

Models for the Temperature and Gas Partial Pressure Dependence of Conductance

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Several models are in common use for the description of the thermal and gas partial pressure dependence of conductance of semiconducting materials. Herein these models are reviewed, including their physical origins and mathematical forms. The models can be divided into three main categories: models based on the Arrhenius equation, models based on power laws, and miscellaneous expressions. In general, the Arrhenius form is used to describe the thermal dependence of conductance where the activation energy arises from the Schottky barrier, band gap, or a combination of the two. Power laws are typically used to describe the gas partial pressure dependence of conductance and have their physical origin in classical reaction kinetics. Despite their simplicity, the Arrhenius equation and power laws have been used successfully to model conductance for a wide range of semiconducting materials. Other models have their own advantages and are here are collected under miscellanea.

KEYWORDS: Model, Theory, Surface Conductance, Gas/Surface Interactions.

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1. INTRODUCTION

The temperature and gas partial pressure dependence of conductance, $G(T, p)$, is an important and somewhat elusive function with far-reaching implications in the fields

of gas sensing, catalysis, organic electronics, pH measurement, etc. Behind the scenes, gas sensors play key roles in automobiles, hydrogen fuel cells, deep-sea diving equipment, anesthesia monitors, respirators, spectrometers, refineries, and water treatment plants. Heterogeneous catalysts are essential components of large-scale industrial synthesis. Organic electronics promise to increase the accessibility and decrease the price of electricity and electronic devices. Finally, pH measurements are paramount in a number of different fields including but not limited to medicine, biology, and chemistry. These applications provide ample motivation for the development of robust mathematical models for $G(T, p)$.

The temperature dependence of conductance is often modeled using the Arrhenius equation where the activation energy is usually assumed to correspond to the band gap or the Schottky barrier at grain boundaries. This model has been applied successfully to many semiconducting thin-films,^{1–7} C_{60}/C_{70} mixture films,⁸ and Cu–Al–O thin-films.^{9,10} In contrast, the dependence of the conductance on the partial pressure of the adsorbing gas molecules is frequently approximated using a power law where the power varies across adsorbing species and substrates. For example, it has been shown that in the presence of a reducing gas at the surface of gallium oxide, conductance follows the relationship,

$$G \propto p_{\text{rg}}^{1/2} \quad (1)$$

where G is the conductance and p_{rg} is the partial pressure of H_2 or CO .¹¹ Similar simple relationships

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have been found for other adsorbate/adsorbent combinations.^{1, 4, 6, 12-14} In addition to the Arrhenius equation and the power law model, which have their physical origins in classical chemical kinetics, there are models derived from quantum mechanics and semiconductor physics that also have been used to describe $G(T, p)$.

This review will present the common models for $G(T, p)$, explain their physical basis, discuss the significance of their important parameters, and note some examples of systems to which they have been applied successfully. This information is generally available in the literature, but it is scattered across journals in several distinct fields and sometimes in difficult-to-acquire references. (It took the authors several months to track down a copy of Ref. [15].) It is hoped that gathering this information together into a single paper will be of value to the community of scholars who are interested in the thermal and gas-partial-pressure dependence of conductance. The paper is organized with one section for each of the following: the Arrhenius Model for $G(T)$, the Power Law Model for $G(p)$, and miscellaneous models for $G(T, p)$.

2. ARRHENIUS EQUATION FOR $G(T)$

The temperature dependence of conductance is most commonly modeled with the Arrhenius equation

$$G(T) = G_0 \exp\left(-\frac{E_a}{kT}\right) \quad (2)$$

Here G_0 is the frequency factor, E_a is the activation energy, k is the Boltzmann constant, and T is the absolute temperature. Basically, this expression is the product of two factors; an “attack frequency” (G_0) times a “hopping

probability,” $\exp(-E_a/kT)$. While it is not surprising that $G(T)$ mirrors the Arrhenius equation when one can identify an energy barrier to charge transport, the physical significance of the activation energy varies across systems. In general, the activation energy arises from some potential barrier that an electron (or other charge carrier) must overcome in order to transfer charge. For electron conduction, the most common forms of this barrier are

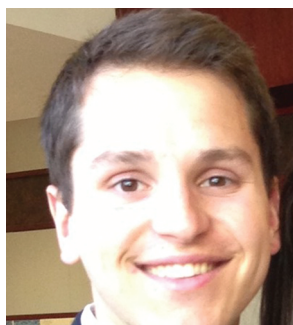
- (1) the energy gap between the highest occupied and lowest unoccupied bands and
- (2) Schottky barriers at grain boundaries.

When charge transport occurs by proton hopping, E_a corresponds to the barrier between two adjacent local minima along the proton hopping path. In the case of charge conduction by electrons, G_0 is the theoretical maximum conductance that the material would have at infinite temperature.¹⁶ In the proton transfer case, G_0 is the vibrational frequency with which a proton in one of the local minima along the hopping path attacks the potential barrier to the next minimum. In other words, it is the vibrational frequency of the local mode vibration of the proton that carries the proton in the direction of the transition state.

Below are several references to particular cases illustrative of the physical interpretation of the energy exponent in the Arrhenius model. Before discussing these cases, however, the physical origins of the barrier are described.

2.1. Arrhenius Energy Parameter Arising from a Band Gap

The gross features of semiconductor band structure are shown in highly stylized fashion in Figure 1. An intrinsic semiconductor will display Arrhenius-type behavior in



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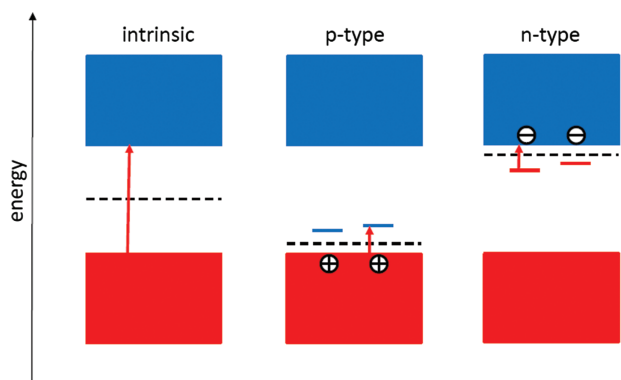


Fig. 1. Schematic of band structure in various semiconductors.

the temperature dependence of conductance when thermal energy is sufficient to excite electrons across the band gap between the valence band and the conduction band. This is shown schematically in the LHS of Figure 1 wherein the red rectangle denotes the valence band, the blue rectangle denotes the conduction band and the Fermi level is noted by the horizontal dashed line.

For a *p*-type semiconductor, holes are introduced into the valence band, (denoted by “+” within a black circle in Fig. 1.) typically by replacing some of the atoms in the material with atoms having fewer valence electrons and often a smaller nuclear charge (e.g., C-for-O substitution). This substitution depletes electrons from the valence band thereby lowering the Fermi level. In addition, due to the weaker nuclear charge associated with the substituent atom, some of the bands “float up” in energy,¹⁷ a few of which may rise into what would constitute the gap in the undoped structure. These bands will be unoccupied owing to depletion of electrons from the valence band due to the substitution. The activation energy then corresponds to promotion of an electron from the valence band into one of these unoccupied gap states.

For an *n*-type semiconductor, electrons are introduced into the conduction band, (denoted by “-” within a black circle in Fig. 1) typically by replacing some of the atoms in the material with atoms having more valence electrons and often a greater nuclear charge. The introduction of an oxygen vacancy in a metal oxide has the same effect, because removal of an oxygen atom depletes more valence spin-orbitals than valence electrons.¹⁷ With the substitution, some bands are pulled down from the conduction band into what would constitute the gap in the undoped structure.¹⁷ These bands will be occupied owing to presence of extra electrons. The activation energy then corresponds to promotion of an electron from one of the occupied gap states into the conduction band.

Cu–Al–O thin films have gained popularity in the last 20 years as ozone sensors, photovoltaic systems, and *p*-type transparent conducting oxides.¹⁰ Their use as ozone sensors has prompted studies of the thermal dependence of conductance, which has been shown to exhibit Arrhenius

behavior.¹⁰ In these systems, the activation energy is generally considered to correspond to the thermal energy required to excite a valence band electron into a low-lying unoccupied acceptor state. For Cu–Al–O and Zn-Doped CuAlO₂, the activation energy ranges from 0.05 to 0.2 eV depending on the oxygen composition.^{9, 10, 18}

Perovskite-type oxides (such as Pr_{0.8}Sr_{0.2}Mn_{0.8}Co_{0.2}O_{3-x}, Sr_{0.85}Ce_{0.15}Fe_{0.5}Co_{0.5}O_{3-x}, and SrFe_yCo_zO_x) are also subjects of intense research because of their applications in solid-state chemical sensors, oxygen permeation membranes, and solid oxide fuel cells.^{19, 20} Like Cu–Al–O, these oxides exhibit *p*-type semiconductor behavior and Arrhenius-type *G*(*T*) dependence, wherein the activation energy corresponds to the energy gap between the valence band and low-lying unoccupied states. For Pr_{0.8}Sr_{0.2}Mn_{0.8}Co_{0.2}O_{3-x} and Sr_{0.85}Ce_{0.15}Fe_{0.5}Co_{0.5}O_{3-x}, the thermal activation energies are reported to be 0.22 and 0.18 eV respectively.^{19, 20} Also of note, perovskite-type oxides that exhibit mixed conductivity are suitable materials for temperature-independent ($E_a \rightarrow 0$ eV) gas sensors.²¹ A mixed conducting material is one that exhibits both hole and electron conductivity. Tunney et al. have shown that $\ln G$ for a perovskite-type oxide with the composition SrFe_{0.25}Co_{0.75}O_x is temperature-independent ($E_a = 0.002$ – 0.04 eV) between 350 and 500 K.¹⁹

The thermal activation of conductance is also observed for polycrystalline tin oxide and Ga₂O₃. For *p*-type Ga₂O₃ thin films, the activation energy in the presence of the reducing gases CO and H₂ is 1.2 eV.¹ Given that the band gap in Ga₂O₃ almost certainly exceeds 4 eV,²² if one assumes that the reducing gas is donating an electron into a hole within the valence band, this result suggests that unoccupied gap states lie far above the valence band edge. For polycrystalline tin oxide, which is an *n*-type semiconductor and commonly used as a CO, H₂, and O₂ sensor, the activation energy ranges from 1.3 to 2.00 eV depending on the sample processing.²³ Lee et al. found that samples prepared via hot isostatic pressing show lower values for the activation energy than those prepared by normal sintering.²³ They were able to demonstrate that the difference in activation energy between normally sintered and hot isotactic pressed samples is essentially independent of grain boundary transport and they therefore concluded that the activation energy in polycrystalline tin oxide results from the blocking effect of the pores that are present in normally sintered samples.

Takashi et al., showed plasma-polymerized C₆₀ to exhibit semiconductor-like properties, specifically Arrhenius-type conductance at high temperatures.⁸ Assuming that C₆₀ is an intrinsic semiconductor and taking the activation energy to be half the band gap ($E_a = \text{Band gap}/2$),²⁴ the predicted band gap is approximately 2.1 eV. This value is consistent with the literature value of 1.9 eV.²⁵

2.2. Arrhenius Energy Parameter Arising from a Schottky Barrier

Schottky barriers arise from the accumulation of charge at surfaces and grain boundaries. Assuming that the radii of the semiconductor grains are much greater than the Debye length (L_D), the one-dimensional Poisson equation,

$$\frac{d^2V(x)}{dx^2} = -\frac{\rho(x)}{\epsilon\epsilon_0} \quad (3)$$

can be used to describe the potential energy $V(x)$ of electrons in the depletion layer around a grain boundary. Here x is the coordinate variable denoting normal distance from the surface, ϵ is the relative permittivity of the material and ϵ_0 is the vacuum permittivity. If all the donor atoms are ionized, the space charge density, $\rho(x)$, can be reasonably approximately using the abrupt change model,

$$\rho(x) = qN_d \quad \forall 0 < x < w \quad (4a)$$

$$\rho(x) = 0 \quad \forall x > w \quad (4b)$$

Here q is the elementary charge and N_d is the density of donors (number per unit volume). The relationship between $\rho(x)$ and the surface charge density (Q_{sc}) is

$$Q_{sc} = -\rho(x)w = -qN_dw \quad (5)$$

where w is the depletion depth. Multiplying $\rho(x)$ by w is equivalent to assuming that all charges in the depletion layer migrate to the surface. This assumption is a key step in connecting the physics of semiconductors to the surface chemistry.

Subject to the boundary conditions, $V(x=w) = dV(x=w) = 0$, the solution to Poisson's Eq. (3) is,

$$qV(x) = q^2 \frac{N_d}{2\epsilon\epsilon_0} (x-w)^2 \quad (6)$$

where Eq. (6) follows directly the work of Sze.²⁶ The surface potential barrier (V_s) is given by Eq. (6) evaluated at $x=0$, which yields,

$$qV_s = q^2 N_d w^2 / 2\epsilon\epsilon_0 \quad (7)$$

Recognizing that the surface charge density arises from the migration of electrons generated by donors within the depletion layer migrating to the surface, one can write

$$Q_{sc} = -N_d w \quad (8)$$

It follows that

$$V_s = qQ_{sc}^2 / 2\epsilon\epsilon_0 N_d \quad (9)$$

which is the well known expression for the Schottky barrier that arises when a density of N_d donors within the depletion region of depth w gives rise to a surface charge density as described in Eq. (8).

Schmitte et al.⁷ and Lantto et al.³ have reported several instances where the activation energy corresponds to the

Schottky barrier at grain boundaries. For SnO_2 in the presence of CO, the Schottky barrier varies from 0.6 to 0.9 eV depending on the SnO_2 film thickness.⁷ Theoretical analysis of the thermal dependence of the Schottky barrier corroborates this finding. Lantto's³ derivation will be followed closely here.

The starting assumption is that ambient oxygen "ionisorbs" to the surface wherein after adsorption, the O_2 molecules become anionic by capturing electrons from the bulk. (See Ref. [27] Chapter 2) By Eq. (9), the Schottky equation for the barrier energy (eV_s) on the surface is

$$eV_s = e^2 Q_{sc}^2 / 2\epsilon\epsilon_0 N_d \quad (10)$$

where e is the elementary charge, Q_{sc} is the surface charge density arising from ionisorbed oxygen, $\epsilon\epsilon_0$ is the permittivity of the semiconductor, and N_d is the concentration of electrons arising from donors. If the energy of the surface states to which oxygen ionisorbs is denoted E_t , for E_t substantially above the Fermi level $e\eta$, an approximate expression for the population of the surface states from Fermi-Dirac statistics is,

$$Q_{sc} = N_p(p_{\text{O}_2}, T) \exp\left(\frac{-(E_t - e\eta)}{kT}\right) \quad (11)$$

here N_p is the surface density of physisorbed oxygen, which depends on the partial pressure of oxygen p_{O_2} and the absolute temperature T . Defining ΔE to be the energy difference between the surface states (E_t) and the top of the Schottky barrier, (i.e., the energy of the conduction band at the surface) Eq. (11) can be re-written as,

$$Q_{sc} = N_p(p_{\text{O}_2}, T) \exp\left(\frac{(\Delta E - e\eta)}{kT}\right) \exp\left(\frac{-eV_s}{kT}\right) \quad (12)$$

As discussed by Morrison,²⁷ for any physically reasonable value the barrier potential severely restricts the magnitude of the surface charge to a small near-constant, (the so-called "Weisz limitation"²⁸) so E_t is effectively constant. This is used to justify the rearrangement of Eq. (12) to yield,

$$\frac{N_p(p_{\text{O}_2}, T)}{Q_{sc}} = \frac{\exp(-(\Delta E - e\eta)/kT)}{\exp(-eV_s/kT)} \quad (13)$$

Equation (13) can be solved to find the temperature and gas partial pressure of the barrier energy (eV_s) on the surface if the explicit form of the density of physisorbed molecules ($N_p(p_{\text{O}_2}, T)$) is known. Clifford¹⁵ derived such an expression by assuming that a quasi-equilibrium is established between adsorption and desorption processes on an exponential distribution for surface sites. The resulting areal density of physisorbed molecules (the derivation of the areal density, which is non-intuitive, appears in Clifford's thesis,¹⁵ but this source is not readily available so it is reviewed here in Appendix A) is given by,

$$N_p(p_{\text{O}_2}, T) = N_0 (aP_{\text{O}_2})^{kT/E_0} \quad (14)$$

Here N_0 and a are experimentally determined constants. E_0 is a parameter characteristic of the surface and has units of energy. a is a scaling factor with units of reciprocal pressure that is related to the rate constant for the desorption process (see Appendix A). Setting the right side of Eqs. (13) and (14) equal to one another and solving for (eV_s) yields the desired thermal and oxygen partial pressure dependence of the Schottky barrier,

$$E_B = eV_s = \Delta E - e\eta + kT \ln(N_0/N_i) + \frac{(kT)^2}{E_0} \ln(aP_{O_2}) \quad (15)$$

It is clear from this model that adsorbing gas molecules play an important role in the temperature dependence of the Schottky barrier and therefore $G(T)$.

2.3. Arrhenius Energy Parameter Arising from a Proton Hopping Barrier

The Arrhenius model has also proven successful for modeling conductance when the charge carriers are other than electrons. Cai et al.^{29,30} used the product of an Arrhenius factor and the Langmuir isotherm (a surface coverage factor) to model thermal dependence of charge transport in γ -alumina.

Cai et al.^{29,30} developed a model based on the assumption that two types of charge carriers contribute to the overall conductance in γ -alumina; protons hopping among vacant cation sites³¹ and hydronium ions moving on the surface. The movement of hydronium is presumed to take place by the Grotthuss mechanism³² whereby successive protons shift across the double-well hydrogen bonding potential between adsorbed water molecules, effectively moving the hydronium. Denoting these carriers as (H) for protons and (w) for hydronium, the conductance may be expressed as,

$$G = B(v_H n_H + v_w n_w) \quad (16)$$

where v_H (v_w) and n_H (n_w) are the drift velocities and concentrations of protons (hydronium) respectively and B is an overall scaling-constant/units-conversion factor, which includes geometric factors specific to the measurement apparatus etc.

The drift velocity is modeled by reference to the hopping mechanism. In a hopping process, the drift velocity is given by the vibrational frequency of the surface-bound charge carrier (v_0), times the distance it must hop to reach an adjacent surface site (d), times the probability of hopping $\rho(T)$,

$$v_i = v_{0i} d_i \rho(T) \quad (17)$$

where the subscript ($i = H, w$) denotes the type of charge carrier. The hopping probability is given by a Boltzmann factor dependent on the hopping energy barrier (E_{bi}),

$$\rho(T) = \exp\left(\frac{E_{bi}}{kT}\right) \quad (18)$$

where k is the Boltzmann constant and T is absolute (Kelvin) temperature. For a particle of charge (q) in the presence of an applied electric field (E), the hopping barrier is decreased by an energy $Eqd_i/2$ in the forward direction and increased by the same quantity in the reverse direction. The overall drift velocity is therefore given by the difference between the forward and reverse velocities,

$$v_i = v_{0i} d_i \rho E > E_{bi} - Eqd_i - v_{0i} d_i \rho E > E_{bi} + Eqd_i \quad (19)$$

Here $(\rho E > E_{bi} + Eqd_i)$ denotes the probability that the charge carrier has an energy in excess of the hopping barrier, $E > E_{bi} + Eqd_i$. Substituting Eqs. (18) into (19) yields,

$$v_i = v_{0i} d_i \exp\left(\frac{E_{bi} - Eqd_i}{kT}\right) - v_{0i} d_i \exp\left(\frac{E_{bi} + Eqd_i}{kT}\right) \quad (20)$$

The concentration n_i is taken to be given by the total concentration (N_i) of possible binding sites for the charge carrier times their fractional occupancy (θ),

$$n_i = N_i \theta(T) \quad (21)$$

The Langmuir isotherm is used to model the temperature (T) and gas partial pressure (p) dependence of the fractional occupancy,

$$\theta(T, p) = \frac{K_i p_i}{1 + K_i p_i} \quad (22)$$

where K_i is the equilibrium constant expressing the partitioning between the gas and surface-bound states of the adsorbate species that gives rise to the surface charge carrier. This equilibrium constant may be written in terms of the molar free energy of binding (ΔF_i) as,

$$K_i = \exp\left(\frac{-\Delta F_i}{RT}\right) \quad (23)$$

where R is the gas law constant. Subsequent to their original work, Cai et al. elaborated on the partitioning of the free energy of binding into its enthalpic and entropic contributions.³⁰ More recently present authors used the same concepts to extend the model to a wide band gap semiconductor.³³

The overall mathematical model that describes conductance arising from proton and hydronium charge carriers on γ -alumina is arrived at by expanding Eq. (16). The functional form of the concentration factors is arrived at by substituting Eqs. (23) into (22) and subsequently (22) into (21). The functional form of the drift velocity factors is Eq. (20). The overall expression is,

$$G(T, P) = B \{ [v_{\downarrow} H d_{\downarrow} H \exp((E_{\downarrow} bH + Eqd_{\downarrow} H/2)/kT) - v_{\downarrow} H d_{\downarrow} H \exp((E_{\downarrow} bH - Eqd_{\downarrow} H/2)/kT)] \times N_{\downarrow} H ((\exp((-[\Delta F]_{\downarrow} H)/RT) P_{\downarrow} H) / (1 + \exp((-[\Delta F]_{\downarrow} H)/RT) P_{\downarrow} H)) + [v_{\downarrow} w d_{\downarrow} w \exp((E_{\downarrow} bw + Eqd_{\downarrow} w/2)kT) - v_{\downarrow} w d_{\downarrow} w \exp((E_{\downarrow} bw -))] \} \quad (24)$$

In this expression there are two types of Arrhenius-like factors: factors that depend on a hopping barrier ($E_{bi} \pm Eqd_i/2$), and factors that depend on a desorption energy (ΔF_i). Since the energy parameters in these two factors differ, the two factors dominate in different temperature regimes, which produces the dramatic fluctuations with temperature seen in measurements of the conductance of γ -alumina.³⁴

Figure 2 shows data for the thermal dependence of conductance of γ -alumina together with the best fit using the model of Cai et al.²⁹ In region 0 the increasing thermal energy increases the likelihood that H+ in hydronium can surmount E_{bw} and conductance increases with increasing T . In region I, $\theta(T, p)$ decreases as water is desorbed from the surface and conductance decreases with increasing temperature because the scaffold for proton mobility in hydronium is lost. In region II increasing thermal energy increases the likelihood that H+ among cations sites within the alumina can surmount E_{bH} and conductance again increases with increasing T .

3. POWER LAW MODEL FOR $G(p)$

The power law model for the dependence of conductance on the partial pressure of adsorbing gas molecules is given by the expression

$$R(p_g) \propto p_g^n \Rightarrow G(p_g) \propto p_g^{-n} \quad (25)$$

where (p_g) is the partial pressure of the gas and n is a constant that depends on the nature of adsorption, oxidative or reductive, and the species.

3.1. Power Law Arising from Schottky Barriers as Derived from Adsorption Kinetics

Merging the theory of Schottky barriers and adsorption kinetics, Yamazoe and Shimano³⁵ provide a theoretical basis for the value of n for n -type metal oxide semiconductor (MOS) gas sensors.

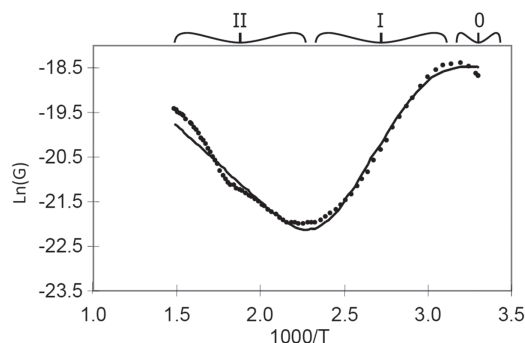


Fig. 2. Data for the thermal dependence of conductance of γ -alumina and best fit using the model of Cai et al. in Ref. [29], from which the figure is adapted. (Reprinted with permission from [29], S. Cai, et al., *J. Phys. Chem. C* 111, 5506 (2007). © 2007, American Chemical Society.)

The first step in the derivation is to establish the relationship between the depletion layer and the sensor resistance.

Solving Eq. (7) for w yields

$$w = \left(\frac{2\epsilon\epsilon_0 V_s}{qN_d} \right)^{1/2} \quad (26)$$

Since the definition of the Debye length is $L_D = (\epsilon\epsilon_0 kT/q^2 N_d)^{1/2}$, Eq. (26) becomes

$$w = L_D \left(\frac{2q}{kT} V_s \right)^{1/2} \quad (27)$$

which can be rearranged to generate

$$V_s = \frac{kT}{2q} \left(\frac{w}{L_D} \right)^2 \quad (28)$$

The concentration of electrons at the surface [e] is then proportional to the density of conduction electrons multiplied by the Boltzmann probability that they will overcome the Schottky barrier, which may be written algebraically as,

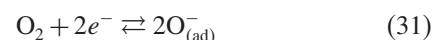
$$[e] = n_0 \exp\left(-\frac{qV_s}{kT}\right) = N_d \exp\left(-\frac{m^2}{2}\right) \quad (29)$$

where n_0 is density of conduction electrons ($n_0 = N_d$), k is the Boltzmann constant, T is the absolute temperature, and m is the reduced depletion depth, defined as $m \equiv w/L_D$. Assuming that Schottky barriers are the main source of internal resistance, Yamazoe and Shimano³⁵ suggest that the resistance is inversely proportional to [e], i.e.,

$$\frac{R}{R_0} = \exp(m^2/2) \quad (30)$$

Here R is the observed resistance of the semiconductor, R_0 is the bulk resistance, and their quotient, R/R_0 , is termed the reduced resistance. Tunneling effects were neglected because they do not affect m , which carries the essential information for deriving the power laws.³⁵

The next step in the derivation is to treat the adsorption of oxygen, (or other oxidizing gasses or reducing gas). This starts with the chemical equation for the adsorption of oxygen to a MOS surface,



Denoting the rate constants for the forward and reverse reactions as k_f and k_r respectively, the rate of formation of $\text{O}_{(\text{ad})}^-$ (the subscript "ad" denotes that the ion is adsorbed on the surface) is then given by,

$$\frac{d[\text{O}_{(\text{ad})}^-]}{dt} = k_f P_{\text{O}_2} [e]^2 - k_r [\text{O}_{(\text{ad})}^-]^2 \quad (32)$$

where P_{O_2} is the partial pressure of molecular oxygen and $[\text{O}_{(\text{ad})}^-]$ is the density of O^- at the surface. Rearrangement

of the expression in Eq. (31) when equilibrium is achieved yields,

$$K_{O_2} P_{O_2} [e]^{-2} = [O_{(ad)}^-]^{-2} \quad (33)$$

Here $K_{O_2} = k_f/k_r$ is the equilibrium constant for the oxygen adsorption reaction in Eq. (31). Assuming that $O_{(ad)}^-$ is the only charged adsorbate, it is solely responsible for Q_{sc} ; therefore,

$$[O_{(ad)}^-] = -\frac{Q_{sc}}{q} = N_d w \quad (34)$$

Inserting Eqs. (29) and (34) into (33), generates,

$$K_{O_2} P_{O_2} N_d^2 \left[\exp\left(-\frac{m^2}{2}\right) \right]^2 = N_d^2 w^2 \quad (35)$$

Dividing both sides by N_d^2 , using $m \equiv w/L_D$ and taking the square root of both sides produces,

$$\frac{\sqrt{K_{O_2} P_{O_2}}}{L_D} \exp\left(-\frac{m^2}{2}\right) = m \quad (36)$$

If one defines the reduced absorptive strength of oxygen as $x = (K_{O_2} P_{O_2})^{1/2}/L_D$, the above expression may be written in the simplified form,

$$x = m \exp\left(\frac{m^2}{2}\right) \quad (37)$$

Referencing Eq. (30), Yamazoe and Shimano³⁵ obtain the following expression for R/R_0 ,

$$\frac{R}{R_0} = \frac{x}{m} = \frac{(K_{O_2} P_{O_2})^{1/2}}{w} \quad (38)$$

Given that the power-law exponent may be defined by,

$$n \equiv \frac{\partial \log R}{\partial \log P_{O_2}} \quad (39)$$

using the expression for resistance given in Eq. (38), differentiation of $\log R$ with respect to $\log P_{O_2}$ therefore yields the power law exponent for oxygen adsorption,

$$n = \frac{1}{2} [1 - (1 + m^2)^{-1}] \quad (40)$$

According to Ref. [36] the experimental power law exponent for oxygen adsorption on tin dioxide is 1/2. This suggests that the depletion region formed by the formation of surface O^- is large, since Eq. (40) approaches 1/2 as m increases. Experimentally determined m values for SnO_2 range from 4 to 5.12, validating the power law model.³⁷

The kinetic methods employed in determining the power law exponent for reducing and oxidizing gases are very similar to the above case for oxygen and may be found in Ref. [35]. Thus, for the sake of brevity, a full derivation of the power law exponent for reducing and oxidizing gases will not be presented. For reducing gases, n becomes,

$$n_{rg} = -\frac{p/2}{[1 + q/(2m^{-2})]} \quad (41)$$

where p and q are the number of moles of reducing gas molecules and ions respectively. For oxidizing gases, n becomes,

$$n_{og} = \frac{z/(x+z)}{1+m^{-2}} \quad (42)$$

where $z = K_A P_A/L_D$, K_A is the equilibrium constant for adsorption of the oxidizing gas, P_A is the equilibrium partial pressure of the oxidizing gas, K_{O_2} is the equilibrium constant for O_2 adsorption, and P_{O_2} is the equilibrium partial pressure of O_2 . This model is consistent with findings for SnO_2 , WO_3 , and In_2O_3 by Clifford and Tuma,³⁶ Akiyama et al.,³⁸ Guerin et al.,³⁹ and Vuong et al.,⁴⁰ respectively. The n values as predicted by the Yamazoe-Shimano model are shown in Table I.

3.2. Power Law Arising from the Volkenstein Theory of Catalysis

Regarding the Yamazoe-Shimano model, Geistlinger has pointed out that, "The main point of criticism is that there is no rigorous connection between the electronic state of the surface and the electronic state of the bulk"¹¹ and has developed a model to address this shortcoming.

In Geistlinger's approach, conductivity (σ) is assumed to arise from free conduction band electrons in the depletion region near the surface, which may be given by,

$$\sigma(p) = e\mu^{SCR} \langle n(z, p) \rangle \quad (43)$$

where e is the unit charge, μ^{SCR} is the charge mobility in the space charge region (depletion layer) and $\langle n(z, p) \rangle$ is the average charge density, z being the surface normal. A key in Geistlinger's approach is therefore to relate the concentration of electrons in surface states to adsorbate partial pressure (p). Ultimately, the n values in the power law (Eq. (16)) for the adsorption of H_2 and CO on Ga_2O_3 are computed using the Volkenstein theory of catalysis.¹¹

The Volkenstein model (VM) assumes that there exists a spectrum of surface energy states that engage in varying degrees of partial charge transfer between the adsorbate and the surface. Within the spectrum there are two levels, corresponding to neutral-weak and charged-strong chemisorption. Geistlinger suggests that these states can be identified in the solutions to the time independent Schrödinger equation based on the following Hamiltonian,

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_r^2 + V_{lattice}(\vec{r}) + W(\vec{r} - \vec{d}) + U(\vec{d}) \quad (44)$$

Here $V_{lattice}(\vec{r})$ is the periodic potential of the lattice ions, $W(\vec{r} - \vec{d})$ is the coulomb potential of the adion, $U(\vec{d})$ is the electrostatic potential between the lattice and the adion, m is mass and \hbar is the reduced Planck constant. The occupation probabilities of the two states corresponding to neutral-weak and charged-strong chemisorption can be calculated using Gibb's grand partition function (Z_{chem}),

$$Z_{chem} = \sum_j \sum_m \square \exp\left(\frac{j\mu - E_{jm}}{kT}\right) \quad (45)$$

Table I. n values as predicted by the Yamazoe-Shimanoie (YS) and Geistlinger models, together with values derived from experiments.

Model	Gas	Sensing material	n	Temperature (°C)	References
YS	O ₂	n -type	1/2	≥200	[35]
	Reducing gas	Semiconducting	-1/2		[35]
	Oxidizing gas	Oxides	1		[35]
Geistlinger	H ₂	Ga ₂ O ₃	-1/3	577 to 677	[11]*
	CO	Ga ₂ O ₃	-1/3		[11]*
Experiment	O ₂	SnO ₂	1/2	445	[36]**
	NO ₂	WO ₃	1	300	[38]**
	O ₃	WO ₃	1	250	[39]**
	H ₂	SnO ₂	-1/2	250	[40]**
	CO	SnO ₂	-1/2	445	[36]**
	O ₂	SnO ₂ :Cu	1/6...1/2	374	[14]*
	CO	SnO _x	-1/2	200-500	[13]*
	O ₂	SnO ₂	1/4	230	[4]*
	CO	SnO ₂	-0.8...-0.3	Not reported	[4]*
	CO and H ₂	Ga ₂ O ₃	-1/3	550 to 650	[1]*
	O ₂	Ga ₂ O ₃	1/4	900 to 1000	[1]*
O ₂	ZnO	1/6...1/4	527 to 1627	[41]*	

Notes: *These sources report $G \propto p^n \Rightarrow R \propto p^{-n}$. **As reported in Ref. [35].

Here, j is the number of electrons that occupy the surface state (the index runs from 0 to 1 in the present case), μ is the chemical potential, and E_{jm} is the energy of the m th quantum state with j electrons. The subscripts j and m in Eq. (45) are the same as the j and m in Table II. In terms of j , m , and E_{jm} , the neutral-weak and charged-strong chemisorption states for the donor-type adsorption of H₂ on Ga₂O₃ are shown in Table II.

Plugging the values in Table II into Eq. (45) yields,

$$Z_{\text{chem}} = 2 \exp\left(\frac{\mu - E_a^0}{kT}\right) + \exp\left(-\frac{E_{\text{ion}}^+}{kT}\right) \quad (46)$$

The first (second) term in Eq. (46) corresponds to the neutral-weak (charged-strong) chemisorbed state. The neutral state contains one electron, which can be spin-up or spin-down, hence the degeneracy 2. The probability of occupying the neutral-weak chemisorbed state (f^0) is given by,

$$f^0 = \frac{2 \exp(\mu - E_a^0/kT)}{Z_{\text{chem}}} = \frac{1}{(1/2) \exp(E_a^0 - E_{\text{ion}}^+ - \mu/kT) + 1} \quad (47)$$

Since there are only two states, the remaining probability occupies the charged-strong chemisorbed state ($f^+ = 1 - f^0$). In the presence of an electric potential (Φ),

Table II. Classification of the two-level spectrum of surface states according to the Volkenstein theory.

State	j	m	E_{jm}
Neutral-weak	1	Spin up, spin down	E_a^0
Charged-strong	0	0	E_{ion}^+

the energy of the charged-strong chemisorbed state *increases* by $e\Phi$ because the state is positively charged. In contrast, the energy difference between the neutral-weak and charged-strong chemisorbed states decreases by $e\Phi$ because the higher-energy neutral state is unaffected by Φ .

To obtain the expectation value of the charge density in the depletion layer required by Eq. (43), one integrates the product of electron density and Boltzmann probability over distance along the surface normal,

$$\langle n(z, p) \rangle = \frac{1}{D} \int_0^D n^0 \exp\left(-\frac{V(z, p)}{kT}\right) dz \quad (48)$$

Here $V(z, p)$ is the potential energy at the surface. Geistlinger⁴² uses the film thickness as D . n^0 is the charge density evaluated at the zero position.

To obtain the gas pressure dependence of the potential $V(z, p)$, one must solve the 1-D Poisson equation (see Eq. (3)). In this case, the space charge density at the surface, $\rho(z)$, is,

$$\rho(z) = Q_{\text{sc}}(E_f, p) \delta(z) = \frac{en_d}{1 + 2 \exp(E_f - E_d/kT)} + en(z) - ep(z) \quad (49)$$

where $Q_{\text{sc}}(E_f, p)$ is the surface charge density due to chemisorption, $\delta(z)$ is the Dirac delta function, n_d is the concentration of bulk donors, E_f is the Fermi level, E_d is the bulk donor level, $n(z)$ is the electron concentration, and $p(z)$ is the hole concentration (the last of which is neglected in Geistlinger's approach, as justified in a previous section above). The areal surface charge density has the following functional form,

$$Q_{\text{sc}}(E_f, p) = \frac{e\theta^+(E_f, p)N_{\text{chem}}}{A} \quad (50)$$

where A is the area, N_{chem} is the total number of chemisorption sites and θ^+ is the fractional coverage of

charged-strong chemisorbed species. θ^+ is the product of f^+ and the Volkenstein isotherm,¹¹ $\theta(E_f, p)$.

To summarize Geistlinger's approach, he assumes the presence of two chemisorption states in the spectrum of eigenstates of the time independent Schrödinger equation for the surface + adsorbate system: a neutral-weak state and charged-strong state. The occupation probabilities of the two states (f^0, f^+) are obtained with Eq. (47). The product of the occupation probability of the charged-strong chemisorption state and the Volkenstein isotherm gives the fractional coverage of charged-strong chemisorption (θ^+), from which the areal surface charge density due to chemisorption $Q_{sc}(E_f, p)$ may be obtained using Eq. (50). This surface charge density determines the space charge density in the depletion region via Eq. (49).

Using the restrictions of global charge neutrality and Gauss's law, Geistlinger solves the 1-D Poisson equation self-consistently for $V(z, p)$. Inserting $V(z, p)$ into Eq. (48) produces the gas-pressure dependence of expectation value of the charge density in the depletion layer. This quantity together with Eq. (43) yields conductance. A power law is obtained. The exponents n in this derived power law values obtained using Geistlinger's approach (see Table I) agree well with the those determined experimentally by Fleisher and Meixner,¹ Windischmann and Mark,¹³ and McAleer et al.^{4,5} establishing a firm theoretical basis for the power law behavior of thin film gas sensors.

4. MISCELLANEOUS MODELS FOR $G(T, p)$

Three types of models used in the literature are not strictly characterized as Arrhenius-type or power laws:

- (1) Hopping conduction models,
- (2) Mixed Arrhenius + power-law models, and
- (3) Mixed kinetic + semiconductor-physics models.

4.1. Mott's Hopping Models

Mott developed two models of the thermal dependence of conductance based on electron hopping in disordered systems. Both models can be understood by reference to the Miller-Abrahams expression,⁴³

$$G(T) \equiv C_v \exp(-2\gamma R) \exp\left(-\frac{E_{\text{hop}}}{kT}\right) \quad (51)$$

where C_v and γ are constants, R is the distance between localized states, γ is the spatial extent of the wavefunction, and E_{hop} is the energy difference between localized states. Equation (51) has three factors: a constant C_v and two probability factors. The constant C_v can be thought of as the product of an "attempt to escape" frequency and a unit conversion factor that relates the hopping frequency to conductivity. The first exponential effectively describes the degree to which the wavefunctions of the adjacent hopping sites overlap. The second exponential is

a Boltzmann hopping probability. This model was successfully applied by Sayer and Mansingh to semiconducting phosphate glasses⁴⁴ compounds of interest for use in optical fibers and bone scaffolds. Their studies showed that E_{hop} , and thus the conductivity of these materials, correspond to polaron formation and transport.

Mott's first model, nearest neighbor hopping conduction (NNH), describes systems with non-degenerate localized states near the Fermi energy whose wavefunctions overlap appreciably. In the NNH model, the hopping distance is short so the wavefunctions overlap appreciably. The second exponential term in Eq. (51), which arises from thermal activation, becomes the controlling factor and the expression for conductance reduces to the form,⁴⁵

$$\sigma_{\text{NNH}} = C_{\text{nn}} \exp\left(-\frac{E_{\text{hop}}}{kT}\right) \quad (52)$$

Mott's second model, variable range hopping conduction (VRH), describes systems at temperatures lower than the applicable range of NNH. With decreasing temperature, less thermal energy is available to promote endothermic electron hops. For a given energetic and spatial distribution of potential hopping sites, with decreasing temperature the density of energetically accessible sites within the neighboring volume of space decreases and longer hops become more probable. Said another way, the electron must look further afield to find an energetically accessible site to which to hop. To arrive at an analytic expression to describe this condition, one may start with Eq. (52) and assume that the electron hops a distance greater than R by some multiplicative factor p necessarily greater than unity.⁴⁶ The hopping distance becomes pR . A larger hop samples a greater volume of space $(4/3)\pi(pR)^3$ or conversely we may say that the energy difference between hopping sites scales by $1/p^3$ from the case where the sampling volume is $(4/3)\pi R^3$. The hopping probability may then be taken to be proportional to,

$$\exp\left(-2\gamma pR - \frac{E_{\text{hop}}}{kTp^3}\right) \quad (53)$$

The most probable hopping distance can now be seen as arising from a competition between the drive to minimize the distance multiplier p (thereby maximizing the first exponential factor) and the drive to maximize the energy difference divisor p^3 (thereby maximizing the second exponential factor). To find this optimum distance, one takes the second derivative of Eq. (53) with respect to p , sets the resultant expression to zero, and solves for p . It follows that the optimum is

$$p = \left(\frac{3E_{\text{hop}}}{2\gamma kTR}\right)^{1/4} \quad (54)$$

Substitution of the optimal value of p into Eq. (53) yields (after combining terms),

$$\exp\left(-\xi(\gamma R)^{3/4} \left(\frac{E_{\text{hop}}}{kT}\right)^{1/4}\right) \quad (55)$$

where ξ is a collection of constants. This result demonstrates the origin of the $T^{-1/4}$ behavior of conductance in the VRH model. The factor of 1/4 in the exponent may be interpreted as arising because the hopping electron samples states embedded in a 4-dimensional space, 3 spatial dimensions and energy. This may be seen more clearly by defining a range parameter \bar{R} between two states in this 4D space by variable substitution into the argument of the exponential in Eq. (53),

$$-\bar{R} = -2\gamma pR - \frac{E_{\text{hop}}}{kTp^2} \quad (56)$$

so the hopping probability scales with $\exp(-\bar{R})$. In practical application, the functional form for $G(T)$ for the VRH model is usually written in terms of T_0 , the characteristic/Debye temperature,

$$G(T) \propto \sigma_{\text{VRH}} = C_{\text{vr}} \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right] \quad (57)$$

where C_{vr} is an overall scaling-constant/conversion-factor.

Mott's NNH and VRH models fit the experimental data for phosphate glasses^{44,47} and semiconductive polymers⁴⁸ extremely well. This last finding is potentially useful for modeling $G(T, p)$ for organic electronics, which have seen a surge of interest in the last decade. Khanna and Nahar applied the VRH model to Al_2O_3 humidity sensors at low temperatures and obtained an excellent fit to the experimental data.⁴⁹ From this success they concluded that water adsorption can create surface states that lie near the Fermi energy and participate in VRH. More recent work by Cai and colleagues provides an explanation relevant to higher temperatures.^{29,30} Since VRH effectively describes disordered systems,⁵⁰ it has been applied to doped polyaniline⁵¹ and polyacetylene.⁴⁸ For the case of polyaniline doped with sulfonic acid, the power in the exponential was found to be 1/2 as opposed to 1/4, yielding T_0 values similar to those found in the literature [52]. This change in the exponent from 1/4 to 1/2 suggests that the hopping electron is sampling predominantly one spatial dimension. In their investigation of iodine and AsF_5 -doped polyacetylene, Park et al. expanded the VRH model to include the effects of potential barriers at inter-fibril boundaries.⁴⁸ The ability of the extended-VRH model to describe the thermal dependence of conductance for AsF_5 -doped polyacetylene may translate to other organic polymers and, therefore, may find use in the field of polymeric organic electronics, as $G(T)$ surely play a role in their functionality.

4.2. Mixed Arrhenius + Power-Law Model

Kinetic models can also be used to describe $G(T, p)$ for specific adsorbate-adsorbent systems. Wlodek et al. derived an expression for the thermal, temporal, and partial pressure-dependence of conductance using the adsorption kinetics of a reducing gas at the surface of tin oxide

and solving the differential rate equation.⁵³ Both Arrhenius and power law-type function are found in their model for $G(T, t, p)$. Wlodek's model very nicely fits the experimental data for the adsorption of the reducing gases CO , H_2 , and C_3H_8 .⁵³ In his exhaustive review of semiconducting thin-film gas sensors, Sberveglieri points out that the Arrhenius equation and power law model for oxygen can be combined to yield,

$$G(T, P) \propto \sigma = C \exp\left(-\frac{E_a}{kT}\right) P_{\text{O}_2}^{1/m} \quad (58)$$

where C is a scaling-constant/conversion-factor.⁶ The activation energy (E_a) represents the thermal energy necessary to excite an electron to the conduction band. Sberveglieri⁶ presents the values of the activation energy and m for a total of 13 different semiconducting gas sensors spanning 17 references.

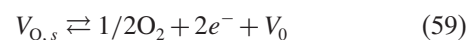
4.3. Two Mixed Kinetic + Power-Law Models

Point defect formation is an important factor in the conductance of semiconductor gas sensors. Fergus showed that a conductance model that incorporates the p_{O_2} -dependence of point defect formation in SrTiO_3 , CaTiO_3 , and BaTiO_3 can be constructed by combining the kinetics of defect formation and gas adsorption.¹² By considering the nature and identity of defects, one can determine the power to which the partial pressure of oxygen is raised in $G(p_{\text{O}_2})$. The general procedure, (which is similar to the YS approach)³⁵ is as follows:

- (i) Define the pertinent point defects,
- (ii) Determine the equilibrium constants for their formation, and
- (iii) Connect the equilibrium constant to the concentration of electrons or holes.

Fergus showed this procedure reproduces the experiment power law behavior for O_2 adsorption on SrTiO_3 , CaTiO_3 , and BaTiO_3 gas sensors¹² and we follow that derivation closely here.

SrTiO_3 forms both oxygen and strontium vacancies. At low oxygen partial pressure, oxygen vacancies are the predominant defects. The chemical equation for the formation of an oxygen vacancy (V_{O}) in SrTiO_3 is,



$V_{\text{O},s}$ is a potential oxygen vacancy site. The equilibrium constant for oxygen vacancy formation (K_{O}) is,

$$K_{\text{O}} = \frac{p_{\text{O}_2}^{1/2} n^2 [V_{\text{O}}]}{[V_{\text{O},s}]} \quad (60)$$

where n is the concentration of electrons. Following standard thermodynamic practice, one may set $[V_{\text{O},s}] = 1$. Assuming oxygen vacancies (which are more likely to

form at low oxygen partial pressure) are the principal source of electrons, the concentration of electrons is

$$n \approx 2[V_0] \quad (61)$$

Combining Eqs. (60) and (61) and solving for n yields its p_{O_2} -dependence:

$$n = \left(\frac{2K_0}{\sqrt{p_{O_2}}} \right)^{1/3} \propto p_{O_2}^{-1/6} \quad (62)$$

This procedure (Eqs. (60) through (62)) can analogously be carried out at high oxygen partial pressure, where strontium vacancies are more likely. Strontium vacancies form hole charge carriers, whose concentration p also depends explicitly on p_{O_2} :

$$p = (2K_{Sr})^{1/3} p_{O_2}^{1/6} \propto p_{O_2}^{1/6} \quad (63)$$

K_{Sr} is the equilibrium constant for the formation of a strontium vacancy.

A model for aqueous proton conduction at a solid- Al_2O_3 surface by Khanna and Nahar is also grounded in kinetics, but contains a fractional power of concentration in the exponent as well.⁴⁹ In this model the dependence of the conductance on the concentration of HSO_4^- is given by the function,

$$G \propto \sigma = e\mu_{Hall} \left[\exp\left(\frac{-\Delta F^0}{RT} - 2P\sqrt{\psi} \right) C_{HSO_4^-} \right]^{1/2} \quad (64)$$

where e is the elementary charge, μ_{Hall} is the Hall mobility, ΔF^0 is the standard free energy change for the dissociation of H_2SO_4 , T is the absolute temperature, ψ is the ionic strength, $C_{HSO_4^-}$ is the concentration of HSO_4^- , and P is the permittivity constant, which is defined as,

$$P = \left(\frac{e^3}{\epsilon_w k_B T} \right)^{3/2} \sqrt{2\pi N_A / 1000} \quad (65)$$

where ϵ_w is the dielectric constant of water, k_B is Boltzmann's constant, and N_A is Avogadro's number. Their model predicts that electronic conduction dominates at low temperature and protonic conduction at high temperature,⁴⁹ which is opposite to the case where no aqueous layer is present.

4.4. Mixed Kinetic + Semiconductor-Physics Model

In an attempt to describe the effect of water vapor on the conductance of tin dioxide, Gaman et al. developed a model that includes the contributions of both band bending/Schottky barriers at grain boundaries and adsorption kinetics.² The authors started with an Arrhenius-type relationship between conductance and temperature where the activation energy physically corresponds to the Schottky barrier due to band bending at SnO_2 grain boundaries. Then, in a similar fashion to the work of Wlodek

et al.⁵³ they developed the following kinetic model for $G(p_{H_2O}, p_{H_2})$. The functional form is,

$$G = \exp \left[\frac{e\varphi_s(p_{H_2O})}{kT} \frac{\eta p_n}{1 + \eta n_{H_2}} \left(2 - \frac{\eta n_{H_2}}{1 + \eta n_{H_2}} \right) \right] \quad (66)$$

where $e\varphi_s$ is the Schottky barrier (which depends on the humidity), η is a simplifying constant, and n_{H_2} is the concentration of H_2 .²

5. CONCLUSIONS

The dependence of the conductance on temperature and the partial pressure of adsorbing gasses is of central importance in several fields, most notably gas sensing and catalysts. This paper reviews the physical origins of various mathematical models that are in common usage, describing in detail the connection between their mathematical form and fundamental physical and chemical principles.

There are two popular simple models for describing $G(T, p)$: the Arrhenius Equation for $G(T)$ and the Power Law Model for $G(p)$.

Models based on the Arrhenius equation are most often used to describe the thermal dependence of conductance. The Arrhenius expression has its origins in microscopic kinetic theory and is generally applicable when there is a key energy barrier to the transport of charge. The barrier can often be identified as a Schottky barrier at a surface or inter-grain interface, but may also arise from the valence-band/conduction-band gap in a semiconductor. When the charge carrier is an atomic or molecular ion, a model with Arrhenius-like terms may arise as well. In such a case, the energy barrier will correspond to a physical hopping barrier to movement of the charged species.

Power-law models are most often used to describe conductance as a function of adsorbate gas partial pressure. They generally have their origins in classical reaction kinetics. The rate equations for these processes are written as functions of the concentrations of the reactant and product species raised to powers of their stoichiometric coefficients, leading to the appearance of power terms in the derived conductance model. More elegantly, the same laws can be derived by reference to the partition function for physisorbed and chemisorbed states that appear in the solution of the Schrödinger equation for the system of an adsorbate interacting with a surface.

In many cases, simple Arrhenius or power-law models are sufficient to reliably describe $G(T, p)$ over the range of temperatures and pressure of interest. Mixed conductance models that incorporate both kinetics and semiconductor physics have also been successfully applied. Mott's conductance models are based on charge-particle hopping theory. Representative applications are to phosphate gasses and conducting polymers.

APPENDIX A

To derive a relationship between the areal density of physisorbed oxygen and temperature and gas partial pressure, roughly following Clifford,¹⁵ we start by considering the adsorption reaction:



where ($\text{O}_{2(\text{g})}$) denotes gas phase molecular oxygen, (V) denotes a vacant surface physisorption site and ($\text{O}_{2(\text{ad})}$) denotes physisorbed molecular oxygen. Assuming that adsorption and desorption are elementary processes we may write the rate (r_f) for the adsorption process as,

$$r_f = k_f p_{\text{O}_2} [S(E) - n_p(E) - n_t(E)] \quad (\text{A2})$$

Here k_f is the rate constant for the adsorption process, p_{O_2} is the partial pressure of oxygen gas, $S(E)$ is the density (in energy) of physisorption sites, n_t is the density (in energy) of ionosorbed oxygen, and n_p is the density (in energy) of physisorbed oxygen. Note that the density of surface vacancies (the quantity in square braces in Eq. (A2)) is given by the total density of physisorption sites minus the density of sites tied up in ionosorption minus the density of sites tied up in physisorption. Similarly, the rate (r_r) for the desorption process may be written as

$$r_r = k_r n_p(E) = v_0 \exp[-(E_g - E)/kT] n_p(E) \quad (\text{A3})$$

Here (k_r) is the rate constant for the desorption process. As shown in the RHS of Eq. (A3), this rate constant may be written as an attack frequency (v_0) times a Boltzmann probability that the system has sufficient energy to reach the desorbed state. The gas-phase potential of the physisorbate is denoted E_g , a value which effectively sets the zero of potential.

Since equilibrium between adsorption and desorption is achieved very rapidly, Eq. (A2) may be equated to (A3) and rearranged to yield an expression for the density (in energy) of physisorbed oxygen ($n_p(E)$),

$$\begin{aligned} k_f p_{\text{O}_2} S(E) - k_f p_{\text{O}_2} n_p(E) - k_f p_{\text{O}_2} n_t(E) \\ = v_0 \exp[-(E_g - E)/kT] n_p(E) \end{aligned} \quad (\text{A4})$$

It follows that the density (in energy) of physisorbed oxygen is given by,

$$n_p(E) = \frac{S(E) - n_t(E)}{1 + (a p_{\text{O}_2})^{-1} \exp[-(E_g - E)/kT]} \quad (\text{A5})$$

where ($k_f/v_0 \equiv a$). Using standard thermodynamics, the chemical potential of the surface physisorbed molecular oxygen (μ_s) is,

$$\mu_s = E_g + kT \ln(a p_{\text{O}_2}) \quad (\text{A6})$$

Substituting for E_g in Eq. (A5) yields,

$$n_p(E) = \frac{S(E) - n_t(E)}{1 + \exp[(E - \mu_s)/kT]} \quad (\text{A7})$$

To find the areal density of physisorbed molecular oxygen one integrates over energy.

$$N_p = \int_{-\infty}^{E_g} n_p(E) dE \quad (\text{A8})$$

Note that Lantto³ refers to this quantity as N_s . Here we are loosely following Clifford¹⁵ and therefore denote it N_p .

To proceed from here, two assumptions are made. First, the Weisz limitation²⁸ restricts the magnitude of the surface charge to a small near constant, $n_t(E)$, which is assumed negligible. Second, the distribution in energy of physisorption sites is assumed to be exponential,

$$S(E) = \frac{N_0}{E_0} \exp[-(E_g - E)/E_0] \quad (\text{A9})$$

where (E_0) is a parameter having units of energy, which is characteristic of the surface and sets the state density. A typical value of E_0 is 0.2 eV.³ With these two assumptions, the areal density of physisorbed molecular oxygen may be approximated by

$$N_p = \frac{N_0}{E_0} \int_{-\infty}^{E_g} \frac{\exp[-(E_g - E)/E_0]}{1 + \exp[(E - \mu_s)/kT]} dE \quad (\text{A10})$$

Note the upper limit of integration is the gas-phase potential of the physisorbate. Physisorbed states higher than this in energy are not relevant since they are not energetically accessible. The lower limit of integration is sometimes set to zero for convenience, but doing so is only valid for $E_g \gg \mu_s \gg 0$; a condition that can typically be met with a judicious choice of the zero of potential. A graph depicting the integrand of Eq. (A10) is shown in Figure A1 for typical values (in eV): $E_g = 2$, $\mu_s = E_g - 0.5$, $E_0 = 0.2$ and $kT = 0.05$.

Note that E_0 sets the rate of growth of the exponential distribution and μ_s sets the point where the distribution

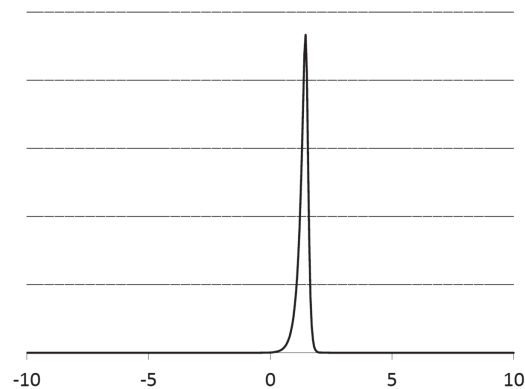


Fig. A1. Integrand of Eq. (A10) as a function of E . Note the dependent variable is essentially zero for values $E \leq 0$.

gets shut off with increasing energy. kT determines the rate at which the function is shut off around μ_s . At higher temperatures, the distribution gets shut off more slowly with increasing energy. Under these conditions the function is effectively zero for $E < 0$, therefore this is a case where the lower limit of integration could be set to zero for convenience. The integrand essentially simplifies to zero for $E > E_g$, so the upper limit of integration may reasonably be set anywhere from E_g to $+\infty$.

The integral in Eq. (A10) can be approximated through application of the Sommerfeld expansion. To apply this technique, the integral is written as

$$N_p = \frac{N_0}{E_0} \int_{-\infty}^{\infty} \frac{H(E)}{1 + \exp[\beta(E - \mu)]} dE \quad (\text{A11})$$

The substitutions,

$$H(E) = \exp[(E - E_g)/E_0] \quad (\text{A12})$$

as well as $\beta = (kT)^{-1}$ and $\mu = \mu_s$ bring Eq. (A10) into the form of (A11). According to the Sommerfeld expansion, the solution may be approximated by

$$N_p \approx \frac{N_0}{E_0} \left\{ \int_{-\infty}^{\mu} H(E) dE + \frac{\pi^2}{6} \left(\frac{1}{\beta} \right)^2 H'(\mu) + O\left(\frac{1}{\beta\mu} \right)^4 \right\} \quad (\text{A13})$$

Here $H'(\mu) = dH(E)/dE|_{E=\mu}$, and $O(1/\beta\mu)^4$ denotes terms of order $(1/\beta\mu)^4$. The latter are neglected here. It follows that

$$N_p \approx \frac{N_0}{E_0} \left\{ \exp(-E_g/E_0) \int_{-\infty}^{\mu} \exp(E/E_0) dE + \frac{\pi^2}{6} \left(\frac{1}{\beta} \right)^2 \frac{dH(E)}{dE} \Big|_{E=\mu} \right\} \quad (\text{A14})$$

Evaluating the integral yields

$$N_p \approx \frac{N_0}{E_0} \left\{ \exp(-E_g/E_0) E_0 [\exp(\mu/E_0) - \exp(-\infty/E_0)] + \frac{\pi^2}{6} \left(\frac{1}{\beta} \right)^2 \frac{dH(E)}{dE} \Big|_{E=\mu} \right\} \quad (\text{A15})$$

Evaluating the derivative yields

$$N_p \approx \frac{N_0}{E_0} \left\{ \exp(-E_g/E_0) E_0 \exp(\mu/E_0) + \frac{\pi^2}{6} \left(\frac{1}{\beta} \right)^2 \times \left(\frac{1}{E_0} \right) \exp(-E_g/E_0) \exp(\mu/E_0) \right\} \quad (\text{A16})$$

Since $E_g \gg E_0$, the second term within the braces effectively evaluates to zero and the expression reduces to

$$N_p \approx \frac{N_0}{E_0} \{ \exp(-E_g/E_0) E_0 \exp(\mu/E_0) \} \quad (\text{A17})$$

which simplifies to

$$N_p \approx N_0 \left\{ \exp\left[\frac{\mu - E_g}{E_0} \right] \right\} \quad (\text{A18})$$

Using the thermodynamic relation between E_g and μ_s given in (A6) together with the identity $\exp \ln(y) = y^x$ yields

$$N_p \approx N_0 (aP_{O_2})^{kT/E_0} \quad (\text{A19})$$

Equation (A19) gives the pressure and temperature dependence of the areal density of physisorbed molecular oxygen under the assumption of a distribution of physisorption sites that is exponentially distributed in energy.

APPENDIX B: NOTATION

The following is a glossary of notation used herein, in order of appearance.

$G(T, p)$	Conductance, often expressed as a function of temperature and/or pressure.
T	Kelvin temperature.
p	Partial pressure, herein typically of an adsorbate gas. Alternatively used to denote number of moles or as a simple multiplicative factor. The meaning should be clear from the context.
p_{rg}	Partial pressure of a reducing gas.
G_0	Conductance at infinite temperature. (a theoretical value only, infinite temperature would vaporize all materials.)
E_a	Activation energy.
k	Boltzmann constant.
$V(x)$	Potential energy, here a function of some spatial coordinate (x).
ϵ	Permittivity relative to free space.
ϵ_0	Vacuum permittivity.
$\rho(x)$	Charge density, here a function of some spatial coordinate.
q	Unit charge. Alternatively used to denote number of moles. The meaning should be clear from the context.
N_d	Volume density of donors.
w	Depletion depth.
Q_{sc}	Surface charge density.
$V_s = E_B$	Surface potential barrier.
e	Elementary charge.
E_t	Energy of state to which ionosorbate adsorbs.
N_p	Surface density of physisorbed oxygen.
p_{O_2}	Partial pressure of molecular oxygen gas.
$e\eta$	Fermi energy.
ΔE	Energy difference between the surface states (E_t) and the top of the Schottky barrier.
N_0	Parameter characteristic of physisorbed state density at energy of gas phase adsorbate.
$a \equiv \frac{k_f}{v_0}$	Constant defined as the ratio of forward rate constant (k_f) to attack frequency (v_0).
E_0	Parameter having units of energy that sets the physisorbed state density.
v_i	Drift velocity of species indicated by subscript.

n_i	Concentration of species indicated by subscript.	$\delta(z)$	Dirac delta function.
B	Scaling/units-conversion constant.	N_{chem}	Total number of chemisorption sites.
v_0	Attach frequency. (may have second subscript to denote specific species.)	C_v	Units-conversion constant and attempt frequency in Miller-Abrahams expression.
d_i	Hopping distance for species denoted by subscript.	γ	Is the spatial extent of the wavefunction in the Miller-Abrahams expression.
$\rho(T)$	Hopping probability, written as a function of temperature.	R	Distance between localized states in the Miller-Abrahams expression.
E_{bi}	Hopping barrier energy for species denoted by second subscript.	E_{hop}	Is the energy difference between localized states.
E	Energy or electric field. Meaning should be clear from context.	σ_{NNH}	Conductance in the nearest neighbor hopping model.
N_i	Concentration of binding sites.	C_{nn}	Scaling/units-conversion constant in the nearest-neighbor hopping model.
$\theta(T, P)$	Fractional occupancy of surface sites, often written as a function of temperature and adsorbate partial pressure.	σ_{VRH}	Conductance in the variable-range hopping model.
n_i	Surface concentration of adsorbate.	C_{vr}	Scaling/units-conversion constant in the variable-range hopping model.
K_i	Equilibrium constant for desorption reaction of species denoted by subscript.	\bar{R}	Range parameter in variable-range hopping model.
ΔF_i	Free energy of desorption for species denoted by subscript.	T_0	Debye temperature.
R	Gas law constant.	K_0	Equilibrium constant for oxygen vacancy formation.
L_D	Debye length.	$[V_0]$	Concentration of oxygen vacancies.
$[e]$	Surface electron concentration.	K_{Sr}	Equilibrium constant for Sr vacancy formation.
$m \equiv w/L_D$	Reduced depletion depth.	ν_{Hall}	Hall mobility.
R	Resistance.	ΔF^0	Standard free energy change for the dissociation of H_2SO_4 .
R_0	Resistance of bulk material.	ψ	Ionic strength.
k_f and k_r	Forward and reverse rate constants.	$S(E)$	Density (in energy) of physisorption sites.
$\sigma(p)$	Conductivity, written here as function of partial pressure.	n_t	Density (in energy) of ionosorbed oxygen.
μ^{SCR}	Surface charge mobility.	n_p	Density (in energy) of physisorbed oxygen.
$n(z, p)$	Charge density, expressed as a function of normal distance and partial pressure.	E_g	Gas-phase potential of the physisorbate, effectively sets the zero of potential.
\hat{H}	Hamiltonian operator.	μ_s	Chemical potential of surface adsorbate.
$h = \frac{h}{2\pi}$	Planck constant.	$\beta = \frac{1}{kT}$	Reduced Boltzmann constant.
$V_{\text{lattice}}(\vec{r})$	Periodic potential arising from a lattice of ions. (\vec{r} is the spatial coordinate vector.)	$H'(\mu)$	Substitution in Sommerfeld expansion.
$W(\vec{r} - \vec{d})$	Coulomb potential arising from an adatom at position \vec{d} .	$O(x)^4$	Terms of order 4th power in x .
$U(\vec{d})$	Electrostatic adatom-lattice interaction.		
Z_{chem}	Partition function.		
E_{jm}	Energy of state m with j electrons.		
f^+ and f^0	Fractional occupancies of charged and neutral states.		
Φ	Electric potential.		
n^0	Charge density evaluated at the zero of potential.		
$\rho(z)$	Space charge density as a function of the surface normal.		
$n(z)$	Electron concentration as a function of the surface normal.		
$p(z)$	Hole concentration as a function of the surface normal. Concentration as a function of the surface normal.		

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