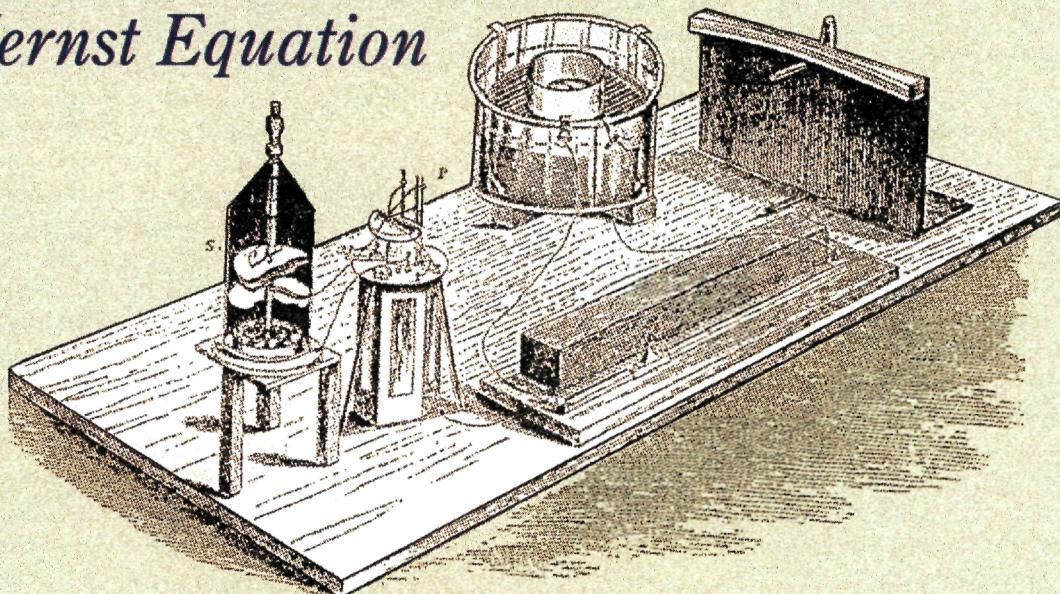


A Fresh Look at Some Old Principles: *The Kelvin Probe and the Nernst Equation*



This month, two 100-year anniversaries are celebrated—those of the still widely used monument of physics, the Kelvin probe (KP), and that bastion of electrochemistry, the Nernst equation. In this Report, we show that the combination of these two principles opens the possibility for including interactions in which only a partial charge transfer occurs between the guest species and the host material. Such an interaction then leads to formation of charge-transfer complexes that cannot be measured by conventional potentiometry, as described by the Nernst equation, but can be followed as a change of the work function of the host matrix using the KP.

Kelvin probe basics

The energy with which electrons are bound in conducting materials is known as the "electron affinity". Those materials that strongly bind electrons, gold for ex-

The combination of two old ideas leads to a new class of chemical sensors

ample, exhibit "noble" behavior; that is, they are relatively inert and do not oxidize spontaneously in air. However, other metals, such as aluminum or copper, are "less noble" and their surfaces are readily oxidized. When two dissimilar electronic conductors are in contact, electrons flow from the material that is less noble to the one that is more noble until an equilibrium is

reached and the contact potential V_c is formed at the junction. Because of the multitude of combinations of conductors, contact potential is the most ubiquitous of all junction potentials.

A simple electrical circuit can be constructed from such a pair of metals. The ends of the two metals are arranged to form a parallel plate capacitor (Figure 1). An electric field is generated between the two plates, which is the result of the spontaneous separation of electrons. In the case of a copper/palladium junction, the copper plate becomes positively charged and the palladium plate negatively charged. A galvanometer and a battery placed in series complete the circuit. As the distance between the two plates is periodically changed, the galvanometer registers an alternating current, which is the result of the mechanical vibration of the two plates in an electric field. A compensating voltage from a variable source is then applied until the electric field

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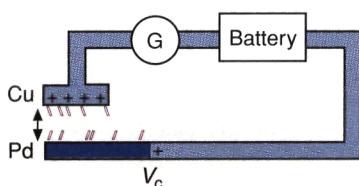


Figure 1. KP operating principles.

The distance between the Cu and Pd plates is periodically changed, causing an alternating current in the external circuit. Dipoles shown / are illustrated at both surfaces.

is nulled out and the galvanometer registers zero alternating current.

This was the experiment that Lord Kelvin described on May 17, 1897, to the Royal Institution in a lecture in which he also discussed Volta potentials, thermoelectricity, contact potentials, and other things that analytical chemists prefer to avoid (1). This instrument became known as the KP, although Kelvin himself acknowledged that a similar experiment was performed by Pellat in 1881 (2). Since then the KP has been widely used by physicists, material scientists, and, to some extent, physical chemists to measure "contact potentials", "surface potentials", or the "work function" of materials—a confusing variety of misnomers for the same measurement. It was first used for analytical purposes by Phillips in 1951 as a nonspecific detector for GC (3). The invention of other detectors eventually eclipsed the use of the KP as an analytical instrument.

The KP operation depends on the contact and surface potentials, which are combined in one of the most fundamental properties of any electronically conducting material—the work function Φ . It is defined as "the minimum work required to extract an electron in vacuum from the Fermi level ϵ_F of a conducting phase through a surface" and to place it just outside the reach of the electrostatic forces of that phase, in a so-called vacuum level (4). This work can be conceptually divided between the work required to free the electron from its bulk electron-ion or electron-electron interactions, and the work expended on its passage through the electric field of the surface dipole χ that exists even at absolutely clean surfaces.

To change this discussion to more familiar chemical grounds, we make a

change from a single electron to a mole of electrons by multiplying Φ by Avogadro's number N_A . The chemist's definition of the work function then becomes

$$\Phi = -\mu_e/N_A + e\chi \quad (1)$$

where μ_e is the chemical potential of the electron and e is the charge of the electron. The chemical potential of any species indicates "affinity" or the degree of interactions that species will have within the system in which it exists. Therefore, a "high affinity" of a metal for electrons (i.e., its high work function) makes it noble.

The experimentally determined value of the work function depends on the way in which the electron is removed from the conducting phases. In addition, an electron

different fatty acids to one of the plates of his KP detector and achieved some selectivity to the passing organic vapors (3).

Demonstrating the modulation of the work function by the bulk term has been difficult because both plates must be electronically conducting and the species that would modulate the bulk contribution must penetrate the interior of one of the plates. This latter condition is not readily achieved except for a few metals, such as palladium, that dissolve hydrogen. Thus, exposure to hydrogen of the two metals forming a Cu/Pd junction results in a lowering of the work function of palladium that can be related to the partial pressure of hydrogen in the ambient atmosphere.

When interpreting the resulting signal, we can only assume that the work function of the reference material (e.g., copper) has not changed. This "act of faith" is the fundamental bane of all electroanalytical potentiometry, in which the invariability of the reference potential can only be assumed but never thermodynamically proven. In KP measurements, this situation is worsened because both the surface and the bulk contributions of the work function of the "reference" plate can be affected.

To summarize, KP measures $\Delta\Phi$ of the work function of the two conductors; a single contact potential or the absolute value of the work function of one material cannot be measured by the KP; adsorption of a species at the surface of the plate(s) modulates the contribution of the dipoles and surface charges, whereas the absorption of the same species in the bulk modulates the contribution to the work function from the Fermi level(s); and to perform the KP measurement, the two plates must be capacitively coupled.

IGFETs and SGFETs

The closest cousin of the KP is the group of solid-state devices that operate on the basis of the so-called "semiconductor field effect". The heart of their operation is a capacitor formed by a metal plate (e.g., palladium) that is separated from a silicon plate by a thin insulator (Figure 2). Because silicon is a semiconductor, the charge is located near its interface with the insulator in an area called the space charge region. The total space charge equals the charge on the metal plate. The back of the silicon is ohmically connected

The KP and the IGFET are important analytical tools in their own right.

cannot just be taken out of a phase—it must also be deposited elsewhere. The measurement of the work function by any method thus always involves two functions, the donor and the acceptor phases; KP is no exception. Because there are two capacitor plates involved, the KP measurement is the difference of work functions $\Delta\Phi$ of the two plate materials

$$\Delta\Phi = \Phi_1 - \Phi_2 = (\mu_1 - \mu_2)/N_A + e(\chi_1 - \chi_2) = (\Delta\mu_e + F\Delta\chi)/N_A \quad (2)$$

in which $\Delta\mu_e$ represents the bulk modulation and $F\Delta\chi$ corresponds to the surface contribution to the work function difference.

Lord Kelvin also demonstrated that two pieces of copper subjected to a different surface treatment (polishing and flaming) required several hundred millivolts of compensating voltage to null out the KP. This voltage was brought to zero by identical polishing of the two plates. This was clear proof of the contribution of the surface dipoles. Similarly, Phillips applied

to the palladium plate through a variable voltage source, and the electrons in the palladium and the silicon are again in equilibrium, forming the Si/Pd contact potential. The trapped surface charges in the insulator and the surface dipoles also contribute to the resulting electric field in the insulator.

This situation is identical to the conventional KP with one important difference: The distance between the two plates forming the capacitor cannot be varied. Therefore, another method of interrogating the charge must be introduced. In insulated gate field-effect transistors (IGFETs), this is accomplished by a pair of electrodes designated "drain" and "source" (Figure 2a) at the two ends of the virtual channel near the surface of the silicon. A voltage applied between the two electrodes produces the drain current, and the magnitude of the current depends on the channel resistance. That, in turn, depends on the electron density in the channel, which depends on the work function difference between the palladium and silicon and on the applied gate voltage V_g .

The chemical modulation of the signal by the hydrogen from the palladium-gate IGFET reveals two important differences as compared with the Cu/Pd KP. First, hydrogen can enter only from the top of the palladium metal and must penetrate through the bulk to reach the palladium/insulator interface. Second, silicon and the silicon/silicon oxide interface are virtually sealed from all gases; therefore, it is a far better reference than any material used in the KP. However, the price for this advantage is quite high. Because the ability of hydrogen to pene-

trate palladium is unique, only hydrogen and hydrogen-producing compounds can modulate the response of the palladium IGFET in this configuration.

To overcome this problem, we have constructed a suspended gate field-effect transistor (SGFET) in which the gate metal is suspended above the gate insulator by a narrow gap (5). It resembles the macroscopic KP, but in the SGFET the capacitor does not vibrate (Figure 2b). The silicon plate is protected by the insulator, which prevents the modulation of its work function. In that respect, silicon is almost an ideal reference plate. Most importantly, the transistors are small and can be microfabricated.

The Nernst equation and chemical aspects of the contact potential

Transferring an electron from one conductor to another clearly affects the electrostatic potentials Φ_1 and Φ_2 of the two phases, or, said another way, a contact potential V_c (which equals $\Phi_1 - \Phi_2$) is formed at their interface. A similar situation exists when ions are partitioned between a solution of electrolyte and an ion-selective membrane. Thus, the interfacial potential of an ion-selective electrode is a form of a contact potential

$$V_c = (RT/zF)\ln(a_1/a_2) \quad (3)$$

in which R , T , z , and F are the gas constant, temperature, charge, and Faraday constant, respectively, and a_1 and a_2 are the activities of the partitioning ion in the solution and the membrane. In this

case, the contact is made by the transferring ion. Nernst presented his equation at the meeting of the German Chemical Society on May 24, 1897 (6), a week after Lord Kelvin's lecture at the Royal Institution.

It is important to realize that an integral charge (i.e., one electron or one ion) is transferred across the interface, resulting in an integral value of the slope of the dependence of the interfacial potential on the logarithm of the activity of the charged species. In the case of a multivalent ion with charge z , this slope has a value of RT/zF . For example, at 25 °C the slope is 59 mV/decade for the univalent ion, 29 mV/decade for the divalent ion, etc.

The situation differs substantially in the chemical modulation of the work function. When electrically neutral hydrogen molecules dissolve in palladium, the work function is lowered and consequently the contact potential between palladium and copper is also lowered. The origin of the contact potential is again the distribution of electrons between palladium and copper, but it is important to note that the cause of the change of this distribution is the interaction between the palladium and hydrogen. To follow this change, a KP (Figure 1) must be used rather than a voltmeter, which is normally used to measure the Nernst potential. Thus, there are striking similarities and differences between these two modes of potentiometry. In this light, the KP and the IGFET become important analytical tools in their own right.

To ascertain their full analytical potential, we need to look at a more general interaction of neutral gas molecules with a semiconductor. The ease with which a molecule forms an ion, either by accepting or donating an electron, is indicated by its Mulliken electronegativity coefficient η (7), which is the average of its molecular electron affinity E_a and its ionization potential I_p .

On the other hand, the ability of a semiconducting solid to donate or accept electrons is related to the energy of its Fermi level ϵ_F or the electron affinity of the material. Thus the transfer of charge δ can be viewed as a simple redox equilibrium between the gaseous dopant (the guest) and the solid matrix (the host), in

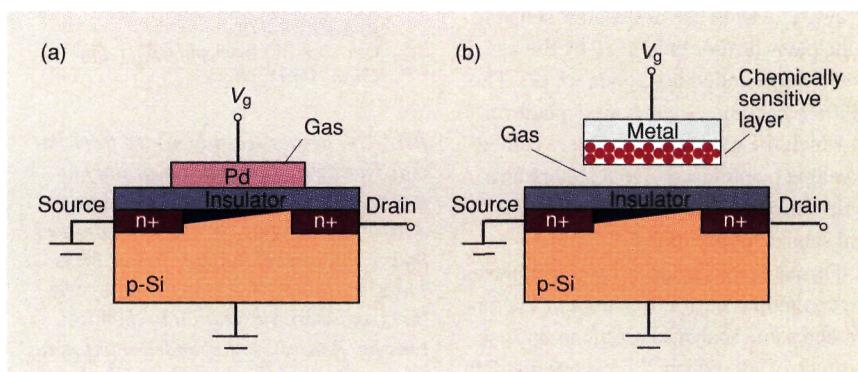


Figure 2. (a) Insulated gate field-effect transistor (IGFET) and (b) suspended gate field-effect transistor (SGFET).

which the role of the electron donor and electron acceptor can be played by either of the two and δ depends on the values of the η and ϵ_F , respectively. The amount of the transferred fractional charge is proportional to the difference of these two quantities.

Substitution of these relationships into the Fermi-Dirac distribution function yields a simple expression of dependence of the ϵ_F on the partial pressure P_D of the dopant gas

$$\epsilon_F = \epsilon^* + \frac{RT}{2\delta F} \ln P_D \quad (4)$$

(when $P_D = 1$, $\epsilon_F = \epsilon^*$). The resemblance of this equation to the Nernst equation is more than casual. However, the fundamental difference lies in the fact that the change of the experimentally observable parameter ϵ_F with the partial pressure of dopant gas has a fractional value given by δ , whereas in the Nernst equation this slope has an integral value given by the integral charge z on the partitioning ion. Thus, Eq. 4 can be regarded as a more general form of the Nernst equation (8).

Eq. 4 describes the changes of the ϵ_F of the material caused by its bulk interactions with guest molecules. Surface interactions are expected to lead to the modulation of the surface potential. The overall change of the work function would then follow some form of adsorption isotherm until the surface sites are fully occupied. At higher concentrations, the response would become logarithmic, corresponding to the partitioning process.

Thus, the combination of these two principles opens the door to an entirely new class of modern chemical sensors for electrically neutral species based on the semiconductor field effect. Not the only one, but probably the most convenient, is the IGFET, which can be microfabricated in silicon and arranged in multisensing arrays. The wide use of this new sensing principle is further enhanced by the use of electrically conducting polymers (9). The KP then becomes a convenient platform on which the new selective layers can be developed, optimized, and tested before their transfer to the SGFET format for real sensing applications (10, 11).

Formation of charge-transfer complexes is a common occurrence in organic chemistry, and some analytical reactions also use this type of interaction. We believe that this is the first time that charge-transfer complexes have been used as the transduction mechanism for direct sensing purposes.

Organic semiconductors are particularly suitable for this type of transduction. The work function of the polymer can be adjusted electrochemically over a broad range of initial values (12), and when these materials are exposed to the same amount of different organic vapors (Figure 3), a different response is obtained for each vapor. When the work function of the polymer is high, the electronic charge is transferred from the organic vapor to the polymer. When the work function of the polymer is low, the charge is transferred to the vapor. When the Mulliken electronegativity of the gas and the ϵ_F of the polymer are approximately equal, no charge transfer occurs.

These experiments clearly show that electrochemical tuning of "selectivity" is possible. Electrochemical generation and processing of selective layers for chemical sensors is an ideal approach because it allows precise control of the properties of materials and different selective layers can be addressed individually.

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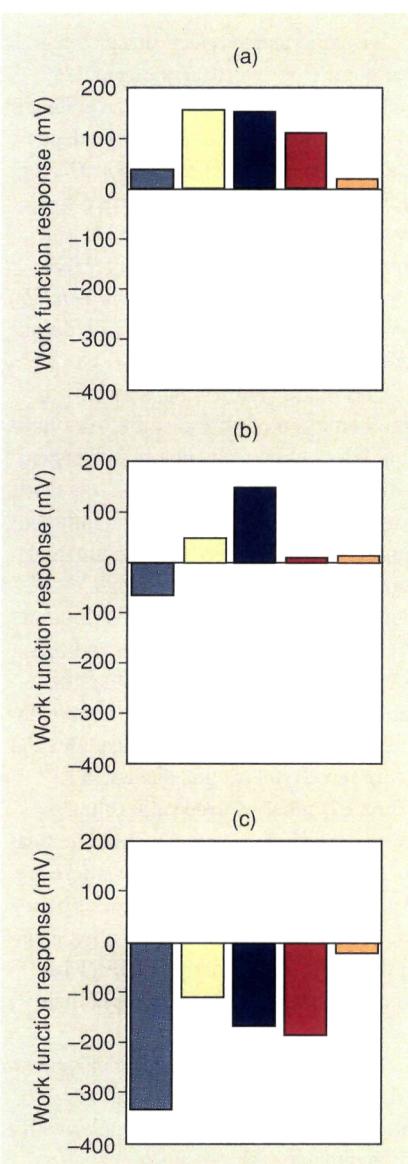


Figure 3. Chemical modulation of the work function of three electrochemically prepared polypyrrole layers with different initial values of the work function.

Initial work function values are (a) 60 mV, (b) 210 mV, and (c) 590 mV. The responses for the changes in the work function were obtained by injecting and evaporating 10 μ L of neat liquid samples (represented by the colored bars) into the sample in a stream of nitrogen. Lt. blue = methanol; yellow = chloroform; blue = dichloromethane; red = isopropanol; and orange = *n*-hexane. The positive values of the work function response correspond to the transfer of electron density from the polypyrrole matrix to the gas molecule. (Data from Ref. 12.)

Jiří "Art" Janata recently moved from Pacific Northwest National Laboratory to Georgia Tech, where he will continue research in solid-state chemical sensors and their environmental applications. Mira Josowicz is interested in conducting polymers and their application to chemical sensing. Address correspondence to Janata at the School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400 (jiri.janata@chemistry.gatech.edu).