

Effect of the Electrostatic Field Due to the Surface Monolayer Metal Atoms on the Dissociation of Homonuclear Diatomic Gases in Gas-Metal Surface Reactions

S.V. Raj
Glenn Research Center, Cleveland, Ohio

NASA STI Program . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program plays a key part in helping NASA maintain this important role.

The NASA STI Program operates under the auspices of the Agency Chief Information Officer. It collects, organizes, provides for archiving, and disseminates NASA's STI. The NASA STI Program provides access to the NASA Technical Report Server—Registered (NTRS Reg) and NASA Technical Report Server—Public (NTRS) thus providing one of the largest collections of aeronautical and space science STI in the world. Results are published in both non-NASA channels and by NASA in the NASA STI Report Series, which includes the following report types:

- TECHNICAL PUBLICATION. Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA counter-part of peer-reviewed formal professional papers, but has less stringent limitations on manuscript length and extent of graphic presentations.
- TECHNICAL MEMORANDUM. Scientific and technical findings that are preliminary or of specialized interest, e.g., “quick-release” reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.
- CONTRACTOR REPORT. Scientific and technical findings by NASA-sponsored contractors and grantees.
- CONFERENCE PUBLICATION. Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or co-sponsored by NASA.
- SPECIAL PUBLICATION. Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.
- TECHNICAL TRANSLATION. English-language translations of foreign scientific and technical material pertinent to NASA's mission.

For more information about the NASA STI program, see the following:

- Access the NASA STI program home page at <http://www.sti.nasa.gov>
- E-mail your question to help@sti.nasa.gov
- Fax your question to the NASA STI Information Desk at 757-864-6500
- Telephone the NASA STI Information Desk at 757-864-9658
- Write to:
NASA STI Program
Mail Stop 148
NASA Langley Research Center
Hampton, VA 23681-2199

NASA/TM-20230004019



Effect of the Electrostatic Field Due to the Surface Monolayer Metal Atoms on the Dissociation of Homonuclear Diatomic Gases in Gas-Metal Surface Reactions

S.V. Raj
Glenn Research Center, Cleveland, Ohio

National Aeronautics and
Space Administration

Glenn Research Center
Cleveland, Ohio 44135

April 2023

Acknowledgments

The author thanks Drs. Jon Goldsby and Zach Tuchfeld for reviewing the manuscript and for their valuable comments. This work was supported by the National Aeronautics and Space Administration's (NASA) Space Technology Mission Directorate (STMD) through the Space Nuclear Propulsion (SNP) project.

Level of Review: This material has been technically reviewed by technical management.

Effect of the Electrostatic Field Due to the Surface Monolayer Metal Atoms on the Dissociation of Homonuclear Diatomic Gases in Gas-Metal Surface Reactions

S.V. Raj

National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

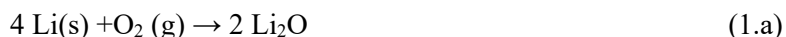
Abstract

The present paper examines the role of an electrostatic field generated by the outermost monolayer of metal ions prior to gas adsorption in aiding the dissociation of homonuclear diatomic gas molecules. The interaction of five homonuclear diatomic gases, Cl₂, F₂, H₂, N₂ and O₂, with several pure metals are examined using Coulomb's law to calculate the attractive and repulsive forces between the electrons or ions in the gas molecule and the free surface metallic electrons or ions assuming a Bohr model. These calculations demonstrate that the total energy of the electrostatic fields from the metals can exceed the molecular binding energies of Cl₂, F₂, and O₂ at some distance from the metallic surface thereby suggesting that these gases interact primarily with the metallic surface in their atomic states after molecular bond dissociation prior to reaction. In contrast, H₂ and N₂ gases do not dissociate prior to reaching the metal surface due to the fact that the effective charge of the gas ions is less than the total electron charge at the outermost electronic shell. The present results correlate linearly with the electrochemical series standard reduction potential as well as with the Pauling electronegativity for several metals.

1.0 Introduction

The corrosive action of reactive gases on metals and alloys is of utmost importance in many engineering applications. The reaction of a gas with the surface of a metal can lead to the formation of either protective or nonprotective reaction products, such as hydrides, nitrides and oxides, between the metal and the gas [1-4]. Therefore, understanding and establishing the fundamental concepts of how corrosive gases react with metallic systems is crucial for developing methods to protect metals and alloys from corrosive attack. The fundamental nature of gas-metal surface reactions has been recognized to be of primary importance of study for over a century [5-15]. Gas-metal surface reactions are commonly encountered in many engineering applications leading to billions of dollars of investment in the development of coatings and other technologies designed to protect components from gaseous corrosive attack. In the specific case of aerospace applications, a few examples of coatings development include thermal barrier coatings for gas turbine engines for aircraft [16,17], and metallic and non-metallic protective coatings for chemical [18] and nuclear thermal propulsion rockets [19].

At a fundamental level, when a gas reacts with a metal surface to form a reaction layer, most chemistry textbooks implicitly assume that the reaction occurs at the surface of the metal involving an electron charge transfer from the metal to the gas atom to form the chemical bond of the reaction product [20,21]. For example, the oxidation of pure lithium with oxygen gas is represented by the chemical equation



This reaction is depicted as a two-step process involving a charge transfer [20]:



In reality, the process is much more complicated involving a number of sub-steps. On deeper reflection, the reaction of the gas with the metal surface must involve other sub-steps, which are not always explicitly stated in textbooks and other publications [2-5], but which must occur before the formation of the final reaction product(s), which in the case of Equation (1.a) is Li_2O . Several sub-steps have been proposed by many models to explain the initiation of a gas-metal surface reaction [2-15]. Briefly, the initiation of a gas-metal surface reaction is assumed to follow the subsequent order of events: (1) The gas molecules collide randomly with the surface of the metal resulting in their velocities being reduced to zero; (2) the gas molecules are adsorbed into the metallic surface by either chemisorption or physisorption; (3) a charge transfer occurs between the adsorbed gas molecule and the metal atoms due to electronegativity differences; (4) the charge transfer results in the dissociation of the gas molecule under the action of Coulomb repulsion and “the filling of antibonding levels” in the adsorbed gas molecules [8]; (5) the direction of the electron spin orientation needs to flip, if necessary, either in the dissociated gas or in the metal atom so as to satisfy Pauli’s exclusion principle before the metal and the dissociated gas atoms can bond [22]; (6) the reaction is formed with the bonding of the gas atom to the metal atom; and (7) the continued growth of the reaction layer occurs by one of the many processes discussed elsewhere primarily involving the diffusion of anions and cations [1-5].

Table I shows the binding energies, $(U_B)_x$ and outer electronic shell configurations, where x is either Cl, F, H, N or O to indicate the gas composition, for five homonuclear diatomic gases [23-25]. It is evident that the magnitudes of $(U_B)_x$, are fairly large so that the dissociation of the stable gaseous molecular bonds would require a lot of energy from an external source. Yet, it is well known that metals, such as aluminum, form a protective oxide scale at room temperature even at very low partial pressures of O_2 . It is also well known that alkali metals are reactive at room temperature if exposed to air or oxygen due to rapid oxidation¹ [3,20,21,26]. These observations suggest that the stable covalent-bonded oxygen molecules had dissociated before recombining with the metal atoms as part of the oxidation process. The fact that the energy required to dissociate the O_2 bond must equal or exceed $498.3 \text{ kJ mol}^{-1}$ (Table I) poses the important question: What is the source of this energy to dissociate the molecular bonds at room temperature? The fact that some metals oxidize at room temperature while others, such as noble metals, do not is indeed curious. Thermal energy alone is insufficient to dissociate oxygen molecules significantly at room temperature since the probability of dissociation of 1 mole of oxygen gas molecules is about 10^{-87} . The dissociation of gaseous molecular bonds by a charge transfer requires a significant diffusion of the gas molecules into the first few atomic layers of the metal. This mechanism is an unlikely rationale at room temperature since the diffusion rates are low for most metals with homologous temperatures less than $0.4 T_m$, where T_m is the absolute melting temperature. Clearly, there must be another force field that is sufficiently strong to dissociate covalent bonded oxygen molecules at room temperature.

¹ The fact that these metals have low melting points does not have any relevance on the dissociation of the oxygen molecules.

TABLE I.—BINDING ENERGIES, (U_B)_x [23], BOND LENGTH, λ [23], OUTER ELECTRON SHELL CONFIGURATION [24], EFFECTIVE NUCLEAR CHARGE AT THE OUTERMOST ELECTRON SHELL, (Z^*)_g [25], NUMBER OF ELECTRONS IN THE DIATOMIC BOND, (q_e)_g [20,21], AND THE VALUES OF CHARGE IN COULOMBS FOR Cl₂, F₂, H₂, N₂ AND O₂

Gas	U_B (T= 298 K), (kJ mol ⁻¹)	Bond length, λ , (m)	Outer shell (Bohr model)	Effective nuclear charge, (Z^*) _g , at the outermost shell (Slater Rules)	Number of electrons in the diatomic bond, (q_e) _g , = 2 x bond order	(Z^*) _g , (C)	(q_e) _g , (C)	(q_e) _g + (Z^*) _g , (C)
Cl ₂	242.6	1.99×10^{-10}	3s ² 3p ⁵	6.10	2	9.76×10^{-19}	-3.2×10^{-19}	6.6×10^{-19}
F ₂	156.9	1.42×10^{-10}	2s ² 2p ⁵	5.20	2	8.32×10^{-19}	-3.2×10^{-19}	5.1×10^{-19}
H ₂	436.0	7.46×10^{-11}	1s ¹	1.00	2	1.60×10^{-19}	-3.2×10^{-19}	-1.6×10^{-19}
N ₂	945.3	1.10×10^{-10}	2s ² 2p ³	3.90	6	6.24×10^{-19}	-9.6×10^{-19}	-3.4×10^{-19}
O ₂	498.3	1.21×10^{-10}	2s ² 2p ⁴	4.55	4	7.28×10^{-19}	-6.4×10^{-19}	8.8×10^{-20}

The objective of the present paper is to examine whether an electrostatic field created by the presence of a positively charged metallic ion surface monolayer at the outermost external surface [27] is adequately strong to cause the dissociation of gas molecules significantly at room temperature. Using Coulomb's law, and assuming a Bohr atomic model for evaluating the effective charges of gas and metal ions for simplicity, the total electrostatic interaction energy, (U_E)_m, of the electrostatic field of a surface metal (m) atom acting on a gas (g) molecule is calculated as a function of the distance between the gas molecules and the metal surface for different metals and five homonuclear diatomic gases, Cl₂, F₂, H₂, N₂ and O₂. The values of (U_E)_m for each metal are compared with the room temperature values of (U_B)_x, (Table I) [23] for each gas in order to examine if (U_E)_m \geq (U_B)_x, which is the condition for the dissociation of the gas molecules. For simplicity, the additional effect of temperature is not considered so that the present calculations are conservative since the effect of temperature would reduce the critical strength of the electrostatic field required to dissociate the gas molecules. For simplicity, it is noted that the present model considers the Coulombic forces between the outermost electronic shell of a metal atom and the bond plane of a gas molecule. The essential question that the paper tries to answer is: Are the electrostatic Coulomb forces exerted by the outermost electronic shells of the metallic surfaces sufficiently strong to break up the molecular bonds of the homonuclear diatomic gases? While more refined calculations using wave mechanics may provide additional insights, the answer to this question is unlikely to change significantly from the simple approach adopted in the present paper.

2.0 Coulombic Force and Energy Calculations

2.1 Theoretical Approach and Model

Figure 1 is a schematic representation of the metallic bond showing the metal ions surrounded by a sea of electrons in the first few layers of atoms at the free surface. The model considers the total electrostatic field, (E_E)_m, generated by the metal ions of the outermost layer of surface atoms, AA, with an effective nuclear charge of Z_m^* . The total electrostatic force, (F_E)_m, due to (E_E)_m, acting on the gas molecular bond plane, BB, at a distance, d, from the outermost electronic shell of the surface atoms was determined in order to calculate (U_E)_m = (F_E)_m•d.

The magnitude of (F_E)_m is given by

$$(F_E)_m = (F_R)_{mg} + (F_R)_{gm} + (F_A)_{mg} + (F_A)_{gm} \quad (2)$$

where $(F_R)_{mg}$ is the repulsive force between Z_m^* , and the gas, Z_g^* , nuclei, $(F_R)_{gm}$ is the repulsive force between the outer shell metal electrons, $(q_e)_m$, and the number of bonding gas electrons in the diatomic covalent bond, $(q_e)_g$, $(F_A)_{mg}$ is the attractive force between Z_m^* and $(q_e)_m$, and $(F_A)_{gm}$ is the attractive force between Z_m^* and $(q_e)_g$.

The attractive and repulsive forces are given by Coulomb's law [28]

$$(F_A)_{mg} = \left(\frac{(q_e)_m}{4\pi\epsilon_0} \right) \left(\frac{Z_g^*}{d^2} \right) \quad (3.a)$$

$$(F_A)_{gm} = \left(\frac{(q_e)_g}{4\pi\epsilon_0} \right) \left(\frac{Z_m^*}{d^2} \right) \quad (3.b)$$

$$(F_R)_{mg} = \left(\frac{Z_m^*}{4\pi\epsilon_0} \right) \left(\frac{Z_g^*}{d^2} \right) \quad (3.c)$$

$$(F_R)_{gm} = \left(\frac{(q_e)_g}{4\pi\epsilon_0} \right) \left(\frac{(q_e)_m}{d^2} \right) \quad (3.d)$$

where ϵ_0 is the permittivity constant and $\left(\frac{1}{4\pi\epsilon_0} \right) = 8.99 \times 10^9 \text{ N}\cdot\text{m}^2/\text{C}$. Thus,

$$(U_E)_m = (F_E)_m \cdot d = \left(\frac{1}{4\pi\epsilon_0} \right) \left(\frac{(Z_m^* + (q_e)_m)}{d} \right) (Z_g^* + (q_e)_g) \quad (4)$$

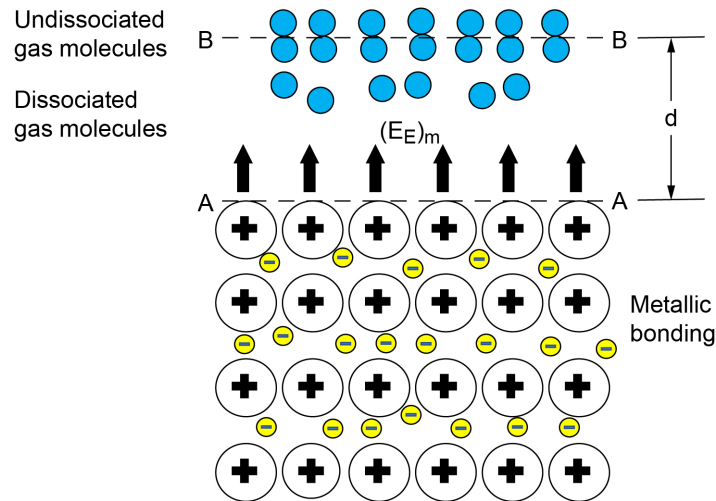


Figure 1.—Schematic showing the metal (m) ions surrounded by a sea of electrons in the first few layers of surface atoms. The electrostatic field, $(E_E)_m$, due to the outermost electron shell of the first layer of atoms in plane, AA, acts on the gas (g) molecules at some distance, d, from the molecular bond plane, BB causing their dissociation when $(U_E)_m \geq (U_B)_x$. where x is either Cl_2 , F_2 , H_2 , N_2 and O_2 .

2.2 Assumptions and Data References

The values of $(U_E)_m$ were calculated for the interaction of several different pure metals (Table II) with five homonuclear diatomic gases, Cl_2 , F_2 , H_2 , N_2 and O_2 (Table I). Table I shows the binding energies, $(U_B)_x$ [23], bond length, λ [23], outer electron shell configuration of the gas atom [24], the magnitudes of $(Z^*)_g$ [25], the magnitudes of $(q_e)_g$ [20,21], and the values of the charges in Coulombs for Cl_2 , F_2 , H_2 , N_2 and O_2 . Table II shows twenty four different pure metals including alkaline, noble, and refractory metals that were analyzed. Other data shown in Table II include the electron configuration in the outermost shell of the metal [20], the magnitudes of $(q_e)_m$ [24], the magnitudes of $(Z^*)_m$ [25], the values of the charges in Coulombs, Pauling electronegativity, χ , [21], and electrochemical series standard reduction potential, E^0 , [29].

TABLE II.—DESCRIPTION OF THE PURE METAL, ELECTRON CONFIGURATION IN THE OUTERMOST SHELL, NUMBER OF ELECTRONS IN THE OUTERMOST SHELL, $(q_e)_m$, [24], EFFECTIVE NUCLEAR CHARGE AT THE OUTERMOST ELECTRON SHELL, $(Z^*)_m$ [25], THE VALUES OF CHARGE IN COULOMBS, ELECTRONEGATIVITY, χ , [21], AND ELECTROCHEMICAL SERIES STANDARD REDUCTION POTENTIAL, E^0 , [23,29]

Metal	Outer shell (Bohr model)	Number of electrons in the outer shell, $(q_e)_m$	Effective nuclear charge, $(Z^*)_m$, at the outermost shell (Slater rules)	$(Z^*)_m$, (C)	$(q_e)_m$ (C)	$[(Z^*)_m+(q_e)_m]$ (C)	Electronegativity, χ	E^0 (V)
Al	3s ² 3p ¹	3	3.50	5.60×10 ⁻¹⁹	-4.8×10 ⁻¹⁹	8.0×10 ⁻²⁰	1.5	-1.6620
Ag	5s ¹	1	4.20	6.72×10 ⁻¹⁹	-1.6×10 ⁻¹⁹	5.1×10 ⁻¹⁹	1.9	0.7996
Au	6s ¹	1	3.70	5.92×10 ⁻¹⁹	-1.6×10 ⁻¹⁹	4.3×10 ⁻¹⁹	2.4	1.6800
Be	2s ²	2	1.95	3.12×10 ⁻¹⁹	-3.2×10 ⁻¹⁹	-8.0×10 ⁻²¹	1.5	-1.8470
Ca	4s ²	2	2.85	4.56×10 ⁻¹⁹	-3.2×10 ⁻¹⁹	1.4×10 ⁻¹⁹	1.0	-2.7600
Co	4s ²	2	3.90	6.24×10 ⁻¹⁹	-3.2×10 ⁻¹⁹	3.0×10 ⁻¹⁹	1.9	-0.2800
Cr	4s ¹	1	3.45	5.52×10 ⁻¹⁹	-1.6×10 ⁻¹⁹	3.9×10 ⁻¹⁹	1.6	-0.9130
Cu	4s ¹	1	4.20	6.72×10 ⁻¹⁹	-1.6×10 ⁻¹⁹	5.1×10 ⁻¹⁹	1.9	0.5220
Fe	4s ²	2	3.75	6.00×10 ⁻¹⁹	-3.2×10 ⁻¹⁹	2.8×10 ⁻¹⁹	1.8	-0.4090
Hf	6s ²	2	3.15	5.04×10 ⁻¹⁹	-3.2×10 ⁻¹⁹	1.8×10 ⁻¹⁹	1.3	-1.5500
Li	2s ¹	1	1.30	2.08×10 ⁻¹⁹	-1.6×10 ⁻¹⁹	4.8×10 ⁻²⁰	1.0	-3.0450
Mg	3s ²	2	2.85	4.56×10 ⁻¹⁹	-3.2×10 ⁻¹⁹	1.4×10 ⁻¹⁹	1.2	-2.3750
Mo	5s ¹	1	3.45	5.52×10 ⁻¹⁹	-1.6×10 ⁻¹⁹	3.9×10 ⁻¹⁹	1.8	-0.2000
Na	3s ¹	1	2.20	3.52×10 ⁻¹⁹	-1.6×10 ⁻¹⁹	1.9×10 ⁻¹⁹	0.9	-2.7100
Nb	5s ¹	1	3.30	5.28×10 ⁻¹⁹	-1.6×10 ⁻¹⁹	3.7×10 ⁻¹⁹	1.6	-1.0990
Ni	4s ²	2	4.05	6.48×10 ⁻¹⁹	-3.2×10 ⁻¹⁹	3.3×10 ⁻¹⁹	1.9	-0.2300
Pb	6s ² 6p ²	4	5.65	9.04×10 ⁻¹⁹	-6.4×10 ⁻¹⁹	2.6×10 ⁻¹⁹	1.9	-0.1263
Pt	6s ¹	1	3.55	5.68×10 ⁻¹⁹	-1.6×10 ⁻¹⁹	4.1×10 ⁻¹⁹	2.2	1.1800
Ta	6s ²	2	3.30	5.28×10 ⁻¹⁹	-3.2×10 ⁻¹⁹	2.1×10 ⁻¹⁹	1.5	-0.6000
Ti	4s ²	2	3.15	5.04×10 ⁻¹⁹	-3.2×10 ⁻¹⁹	1.8×10 ⁻¹⁹	1.5	-1.6300
V	4s ²	2	3.30	5.28×10 ⁻¹⁹	-3.2×10 ⁻¹⁹	2.1×10 ⁻¹⁹	1.6	-1.1750
W	6s ²	2	3.45	5.52×10 ⁻¹⁹	-3.2×10 ⁻¹⁹	2.3×10 ⁻¹⁹	1.7	0.1000
Y	5s ²	2	3.00	4.80×10 ⁻¹⁹	-3.2×10 ⁻¹⁹	1.6×10 ⁻¹⁹	1.2	-2.3720
Zn	4s ²	2	4.35	6.96×10 ⁻¹⁹	-3.2×10 ⁻¹⁹	3.8×10 ⁻¹⁹	1.6	-0.7628
Zr	5s ²	2	3.15	5.04×10 ⁻¹⁹	-3.2×10 ⁻¹⁹	1.8×10 ⁻¹⁹	1.4	-1.4500

Certain assumptions were made to simplify the calculations of $(U_E)_m$ without getting into details of quantum mechanics as discussed below:

- a) As mentioned earlier, the effect of temperature is ignored. Thus, the values of $(U_E)_m$ calculated in this paper are higher than the energy actually required to dissociate the molecular bonds of the gases if thermal energy is included. Although the calculations are strictly valid for 0 K, the fact that the experimental values of $(U_B)_x$ are reported for 298 K [23], the figures indicate that the comparisons are made at 298 K instead of 0 K. The crossover points of the curves for the different metals would shift to higher values of d if thermal energy was included.
- b) The values of Z_g^* and Z_m^* were calculated for the outermost electron shell of the atoms using the Slater rule to account for electron shielding effects assuming that the atoms can be represented by a Bohr model [30]. An online calculator was used for calculating these values for each metal and gas [25].
- c) Since the five homonuclear diatomic gases investigated in this paper form a covalent bond with a bond order, N , each containing two electrons that need to be separated by $(F_E)_m$ to cause the complete dissociation of the gases, the magnitude of $(q_e)_g = 2N$.
- d) The magnitudes of $(q_e)_m$ for the metal atoms were determined for the outermost electron shell [20,24]. An online tool was used to determine the number of valence electrons in the outermost shell [24].
- e) The present analyses implicitly assume that the gases are dry. The effect of moisture in the gases is likely to change the magnitudes of the electrostatic forces.

3.0 Results and Discussion

3.1 Metal-Chlorine Interactions

Figure 2 shows the variation of $(U_E)_m$ with increasing values of d for metal- Cl_2 gas interaction for Al, Ag, Cr, Li, Mg, Mo, Na, and Zr, where the horizontal broken line represents the value of $(U_B)_{\text{Cl}} = 242.6 \text{ kJ mol}^{-1}$ at 298 K [23] so that the gas molecules will dissociate when $(U_E)_m > (U_B)_{\text{Cl}}$ under the electrostatic field. It is important to note that $d = 0 \text{ nm}$ is the free surface of the metal so that $(U_E)_m \leq (U_B)_{\text{Cl}}$ at a value of $d = 0 \text{ nm}$ indicates that the undissociated gas molecules are adsorbed at the metal surface.² An examination of Figure 2 reveals that Cl_2 is not adsorbed by any of the metals shown in the figure.³ Instead, the gas molecules dissociate due to the force generated by $(E_E)_m$ when $0 < d \leq d_c$, where d_c is the critical distance at which $(U_E)_m = (U_B)_{\text{Cl}}$, depending on the metal. Interestingly, the $(U_E)_m - d$ curves shift to lower values of d for more reactive metals, such as Al and Li, where the position of the curve for each metal with respect to other metals is acutely dependent on the relative magnitudes of $(Z_m^* + (q_e)_m)$. Metals with lower values of $(Z_m^* + (q_e)_m)$ generate weaker Coulombic forces, $(F_E)_m$, so that the dissociation of the gas molecular bonds are more likely to occur closer to the free surface of the metal as $(F_E)_m$ increases with decreasing values of d than for noble metals, such as Ag and Au, with higher values of $(Z_m^* + (q_e)_m)$. When the bond dissociation occurs closer to the metal surface, it is more

² A negative value of $d < 0 \text{ nm}$ does not have any physical meaning. Thus, only values of $d \geq 0 \text{ nm}$ are considered in this paper so that $d < 0 \text{ nm}$ is assumed to be $d = 0 \text{ nm}$.

³ Beryllium is an exception for which $(Z_m^* + (q_e)_m) = -4.8 \times 10^{-21} \text{ C}$ due to the fact that Z_m^* is smaller than $(q_e)_m$. Thus, the magnitudes of $(U_E)_{\text{Be}} < (U_B)_x$ as a function of d are negative when the metal interacts with Cl_2 , F_2 and O_2 . Notably, $(U_E)_{\text{Be}} < (U_B)_x$ for H_2 and N_2 for $d > d_c = 0.01 \text{ nm}$. Thus, H_2 and N_2 may either dissociate very close to the Be surface or be adsorbed at the surface due to the very low value of d_c .

likely that the gas atoms will react with the metal as the attractive forces of the metal ions pull the dissociated gas molecules towards them. In contrast, when the bond dissociation occurs at a greater distance from the metal surface, it is more likely that the dissociated gas molecules will disperse away from the metal surface under the action of thermal convection. Thus, the gas is less likely to react with the metal, and these metals are less reactive, such as the noble metals.

Figure 3(a) and (b) show the variations of E^0 and χ against d_c . Both plots show that E^0 and χ increase linearly with increasing d_c . The most reactive metals with more negative values of E^0 and lower values of χ are clustered at lower values of d_c while the more noble metals exhibit more positive values of E^0 and higher values of χ clustering at higher values of d_c . The linear relation between E^0 and d_c and that between χ and d_c are given by Equations (5.a) and (5.b), respectively:

$$E^0 = 0.50d_c - 2.82 \quad (\text{V}) \quad (R_d^2 = 0.648) \quad (5.a)$$

$$\chi = 0.13d_c + 1.10 \quad (R_d^2 = 0.509) \quad (5.b)$$

In Equation (5.a), E^0 has a unit of V with the slope and the intercept having units of V/nm and V, respectively. On the other hand, Equation (5.b) is unitless.

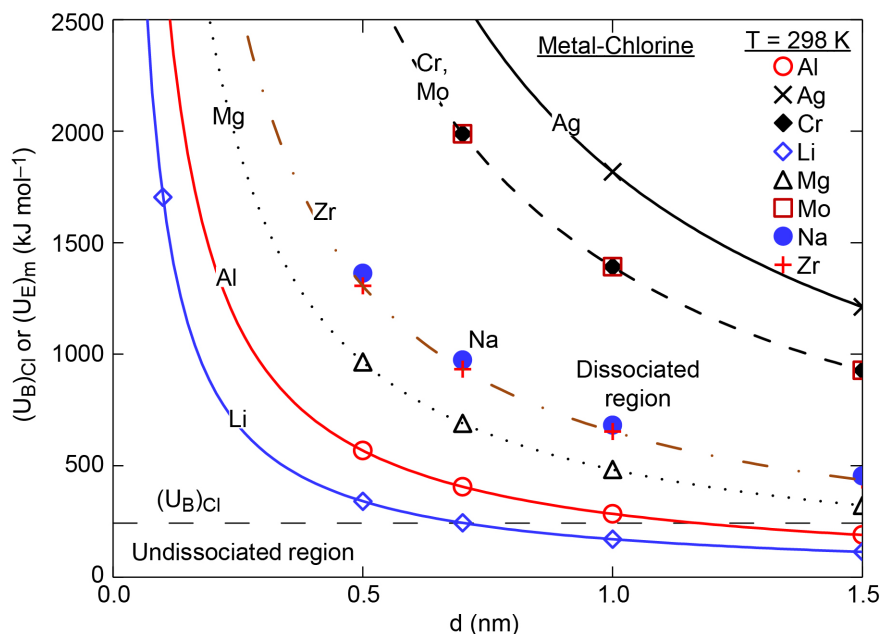


Figure 2.—Plot of $(U_E)_m$ against d for Al, Ag, Cr, Li, Mg, Mo, Na, and Zr, where $d = 0$ is the surface of the metal. The magnitude of $(U_B)_{Cl} = 242.6 \text{ kJ mol}^{-1}$ [23] is represented by the broken horizontal line, where the region $(U_E)_m > (U_B)_{Cl}$ indicates that the Cl_2 molecules dissociate under the action of $(E_E)_m$.

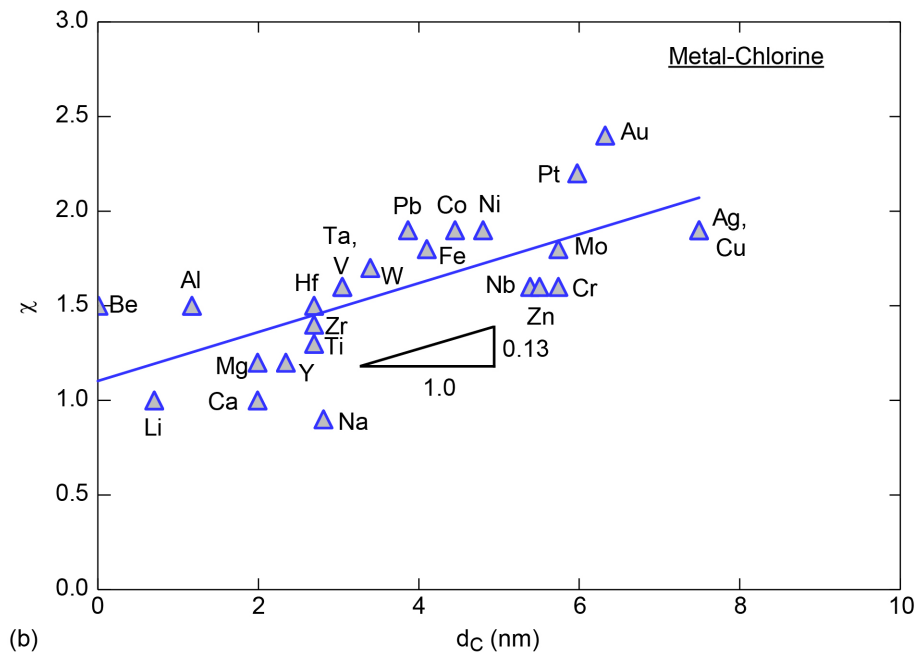
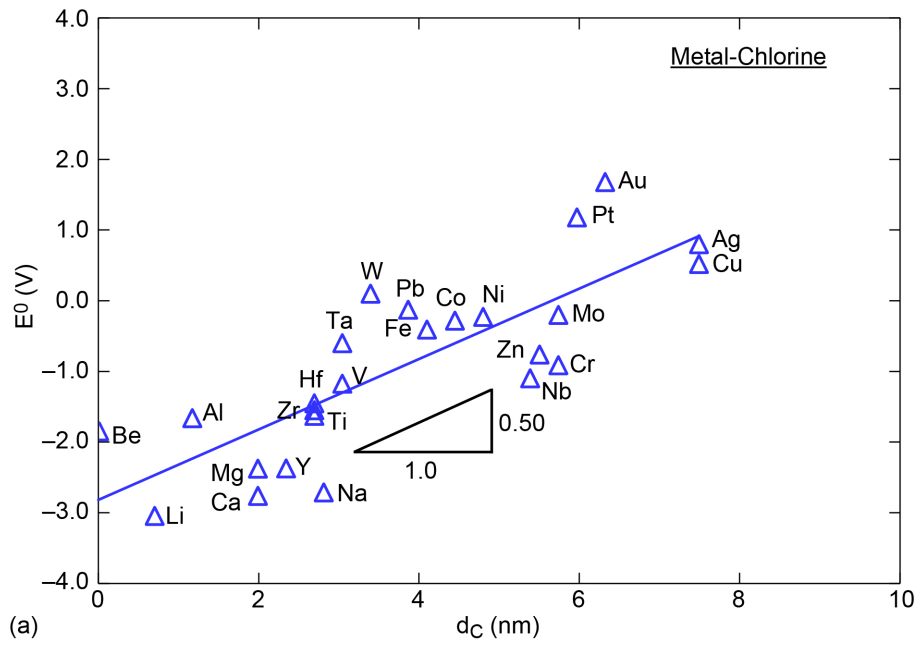


Figure 3.—Correlation of (a) E^0 [23,29] and (b) χ [21] with d_c for several metals prior to reacting with chlorine gas demonstrating that reactive metals with lower values of E^0 and χ have low values of d_c and noble metals have high values of d_c .

3.2 Metal-Fluorine Interactions

Figure 4 shows a similar variation of $(U_E)_m$ with increasing values of d for metal- F_2 gas interactions for Al, Ag, Cr, Li, Mg, Mo, Na, and Zr as in Figure 2. The horizontal broken line represents the value of $(U_B)_F = 156.9 \text{ kJ mol}^{-1}$ at 298 K [23]. Just as in the case of the chlorine molecules, the fluorine molecules also dissociate prior to reaching the metal surface under the action of the electrostatic field. One significant difference between the metal-chlorine and the metal-fluorine interactions is that the values of $(d_c)_F > (d_c)_{Cl}$, where $(d_c)_F$ and $(d_c)_{Cl}$ are the values of d_c for F_2 and Cl_2 , respectively. Figure 5(a) and (b) confirm that E^0 and χ increase linearly with increasing d_c consistent with the results shown in Figure 3(a) and (b) including identical magnitudes of the intercepts at $d_c = 0 \text{ nm}$.

The linear relation between E^0 and d_c and that between χ and d_c are given by Equations (6.a) and (6.b), respectively:

$$E^0 = 0.41d_c - 2.82 \quad (\text{V}) \quad (R_d^2 = 0.648) \quad (6.a)$$

$$\chi = 0.11d_c + 1.10 \quad (R_d^2 = 0.509) \quad (6.b)$$

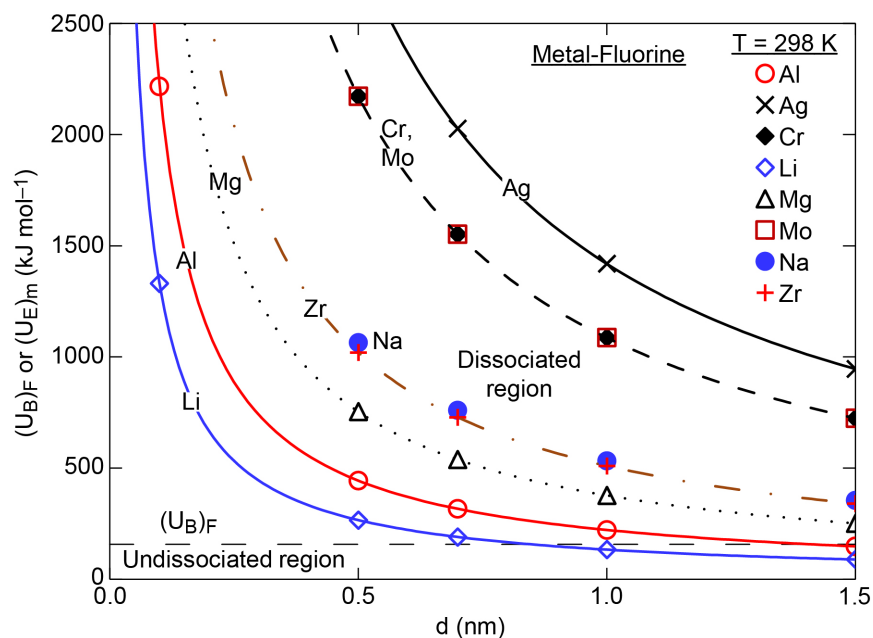


Figure 4.—Plot of $(U_E)_m$ against d for Al, Ag, Cr, Li, Mg, Mo, Na, and Zr, where $d = 0$ is the surface of the metal. The magnitude of $(U_B)_F = 156.9 \text{ kJ mol}^{-1}$ [23] is represented by the broken horizontal line, where the region $(U_E)_m > (U_B)_F$ indicates that the F_2 molecules dissociate under the action of $(E_E)_m$.

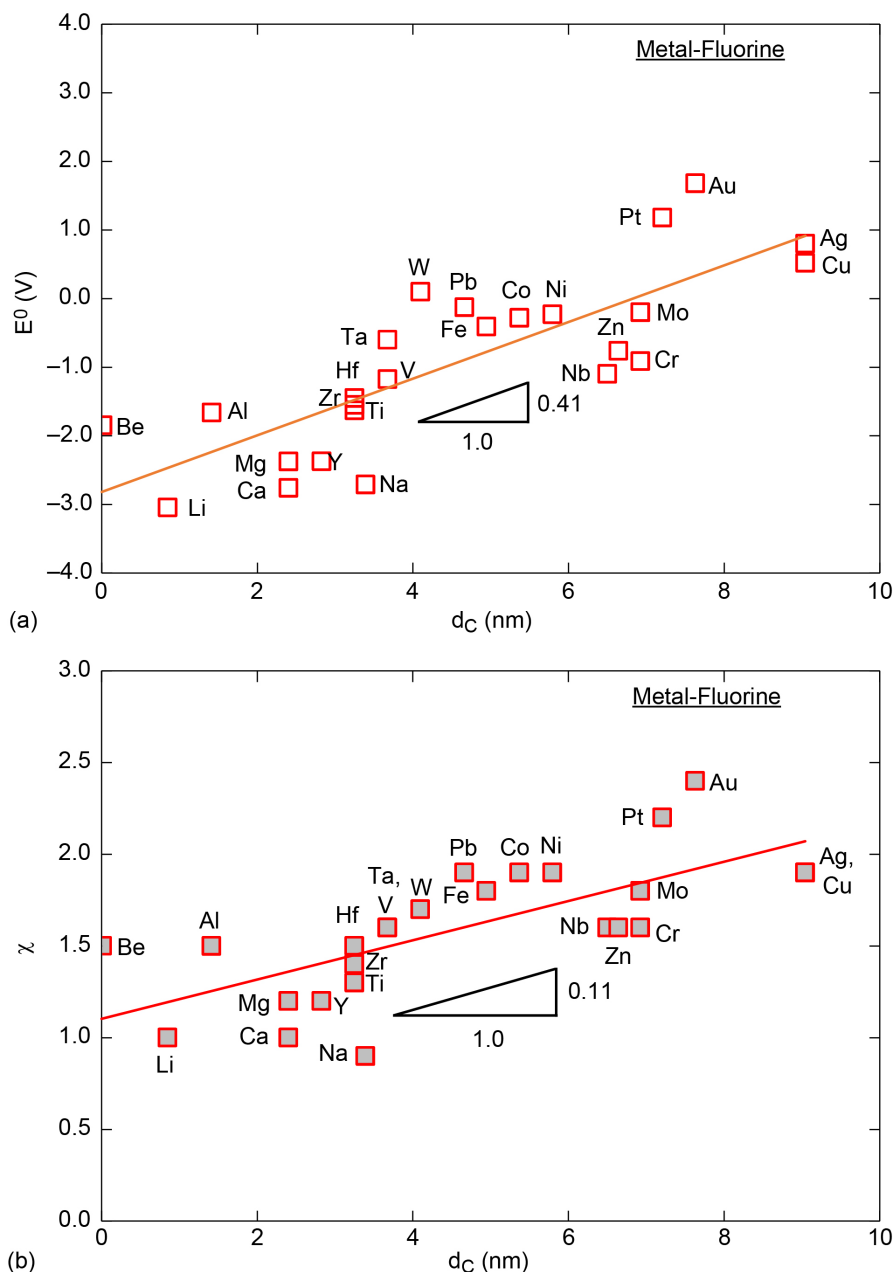


Figure 5.—Correlation of (a) E^0 [23,29] and (b) χ [21] with d_c for several metals prior to reacting with fluorine gas demonstrating that reactive metals with lower values of E^0 and χ have low values of d_c and noble metals have high values of d_c .

3.3 Metal-Hydrogen and Metal-Nitrogen Interactions

The plots of $(U_E)_m$ against d for Al, Ag, Cr, Li, Mg, Mo, Na, and Zr are vastly different for metal-hydrogen (Figure 6) and metal-nitrogen interactions (Figure 7) than those for Cl_2 (Figure 2) and F_2 (Figure 4). An examination of Figure 6 and Figure 7 reveals that $(U_E)_m < (U_B)_H$ and $(U_E)_m < (U_B)_N$ for hydrogen and nitrogen, respectively, where $(U_B)_H = 436.0 \text{ kJ mol}^{-1}$ and $(U_B)_N = 945.3 \text{ kJ/mol}$ (Table I) [23], with the values of $(U_E)_m$ increasingly negative in magnitude with decreasing values of d . Both these gases do not dissociate under the action of the electrostatic field because $(Z_g^* + (q_e)_g) < 0$ (Table I). Unlike Cl_2 , F_2 and O_2 for which $Z_g^* > (q_e)_g$, the values of $Z_g^* < (q_e)_g$ for H_2 and N_2 so that the latter

gases are adsorbed at the metal surface where the dissociation of the gas molecules presumably occurs by a different mechanism similar to those described elsewhere [8,9,11,12,14,15].

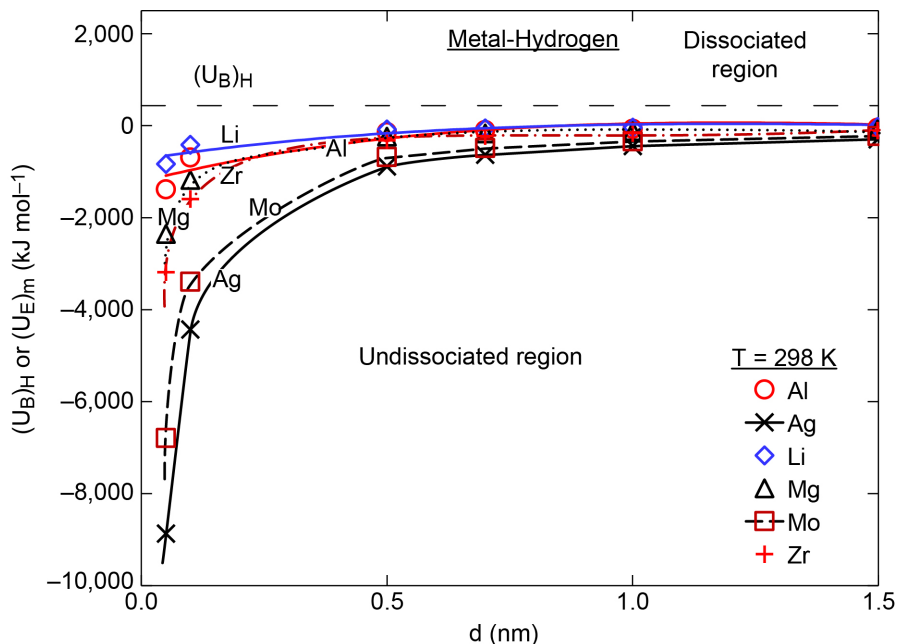


Figure 6.—Plot of $(U_E)_m$ against d for Al, Ag, Cr, Li, Mg, Mo, Na, and Zr, where $d = 0$ is the surface of the metal. The magnitude of $(U_B)_H = 436.0 \text{ kJ mol}^{-1}$ [23] is represented by the broken horizontal line, where the region $(U_E)_m > (U_B)_H$ indicates that the region where H_2 molecules dissociate under the action of $(E_E)_m$.

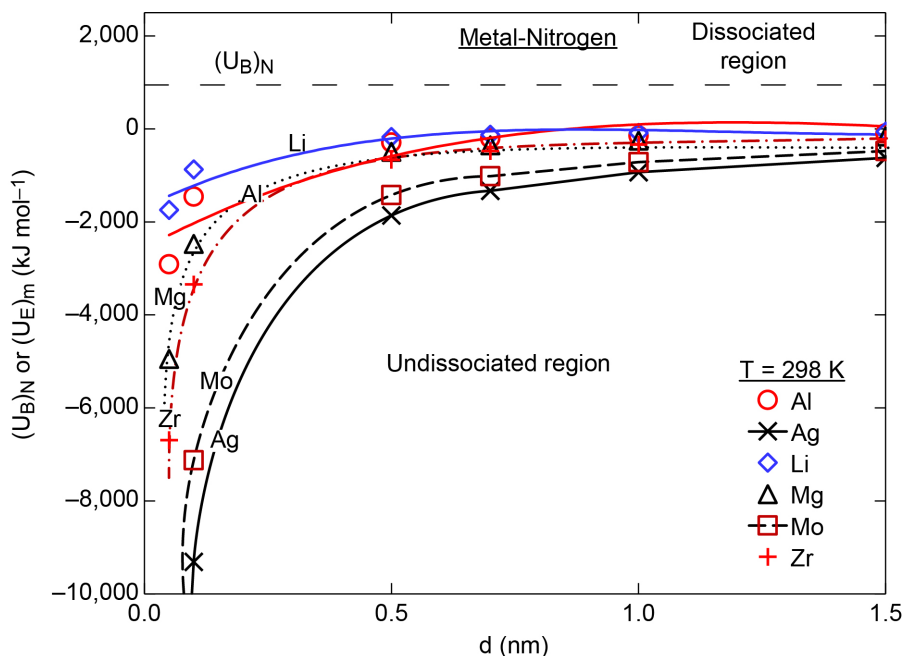


Figure 7.—Plot of $(U_E)_m$ against d for Al, Ag, Cr, Li, Mg, Mo, Na, and Zr, where $d = 0$ is the surface of the metal. The magnitude of $(U_B)_N = 945.3 \text{ kJ mol}^{-1}$ [23] is represented by the broken horizontal line, where the region $(U_E)_m > (U_B)_N$ indicates that the region where N_2 molecules dissociate under the action of $(E_E)_m$.

3.4 Metal-Oxygen Interactions

Figure 8 shows the variation of $(U_E)_m$ against d for Al, Ag, Cr, Li, Mg, Mo, Na, and Zr for metal-oxygen interactions. The horizontal broken line represents the value of $(U_B)_O = 498.3 \text{ kJ mol}^{-1}$ at 298 K [23]. The variation of $(U_E)_m$ with d follows the same trend as shown in Figure 2 and Figure 4 for Cl_2 and F_2 , respectively, with the magnitudes of $(U_E)_m$ increasing with decreasing values of d . The curves cross the $(U_B)_O$ horizontal line from the undissociated to the dissociated region at $d = d_c$ indicating that the oxygen molecules are dissociated by the electrostatic field before reaching the metal surface. Clearly, the oxygen molecules are not adsorbed by the metal surface but instead react with the metal as individual gas atoms. The O_2 molecules dissociate at higher values of d for the noble metals than for the reactive metals, which suggests that the oxygen atoms can diffuse away from the metal surface instead of reacting with it thereby allowing these metals to remain in their pristine state at room temperature. Significantly, the present results do not support the assumptions made by several metal-oxygen interaction models that assume that the oxygen molecules are first adsorbed at the metal surface prior to their dissociation into atoms and interaction with the metal [5,7,8,10,13].

Figure 9(a) and (b) show that the magnitudes of E^0 and χ increase linearly with increasing values of d_c similar to the observations for the halogen gases (Figure 3 and Figure 4). The linear relation between E^0 and d_c and that between χ and d_c are given by Equations (7.a) and (7.b), respectively:

$$E^0 = 7.63d_c - 2.82 \quad (\text{V}) \quad (R_d^2 = 0.648) \quad (7.a)$$

$$\chi = 1.98d_c + 1.10 \quad (R_d^2 = 0.509) \quad (7.b)$$

These correlations are stronger than those for Cl_2 (Eqs. (5.a) and (5.b)) and F_2 (Eqs. (6.a) and (6.b)). Once again, the magnitudes of the intercepts at $d_c = 0 \text{ nm}$ are identical to the values given by Equations (5.a) and (5.b) and (6.a) and (6.b) for Cl_2 and F_2 , respectively.

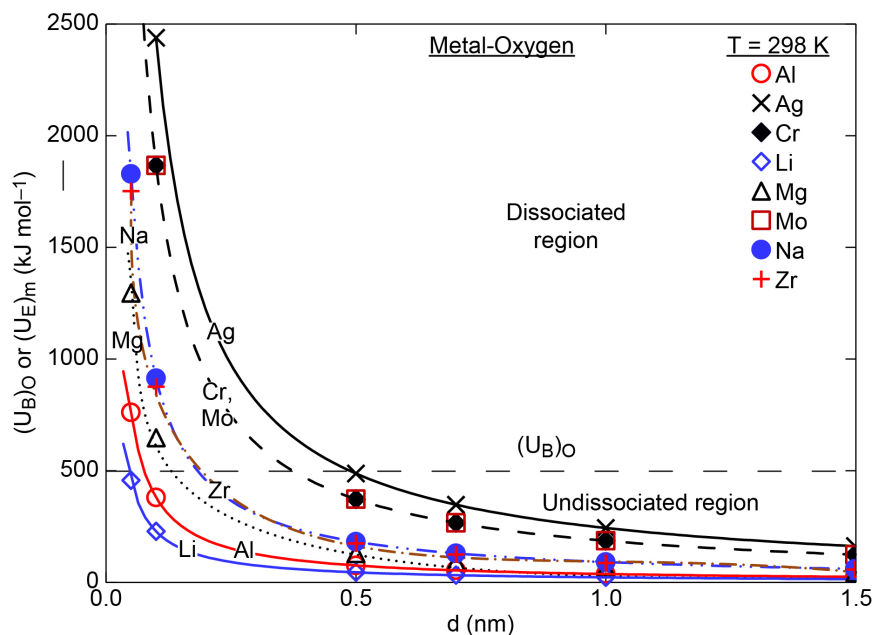


Figure 8.—Plot of $(U_E)_m$ against d for Al, Ag, Cr, Li, Mg, Mo, Na, and Zr, where $d = 0$ is the surface of the metal. The magnitude of $(U_B)_O = 498.3 \text{ kJ mol}^{-1}$ [23] is represented by the broken horizontal line, where the region $(U_E)_m > (U_B)_O$ indicates that the O_2 molecules dissociate under the action of $(E_E)_m$.

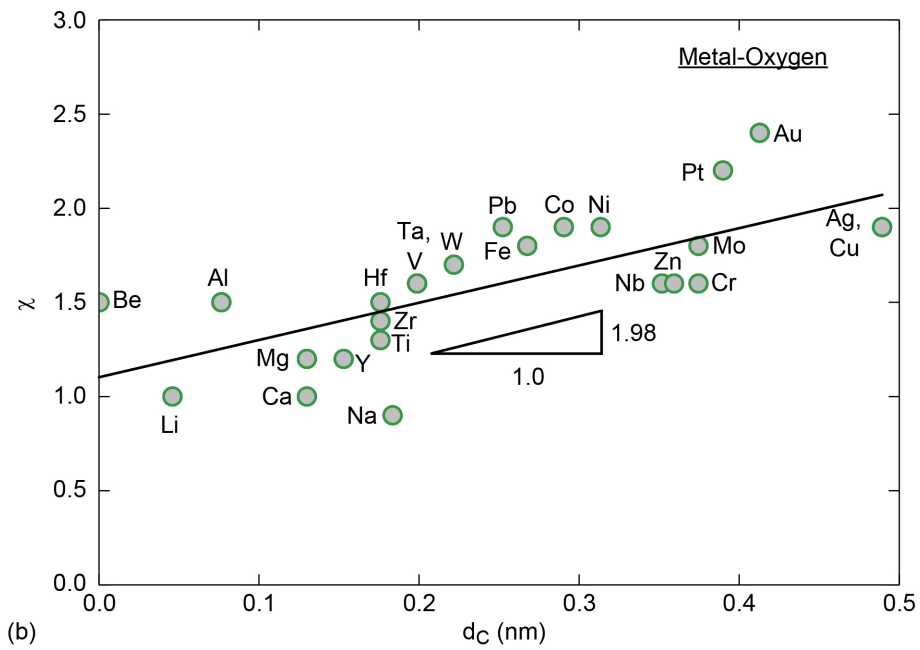
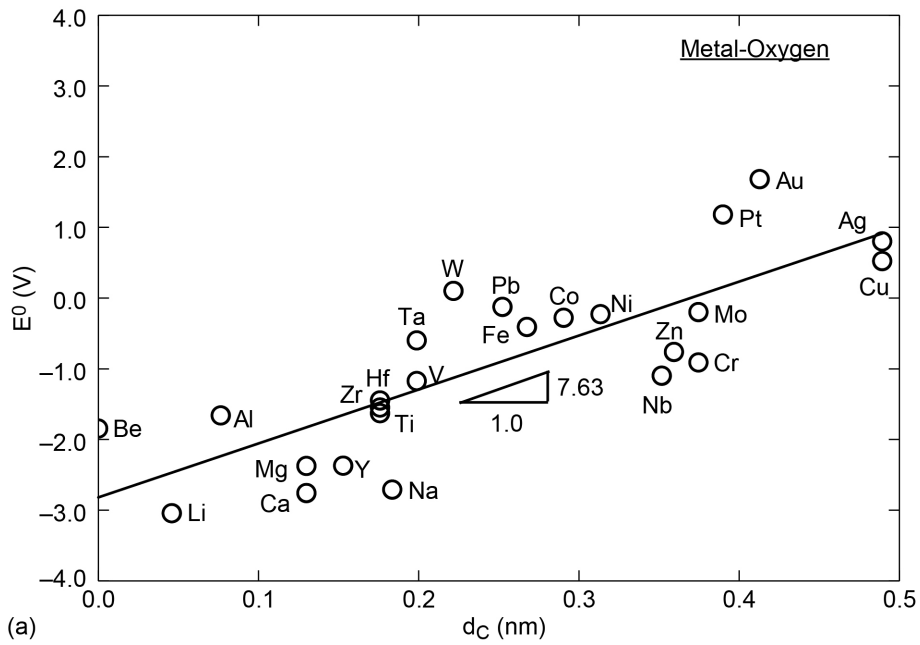


Figure 9.—Correlation of (a) E^0 [23,29] and (b) χ [21] with d_c for several metals prior to reacting with oxygen gas demonstrating that reactive metals with lower values of E^0 and χ have low values of d_c and noble metals have high values of d_c .

3.5 General Comments

The present results have demonstrated that the magnitudes of the total Coulombic forces acting on the Cl₂, F₂ or O₂ gas molecules due to the electrostatic field generated by the first monolayer of metal ions can be sufficiently large to cause them to dissociate. The interactions of these gas molecules with the metal surfaces, except Be, results in an increase in the magnitudes of (U_E)_m with decreasing values of d to values greater than (U_B)_x thus causing the dissociation of the gas molecules (Figure 2, Figure 4, and Figure 8) contrary to assumptions made in theoretical models regarding metal-gas interactions, where it is assumed that the gas molecules are first adsorbed at the surface before dissociation [2-5,7,8,10,13]. The positive values of (U_E)_m and (F_E)_m indicate that the molecular bonds dissociate under the action of a total repulsive force. Conversely, H₂ and N₂ exhibit increasingly negative values of (U_E)_m with decreasing values of d with values less than (U_B)_x thereby suggesting that they are adsorbed at the metal surface as undissociated molecules (Figure 6 and Figure 7) in agreement with theoretical models [9,11,12,14,15]. In this case, the negative values of (U_E)_m and (F_E)_m indicate that the total force acting on the H₂ and N₂ molecular bonds are attractive in nature.

Equations (5) to (7) suggest that the magnitudes of E⁰ and χ increase linearly with the values of d_c for Cl₂, F₂ and O₂ for which (Z_g^{*} + (q_e)_g) > 0. Interestingly, the values of E⁰ and χ converge to identical values of -2.82 V and 1.10, respectively, for these three gases when d_c = 0 nm. This convergence of the three lines to identical intercepts was confirmed by plotting the E⁰ and χ data for the three gases on a single plot. Thus, a generic relationship can be written as

$$E^0 = E^* \cdot d_c - 2.82 \quad (V) \quad (8.a)$$

$$\chi = \theta \cdot d_c + 1.10 \quad (8.b)$$

where E* is a constant with units of V/nm, and θ is a unitless constant. It is important to note that E* has units of an electric field. The exact reason why the values of E⁰ = -2.82 V and χ = 1.10 for d_c = 0 nm are identical for the reactions of Cl₂, F₂ and O₂ with the metals is unclear. It is cautioned that there is a lot of scatter in the data shown in Figure 3(a) and (b), Figure 5(a) and (b), and Figure 9(a) and (b) to draw a definitive conclusion. However, it is possible that E⁰ = -2.82 V and χ = 1.10 represent threshold values of E⁰ and χ for a metal in order to generate sufficiently strong electrostatic forces to dissociate homonuclear diatomic gases for which (Z_g^{*} + (q_e)_g) > 0 at some distance from the free surface. Unlike the other metals, the value of Z_m^{*} < (q_e)_m for Be so that (U_E)_{Be} < (U_B)_x for the five homonuclear diatomic gases. Thus, these gas molecules do not dissociate prior to reaching the Be surface under the action of the electric field and instead they are adsorbed at the metal surface.

4.0 Summary and Conclusions

The present paper examines whether an electrostatic field generated by the outermost monolayer of metal ions at the surface of a metal is strong enough to dissociate the molecular bonds of five homonuclear diatomic gases, Cl₂, F₂, H₂, N₂ and O₂. The total electrostatic fields generated by several pure metals were calculated using Coulomb's law to determine the attractive and repulsive forces between the electrons and ions in the gas molecule and the free surface metal electrons and ions assuming a Bohr model. Except for Be, for which Z_m^{*} < (q_e)_m, the magnitudes of (U_E)_m, due to the electrostatic fields generated by the outermost monolayers of atoms for these metals are greater than (U_B)_x of Cl₂, F₂, and O₂, where x is either Cl₂, F₂, H₂, N₂ or O₂, at some distance from the metal surfaces. This observation suggests that these gases dissociate before they reach the metal surface contrary to assumptions made by

current theoretical models that assume that these gas molecules are adsorbed at the metal surface prior to dissociation of their stable covalent bonds [5,7,10,13]. In contrast, H₂ and N₂ do not dissociate before reaching the metal surface because the values of $Z_g^* < (q_e)_g$ for these gases. Instead, they would be adsorbed at the surfaces of these pure metals prior to the dissociation of their molecular bonds in agreement with current models [9,11,12,14,15]. The magnitudes of E^0 and χ correlate linearly with the critical dissociation distances, d_c , at which $(U_E)_m = (U_B)_x$ as

$$E^0 = E^* \cdot d_c - 2.82$$

$$\chi = \theta \cdot d_c + 1.10$$

where E^* is a constant with units of V/nm, and θ is a unitless constant.

References

1. U.R. Evans: *Trans. Electrochem. Soc.*, 1943, vol. 83, pp. 335-42.
2. P. Kofstad: *High-Temperature Oxidation of Metals*, 1st ed., Wiley, New York, 1966, pp. 21-50.
3. O. Kubaschewski and B.E. Hopkins: *Oxidation of Metals and Alloys*, 2nd ed., Butterworths, London, 1967, pp. 70-82.
4. *Oxidation of Metals and Alloys*, American Society for Metals, Metals Park, OH, 1971.
5. N. Cabrera and N.F. Mott: *Repor. Prog. Phys.*, 1949, vol. 12, pp. 163-84.
6. G. Ehrlich: *Met. Surf.: Struct., Energ. Kinet.*, American Society for Metals, Metals Park, OH, 1963, pp. 221-58.
7. H. Taube: *J. Gen Physiol.*, 1965, vol. 49, pp. 29-50.
8. A.B. Anderson and R. Hoffmann: *J. Chem. Phys.*, 1974, vol. 81, pp. 4545-59.
9. P. Ferrin, S. Kandoi, A.U. Nilekar and M. Mavrikakis: *Surf. Sci.*, 2012, vol. 606, pp. 679-89.
10. C. Carbogno, A. Groß, J. Meyer and K. Reuter: *Dynamics of Gas-Surface Interactions*, R.D. Muiño and H.F. Busnengo, eds., Springer Series in Surface Sciences, 50, Springer-Verlag, Berlin, Ch. 16, 2013, pp. 389-419.
11. G-J. Kroes and C. Diaz: *Chem. Soc. Rev.*, 2016, vol. 45, 3658-700.
12. K. Christmann: *Encyclopedia of Interfacial Chemistry*, Elsevier, New York, NY, 2018, pp. 213-20. <https://doi.org/10.1016/B978-0-12-409547-2.12837-9>.
13. M.M. Montemore, M.A. van Spronsen, R.J. Madix, and C.M. Friend: *Chem. Rev.*, 2018, vol. 118, pp. 2816-62.
14. E.W.F. Smeets, G. Füsichel and G-J Kroes: *J. Phys. Chem.*, 2019, vol. 123, pp. 23049-63.
15. E.C.E. Rönnebro, R.L. Oelrich and R.O. Gates: *Molecules 2022*, 2022, vol. 27, p. 6528.
16. R. Darolia: *Intern. Mater. Rev.*, 2013, vol. 58, pp. 315-48.
17. R. Darolia: *Intern. Mater. Rev.*, 2019, vol. 64, pp. 355-80.
18. S.V. Raj, L.J. Ghosn, C. Robinson and D. Humphrey: *Mater. Sci. Eng.*, 2007, vol. 457, pp. 300-12.
19. S.V. Raj, J.A. Nesbitt, W. Jennings and P. Bonacuse: NASA/TM-202110021453, NASA Glenn Research Center, Cleveland, OH, 2021.
20. W.L. Masterton, E.J. Slowinski and C.L. Stanltski: *Chemical Principles*, 6th ed., Sanders College Publishing, Philadelphia, PA, 1985.
21. S.S. Zumdahl: *Introductory Chemistry: A Foundation*, 5th ed., Houghton Mifflin Company, Boston, MA, 2004.
22. C. Kittel: *Introduction to Solid State Physics*, 4th ed., Wiley Eastern, New Delhi, 1971, p. 105.

23. *CRC Handbook of Chemistry and Physics*, 61st ed. in: R.C. Weast and M.J. Astle, eds., CRC Press, Inc. Boca Raton, FL, 1980-81, pp. D-155-D-157, D-190, F-219, F-222-231.
24. <https://www.periodictable.one/>. Accessed 24 March 2023.
25. <https://www.omnicalculator.com/chemistry/effective-charge>. Accessed 24 March 2023.
26. J. Clark: Libre Texts Chemistry, https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry. Accessed 24 March 2023.
27. N.F. Mott and H. Jones: *The Theory of the Properties of Metals and Alloys*, 1st ed., Dover Publications, New York City, New York, 1958, p. 50.
28. D. Halliday, R. Resnick and K.S. Krane: *Physics vol. 2*, 4th ed., Wiley, Singapore, 1994, p. 597.
29. P. Vanýsek: *CRC Handbook of Chemistry and Physics*, 91st ed., in: W.M. Haynes, ed., CRC Press, Inc., Boca Raton, FL, 2010-11, pp. 8-20 to 8-24.
https://diverdi.colostate.edu/all_courses/CRC%20reference%20data/electrochemical%20series.pdf. Accessed 24 March 2023.
30. J.C. Slater: *Phys. Rev.*, 1930, vol. 36, pp. 57-64.

