady state they must be equal to each other and the transport rate, I_t. Thus, equating I_t to I_r from Eq(6a) and to I_d from Eq(9a), determines *the system departure from chemical equilibrium parameter,* $\bar{\beta}$, and, upon elimination of $\bar{\beta}$, an "Ohm's Law" type of relation for transport, *the transport equation.* Inspection of these equations also show that no straightfoward algebraic elimination of $\bar{\beta}$ can be obtained without some simplifying assumptions. Alternatively, $\bar{\beta}$ can be obtained numerically, but to get some idea of its nature, it is sufficient to look at its behavior in the simplifying regime where $\bar{\beta}\Delta\Phi<<1$, i.e., $T_2<<T_1/\gamma$, which is the approximation used already to obtain Eq (6b).

Thus, for small changes, $\Delta\Phi<<1$, Eq(9a) becomes:

$$I_d=G_dQ_1\gamma\bar{\beta}\Delta\Phi \quad (9b)$$

where $\gamma=(\Delta F-U_1)/(\Delta F-U_2)$.

Thus, one may consider the "potential difference", $Q_1\gamma\bar{\beta}\Delta\Phi$, as producing a "current", I_d across the diffusive conductance, G_d. At steady state:

$$I_t = I_r = I_d,$$

and, $I_t = (1-\bar{\beta})G_s\Delta\Phi + I_p = \bar{\beta}\gamma G_d\Delta\Phi$. From these equations we obtain the system departure from chemical equilibrium parameter, $\bar{\beta}$,

$$\bar{\beta}=(1+(I_pR_s/\Delta\Phi))/(1+\gamma Q_1G_d/G_s) \qquad (14)$$

and the transport equation,

$$\begin{aligned}\Delta\Phi/I_t &= (1/\gamma Q_1G_d + 1/G_s)/(1 + I_p/G_s\Delta\Phi)\\ &=((R_d/\gamma Q_1) + R_s)/(1 + I_pR_s/\Delta\Phi)\\ &=((R_d/\gamma Q_1) + R_{s1} + R_{s2})/(1+I_p(R_{s1}+R_{s2})/\Delta\Phi) \qquad (15)\end{aligned}$$

where we reiterate that $\Delta\Phi$ is the transport reaction driving potential difference, G_d is the diffusive conductance (see Eq(9a)) and G_s is the surface reaction conductance (see Eq(6b)). The reciprocals of these latter two conductances are respectively, the resistances for diffusive transport and for the surface reaction and I_p is the "current" of the product, B, due to flow of the reactant through the reactor. Thus, equation (15), the transport equation, states that the transport reaction potential divided by the transport rate, or transport "current" (say, in moles/sec) is equal to the sum of the diffusive transport resistance and the surface reaction resistance acting consecutively or in series, as required, and that the reactant flow induces a driving potential across the surface reaction resistances. The relation between this transport rate, I_t, and the time rate of change of the film thickness, or the etch rate, $\dot{d}$, is obtained from: $I_t = n_sA_s\dot{d}/N_o$, where $n_s=\rho_s/M_s$, the solid number density, is equal to the solid density divided by its molecular weight, A_s is its exposed area, and N_o is Avogadro's number.

The analogy between this process and an electrical storage battery circuit, with current generators across the surface reaction resistances, is less than fortuitous. Here, the open circuit voltage is analogous to the transport reaction driving potential difference, the surface reaction resistance to the battery internal resistance, the diffusion transport resistance to the load resistance and the flow induced driving potential, to the current generator across the surface reaction resistances (see Fig 7). The application of the above transport equation to a typical PE reactor geometry is given in the Appendix, and leads to a "loading" equation, but some general properties will be discussed below.

d) Effects of Geometry on the Transport Process

From their definitions in Eqns (6b) and (9a), the ratio G_d/G_s is:

$$G_d/G_s=((DC/LVA_{s2})/(\kappa_f a))(1+\alpha) \qquad (16),$$

where $\alpha=A_{s2}/A_{s1}$, so that the effects of the transport geometry are summarized in the ratio $((C/L)/(VA_{s2}))(1+\alpha)$. Thus, by comparison with Eq(14) for $I_p=0$, as the product of the gas volume and transported solid (mean) exposed area, $VA_{s2}/(1+\alpha)$, becomes large with respect to the crossectional area-length ratio of the connecting tube, C/L, it can be seen that $\overline{\beta}$ approaches unity (chemical equilibrium). This is to be expected, since under these conditions the surface reaction rate sufficiently exceeds that of the diffusive transport rate to drive the reactant and product concentrations closer to their equilibrium values. Alternatively, as C/L goes to zero, the two regions are disconnected and each region is forced to its own chemical equilibrium, so that the system departure, $1-\overline{\beta}$, approaches zero.

e) The Temperature Direction of Transport

Both the reaction transport rate described by Eq(6b) and the diffusion transport rate described by Eq(9b) contain the transport driving potential, which, in the absence of a difference in the plasma bombardment energy at the two surfaces, $(\Delta U=0)$, is $\Delta\Phi=((\Delta F-U)/RT)\Delta T/T$. This was obtained for the temperature direction of transport from T_2 to T_1. Thus, for T_2 greater than T_1, and $\Delta F-U$ positive, i.e., the transport reaction is effectively endothermic, and the rates are positive, requires that the product of the effective reaction free energy change and the temperature difference be positive. From this, we see that the endothermic transport reaction transports from hotter to cooler, and conversely for exothermic reactions (where $(\Delta F-U)$ is negative and T_2 is less than T_1). When ΔU is greater than zero, both plasma bombardment differences and temperature differences $(\Delta T \geq 0)$, drive the transport in the same direction. Consistent with this, is the experimental observation of a reduced etch rate when the upper or grounded counter electrode is made hotter than the lower electrode supporting the gold film. Exothermic transport reactions are, for example, commonly used in quartz halogen lamps to minimize evaporative buildup of filament material on the optically transparent envelope, by etching any deposited filament material from the cooler envelope and redepositing it on the hotter filament.

f) The Role of the Plasma in Plasma Chemical Transport

As indicated in references (4) and (5), the plasma can be expected to produce several important modifications of chemical transport occurring in its absence: the plasma can modify the species involved in the transport reaction; it can increase the rate of reaction by decreasing the apparent activation energy; and, finally, as a corollary to the preceding, it can shift the chemical equilibrium by modifying the apparent effective reaction free energy change $\overline{\beta}(\Delta F-U)$ (see Fig 7). Differences in the surface bombardment from the plasma therefore also drive the transport in the absence of a temperature difference between these surfaces, so that $\Delta\Phi = \Delta U/RT$, for $\Delta T = 0$. Here, the plasma bombardment difference is produced by the electrical asymmetry induced DC bias voltage on the lower electrode. This causes the reactant and/or product species bombarding the film, or being bombarded on the film, to be more energetic than those on the other (counter) electrode and thus has the effect of producing a different effective free energy for the transport reaction occurring at that surface. Clearly, any other means of achieving this on the surface of the transport solid will have similar results, e.g., bombardment by ions, photons, atomic beams, electrons, etc.. It is expected that a correlation of the effective thermochemistry and the energy of the species incident from the plasma as a function of the plasma excitation will make this explicit in the future.

g) The Effect of Reactant Flow on the Transport Rate

When $\Delta\Phi=0$, i.e., no temperature difference or bias induced difference in the bombardment parameters, U, exist between the two surfaces, the transport equation, Eq (15), reduces to:

$$I_pR_s/I_t = (R_d/Q_1) + R_s \qquad (17)$$

indicating that the flow of the reactant "drives" the transport by producing a potential across the surface reaction resistance. From its definition, (see Section A) $I_pR_s = \dot{b}_pPV/r_1PV$, we see that the potential driving the transport induced by the flow is a ratio between the rate of product pumping, $\dot{b}_pPV$ and that of the rate at which the surface reaction proceeds, r_1PV, each in (say) cm^3-torr/sec. The mole fraction rate at which the product is removed from the reactor, $\dot{b}_p$, is equal to the net rate of reactant flow through the reactor, or $\dot{b}_p=\dot{a}_i-\dot{a}_p$, for a reaction with zero molar change and constant pressure, as discussed earlier. Thus, $\dot{a}_p=\dot{a}_i/(1+\dot{b}_p/\dot{a}_p)$, so that, assuming that the flow is diffusion controlled and the flow pump inlet is essentially at zero pressure, $\dot{b}_p/\dot{a}_p = D_Bb/D_Aa$, we obtain the following relation between the mole fraction product flow rate, $\dot{b}_p$ (not observable), and the mole fraction reactant input flow rate, $\dot{a}_i$ (an observable): $\dot{b}_p = \dot{a}_i(D_Bb/D_Aa)/(1 + D_Bb/D_Aa)$, where D_A and D_B are the diffusion coefficients of the reactant and the product through the mixture, respectively. Thus we obtain the reactant flow rate induced driving potential, I_pR_s:

$$I_pR_s = (D_Bb/D_Aa)(F_A/F_A{}^o)/(1 + D_Bb/D_Aa), \qquad (18)$$

where $F_A = \dot{a}_iPV$ is the reactant flow rate, and $F_A{}^o = r_1PV$ is the surface reaction rate equivalent flow rate. For endothermic reactions, where b/a is quite small, at the same $F_A{}^o$, flow rates larger by the ratio of the reactant to product pressures are thus required for the same flow driving potential as exothermic reactions, suggesting that, by comparison, little, if any, flow rate dependence is expected for such endothermic transport processes.

h) The Loading Effect

Application of the transport equation to a typical PE geometry, for such endothermic reactions, makes clear the effects of "loading", that is, of the area to be etched. We take the driven and grounded electrode areas as A_o and equal, while the area of the solid to be etched is fA_o, where f is the fraction of the area of the electrode covered by film (the "loading" fraction), and is less than or equal to unity. Thus, the mean exposed area of the solid is $A_o(f/1+f)$ (see discussion following Eq(6b)). The separation of the two electrodes is h, so that the volume of gas V, is (h A_o). Consequently, from the definitions of G_s following Eq(6b) and G_d from Eq(10), the transport rate, Eq(15), for this case becomes:

$$I_t = Xf/(1+Yf)$$

where X and Y are parameters containing the factors independent of the "loading" fraction, f; $X = (\kappa_f aP/RT)hA_o^2\Delta\Phi$ and $Y = 1 + (\kappa_f ah^2A_o/D\gamma Q_1) = 1 + (h/h_o)^2$, with $h_o^2 = D\gamma Q_1/\kappa_f aA_o$.

Finally, since $\dot{d} = I_tN_o/n_sA_of$ (see discussion following Eq (15)), we obtain the etch rate,

$$\dot{d} = \dot{d}_o/(1 + (h/h_o)^2f)$$

where $\dot{d}_o = \kappa_f(N_o/n_s)(aP/RT)hA_o\Delta\Phi$. This is identical with the the form of the "loading" equation given elsewhere(11).

5. *COMPARISON WITH EXPERIMENT*

The following experimental results were obtained to confirm this model:

a- Comparing Fig 1 and 2 with Fig 5, it can be seen that the temperature dependence of the etch rate exhibits a behavior similar to that predicted by theory.

b- The effective endothermicity of the gold-chlorine plasma transport reaction was established, by showing that the direction of transport was from hot to cold, as follows: at zero temperature difference between electrodes, the observed transport from the lower to the upper, is due to a difference in the surface bombardment from the plasma produced by the induced DC bias voltage; futhermore, since an increase in the temperature of the lower electrode (where the gold film is etched) adds to (or increases) this etch rate, the temperature direction of transport is from hot to cold. Alternatively, in the absence of a difference in plasma bombardment conditions, the transport would then be expected to proceed only if one electrode were hotter than the other, and where etching occurs at the hotter and deposition at the colder electrode. Finally, when the upper or counter electrode is made hotter than the lower, the etch rate is found to decrease, as expected.

c- It was found that the lack of reactivity of the stainless steel counter electrode, when free of gold, reduced the etch rate essentially to zero. This is explained by the theory as due to the much smaller chemical reactivity of stainless steel to chlorine than that of gold (i.e., $r_1 = 0$).

d- Comparison of Fig 1b and 2b show that the plasma has the effect of decreasing the negative slope of the high 1/T region of the Arrhenius type plots, yielding an apparent effective free energy in the plasma of 3 kcal/mole, for the stated conditions, and 21 kcal/mole in the absence of the plasma (10). The equilibrium free energy, without the plasma, is about 28 kcal/mole (10). Thus, the slope of the logarithm of the etch rate vs 1/T, yields an apparent effective reaction Gibbs free energy change, $\overline{\beta}(\Delta F - U_2)$, where it was found that this apparent effective free energy change is significantly lower than for the transport in the absence of the plasma, and which , in turn, is lower than that occurring at chemical equilibrium. This is due, in part, to a shift in chemical equilibrium by the plasma $(\Delta F - U)$, and in part, to the departure from chemical equilibrium in which the transport reaction takes place $(0 < \overline{\beta} < 1)$. Other reaction transport processes have also exhibited a region of such straight lines on Arrhenius type plots, but without the peak which occurs for the gold-chlorine transport process, perhaps because the peak occurs at temperatures not investigated, or because they are exothermic. Such processes are, for example, the etching of Si in CF_4-O_2 (11),Ti in $CBrF_3$-He-O_2 (12), and silicate glass in CF_4 (13).

e- The etch rate of about 300 A/min observed at zero temperature difference between electrodes shows that the transport occurs due to the difference in surface bombardment because of the induced bias voltage, as predicted by theory.

f- The etch rate was found to be essentially independent of reactant gas flow rate for this effectively endothermic transport reaction, as predicted by theory, because the deposition rate exceeds the rate of removal possible for endothermic transport reactions, for which the product is a small fraction of the total gas pressure. For exothermic transport reactions, on the other hand, which go more strongly to completion, the total gas pressure is dominantly due to the product and is thus expected to be more sensitive to flow.

6. DISCUSSION

The transport equation (15) is obtained only for the linearized case, but equations (6a) and (9a) are for finite differences, and could be employed without linearization, which requires obtaining the temperature dependence of $\overline{\beta}$ from the condition of steady state. We have chosen here, for simplicity of exposition, to treat the transport reaction as involving no molar changes, but Mandel (3) has shown that this can be incorporated into the model. Fitting the data of the etch rate vs temperature with these improvements will still require assuming that only one reaction mechanism is applicable over the range. There is some indication that there is such a change in the gold-chlorine transport reaction, which shows an anomaly at about 275 °C (see Fig 2a). In addition, some inaccuracy is expected to result from the spatial averaging inherent in this one dimensional model, so that, to reflect the actual physical situation requires extending the above arguments to account for radial variations in the plasma bombardment, i.e., in the electrode planes.

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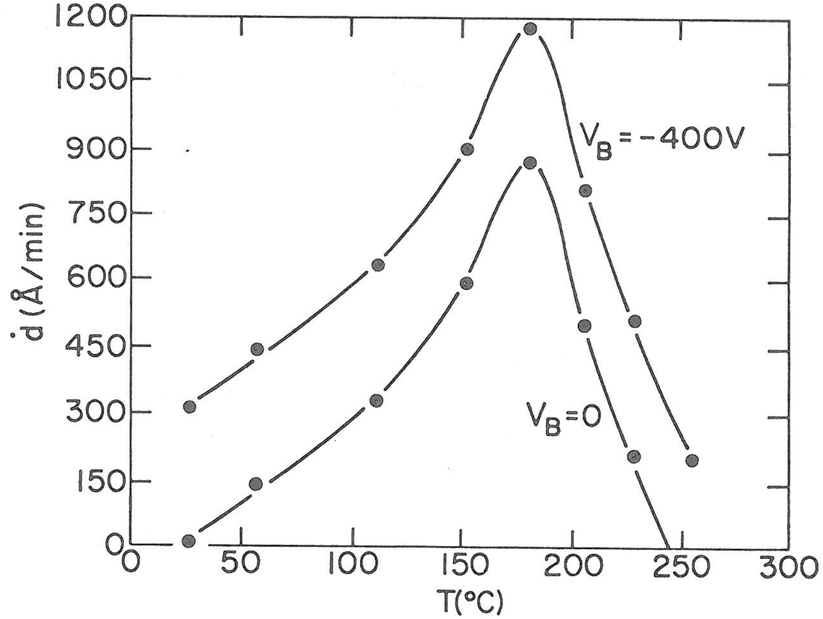


Fig.(1a) Gold Etch Rate vs Temperature

in 40 mTorr Chlorine Plasma

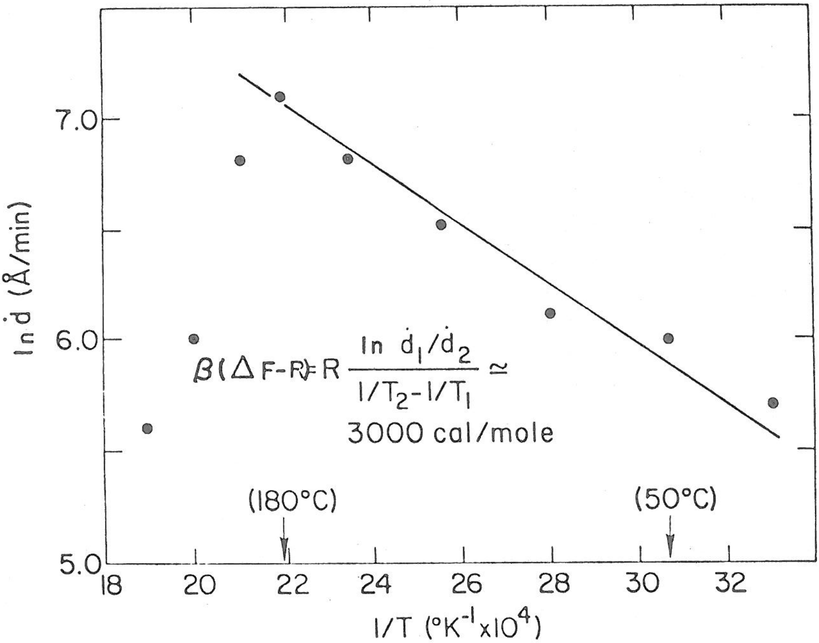
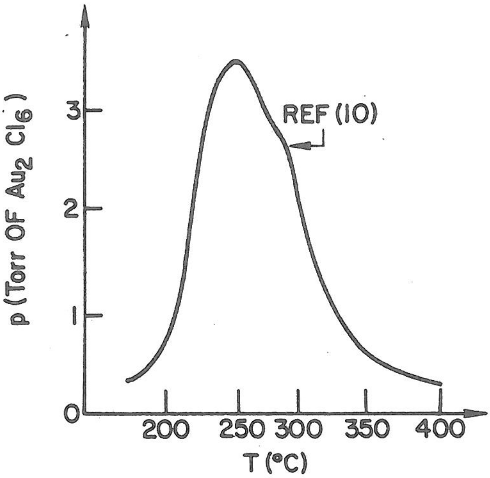


Fig.(1b) Log of Gold Etch Rate vs 1/T

in 40 mTorr Chlorine Plasma

TRANSPORT RATE OF GOLD IN 760 Torr OF CHLORINE vs TEMPERATURE FROM REFERENCE (10)



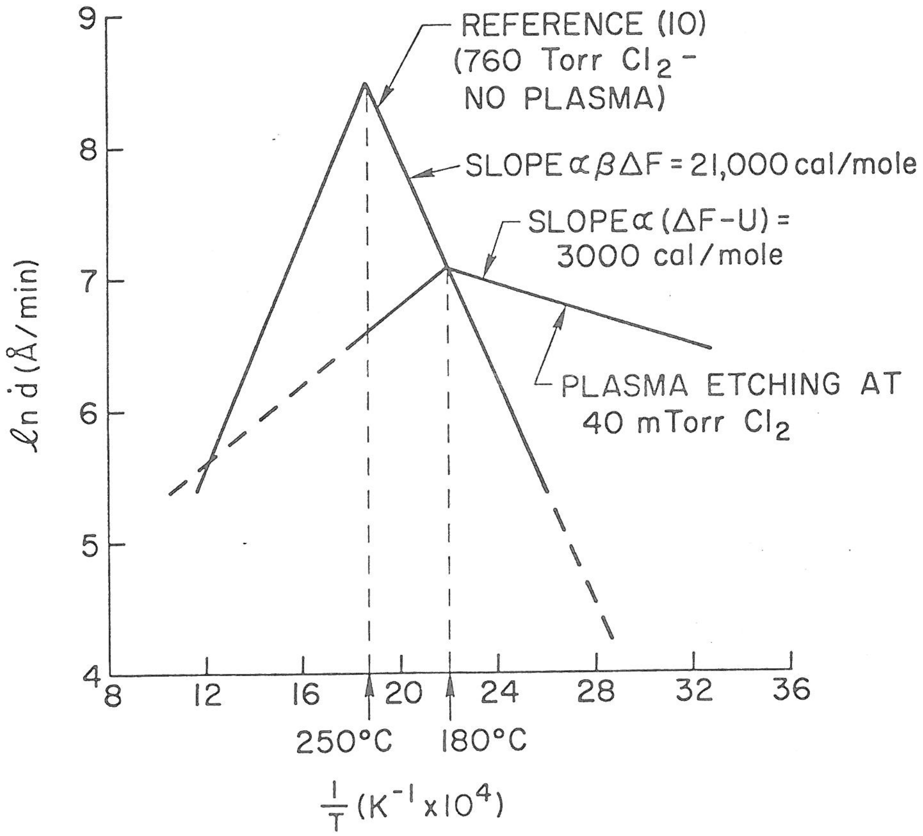
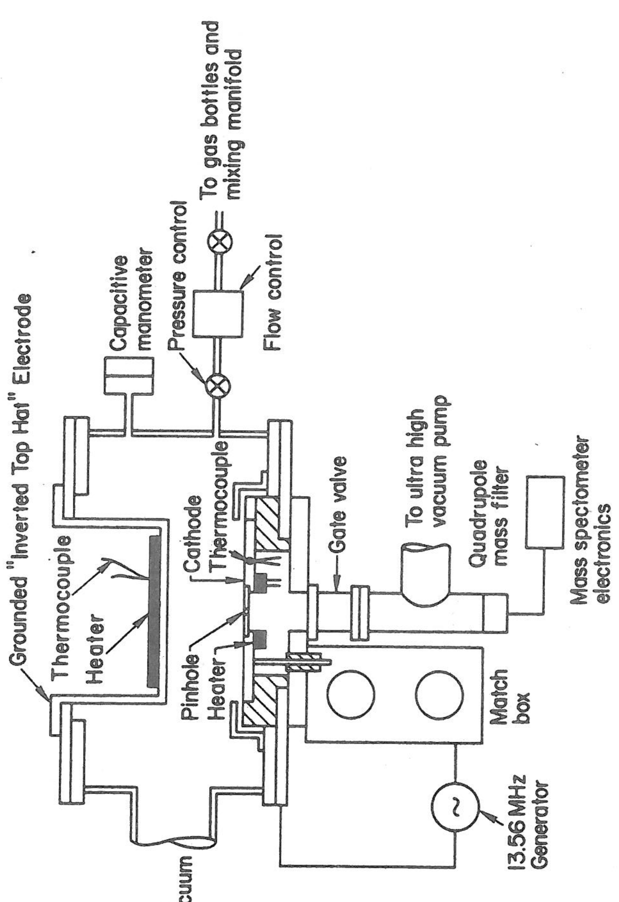


Fig.(2b) Log Etch Rate of Gold in 760 Torr of Chlorine

vs 1/T

REACTIVE ION ETCHING APPARATUS



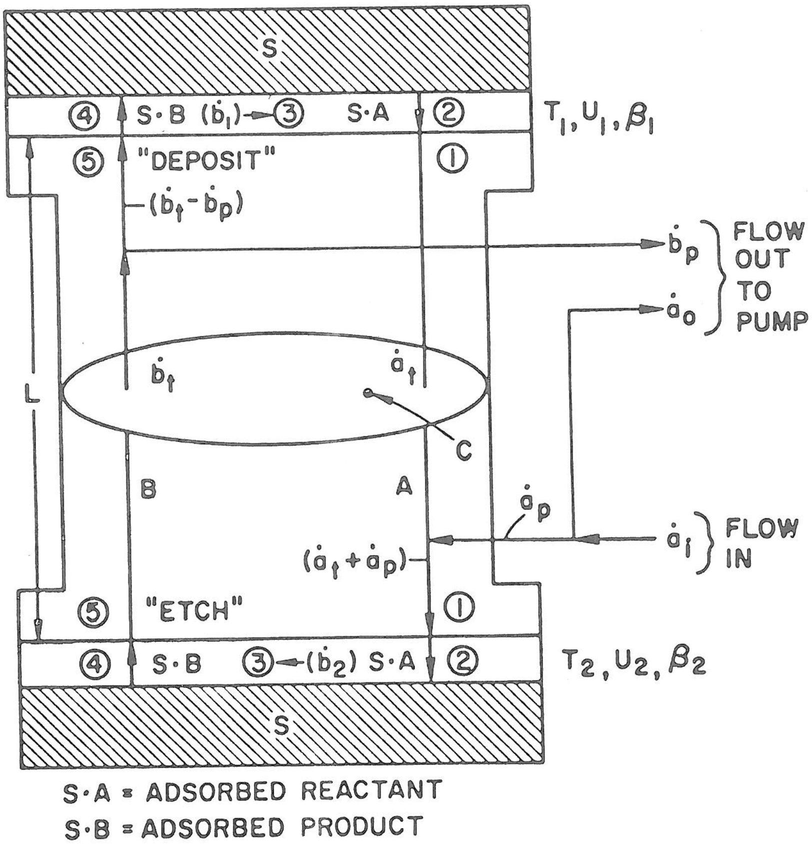


Fig.(4) Schematic of Transport Process

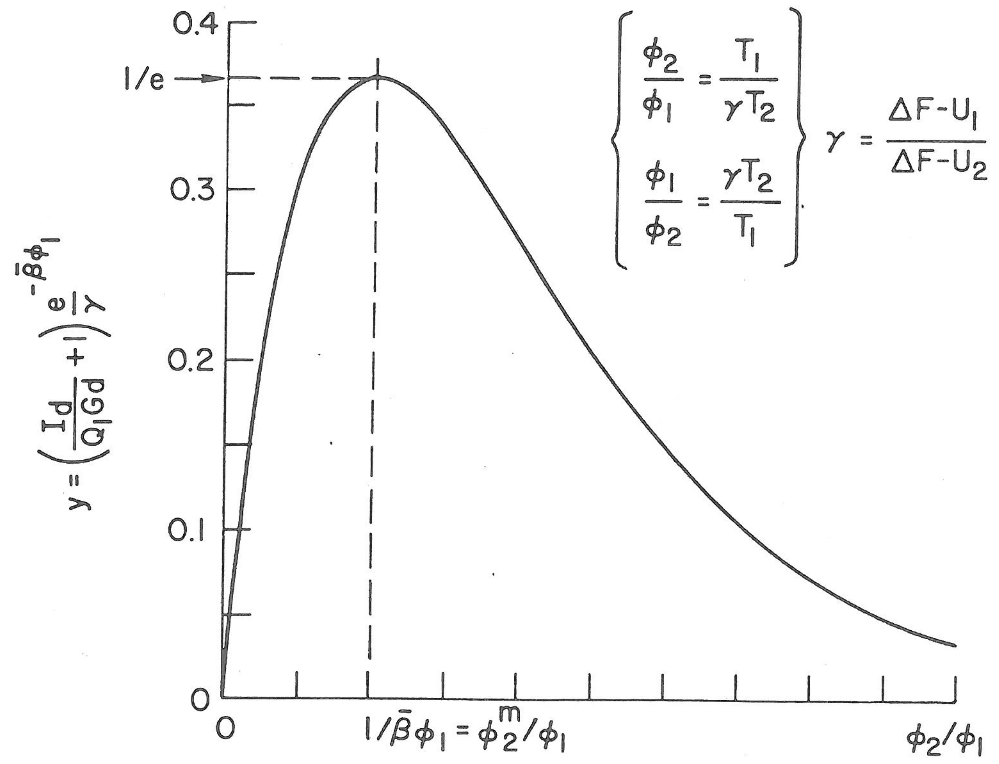


Fig.(5a,b) Plot of Transport Rate vs 1/T,T from Theory

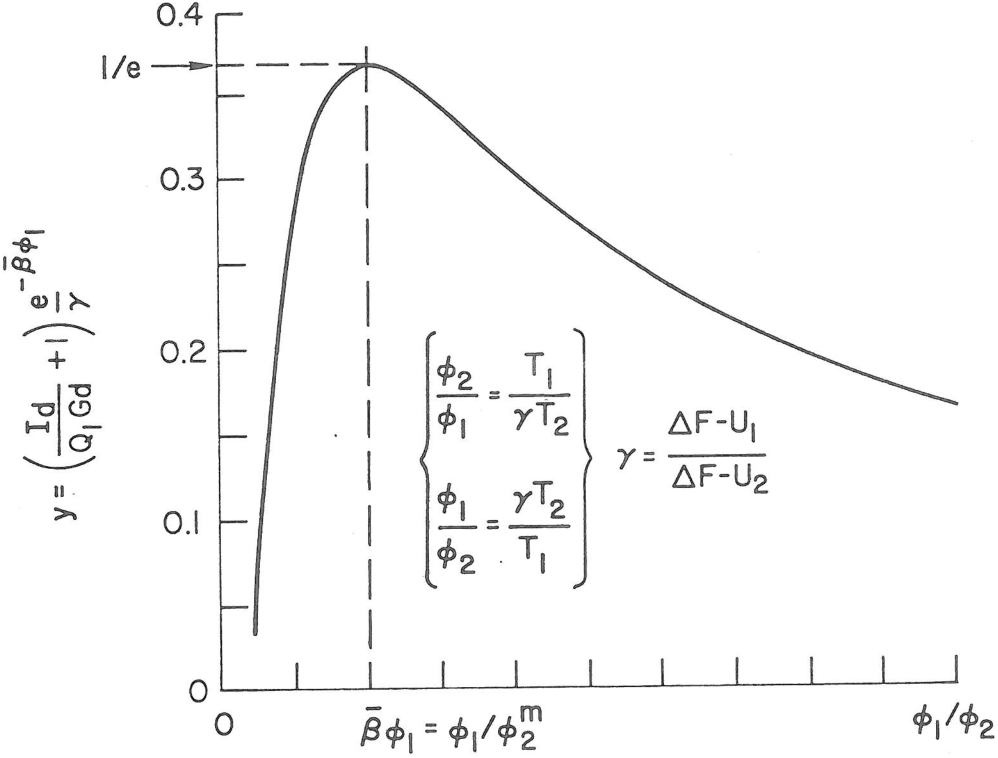
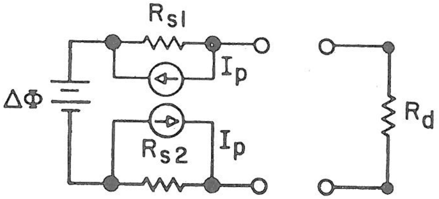


FIG. (5a, b) PLOT OF TRANSPORT RATE vs. 1/T,T FROM THEORY

EQUIVALENT CIRCUIT OF PLASMA CHEMICAL TRANSPORT



$$\Delta\Phi = \frac{\Delta F - U}{RT} \cdot \frac{\Delta T}{T} + \frac{\Delta U}{RT}$$

$$R_{s1} = \frac{RT}{PVa} \cdot \frac{1}{\kappa_{f1} A_{s1}}$$

$$R_{s2} = \frac{RT}{PVa} \cdot \frac{1}{\kappa_{f2} A_{s2}}$$

$$R_d = \frac{RT}{DP} \cdot \frac{L}{C}$$

$$I_p = \frac{\dot{b}_p}{r_1 R_s} \cong \frac{D_B b}{D_A a} \; \frac{F_A}{F_A^0}$$

Fig.(6) Equivalent Circuit of Plasma Chemical Transport

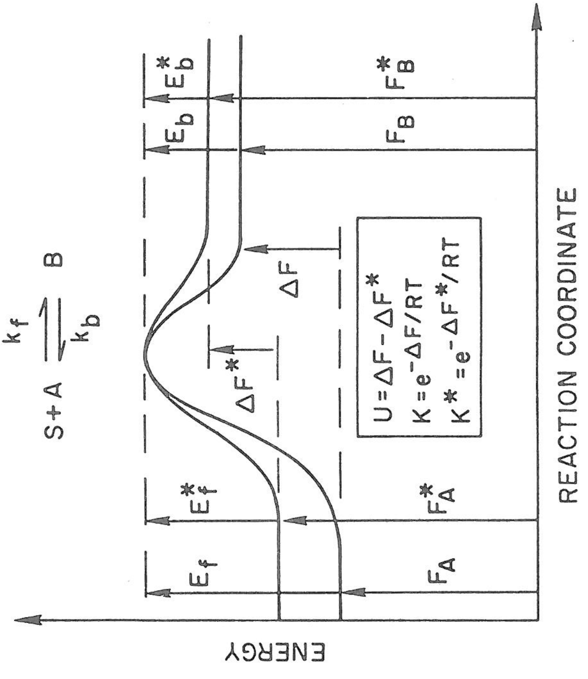


Fig.(7) Schematic Energy Diagram for the Transport Reaction