

Model Predictions for Thermodynamic Behavior of Applied Surfaces and Surface Specimens - An Overview

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Abstract— In order to investigate the growth kinetics of surface film and their characterization using advanced spectroscopic techniques (SEM, TEM, AFM, XPS, and MRAS etc), detailed literature search was carried out preferably on the thermodynamic behavior of surfaces in terms of surface temperature, thermal conductivity, specific heat, entropy and enthalpy, heat of adsorption, heat of dissociation, coefficient of thermal expansion and the relevant model predictions and numerical approaches. The volume of information collected, aims to assist in understanding the probable mechanisms for surface reaction and structural characteristics of the applied surfaces and surface specimens. However, the literature search resulted with incoherent findings with diversity in modeling and simulations studies. The present communication imposes the speculations for unified approaches that can assist in estimating the thermodynamic behavior of the applied surface and surface specimens with much better scientific understanding.

Keywords— Surface temperature, surface functionalization, surface modification, surface films, surface kinetics.

I. INTRODUCTION

Functionlization of fine particles of metal, composite, polymer, fiber and wood specimen involves specific surface (chemical) reactions and help to improve the efficiency of the surface functionalization process there by developing the surface films of successive layers¹⁻²². These functional surfaces are best suited for their advanced application depending upon the physical and chemical nature of surface species and their structural characteristics²³⁻⁴² as well. Detailed thermodynamical analysis of these surface systems is often desirable for understanding the mechanisms of surface functionalization and surface modification of applied surfaces. Thus the thermodynamic behavior of applied surfaces plays significant role and introduces global interests among the researchers. Simultaneously the reduction in consumptions of heat and its measurement contribute significantly to the development of applied surfaces at bulk level and surface level as well. Hence the thermodynamics of surface specimens is known to be the key function for understanding the surface phenomena like surface energy, surface bonding, surface reaction, and reaction kinetics there of. As a consequence, the thermodynamic importance for applied surfaces of various origin like metal surface, ceramic surface, polymer surface, electronic surface and bio surface has been recognized on priority basis for enhancing the overall profile of the applied surface. These have critical considerations for understanding the effect of temperature variation through-out the investigation. As a result, the thermodynamic properties of applied surfaces appear in the form of interdisciplinary research programs and invoke state-of-the-art investigations.

Apart from these, the thermodynamical approaches for layer development and their analysis depends upon the rate of varying stages, and also upon the kinetic equations that describe the whole investigation. The rate of any particular stage for the creation and growth of surface film charges along with the time and temperature. The most slow stage for the

formation of the surface film is the chemical species on the metal surfaces. After the formation of the surface layer in the condition of quasi-equilibrium condition of the diffusion, the transport of chemical species become very slow. Normally the thickness (t_i) of i^{th} phase in n -layer of a surface film is the function of time (τ), temperature (T), reactivity (R_i) and concentration (C_i). These cause the kinetics of the reaction process as major source of complex function. Thus for making an attempt to describe some of the particular stages of the process, it is aimed to mathematically combine the phenomena taking place at any particular stage, even if it is rather difficult to interpret the growth of the surface film due to large member of phenomena involved. Therefore, through a proper selection of thermodynamical parameters involved in the investigation, an optimum and consolidated situation can be achieved at which the well known chemical species govern the successive mode of surface functionalization.

In the present communication the authors aim to attempt emphasize on the validity of the mathematical models for understanding the thermodynamic behavior of applied surfaces that help in pursuing and predicting the effectiveness of the numerical approaches in the varying surface environment. A large number of numerical models have been reported by the surface experts for detailed thermodynamical investigation of the applied surfaces and the interfacial actions there of⁴³⁻⁵². The numerical modles were reported in terms of polymer surface, surface chemicals, electronic surface, condensed matter surface, surface contacts, surface adsorption and surface characterization.

TABLE I. Peak values for XPS data of polyvinyl chloride binder (MR-110).

Peak (eV)	Assignment	References
169.2	S ($2p_{3/2}$) from sulphate group	169.2 [5]
200.6	Cl ($2p_{3/2}$) from $-\text{CH}_2\text{CHCl}-$	200.6 [5]
202.2	Cl ($2p_{1/2}$) from $-\text{CH}_2\text{CHCl}-$	202.2 [5]
285.5	C (1s) from $-\text{CH}_2\text{CHCl}-$	285.5 [5]
286.6	C (1s) from $-\text{CH}_2\text{CHCl}-$	286.5 [5]
532.7	O (1s) from ether or O^{2-}	532.5 [5]
533.2	O (1s) from epoxy	533.1 [5]

TABLE II. Peak values for XPS data of iron particles of known particle size.

Peak (eV)	Assignment	References
74.0	Al (2p _{3/2}) from Al ₂ O ₃	74.0 [7]
74.6	Al (2p _{3/2}) from AlOOH	74.4 [7]
157.8	Y (3d _{5/2})	156.8 [7]
284.8	Al (3d _{5/2}) from Y ₂ O ₃	284.8 [7]
530.1	C (1s) from carbon on MP	530.0 [8]
531.5	O (1s) from Fe ₂ O ₃ / Fe ₃ O ₄ /FeO	531.5 [7]
531.5	O (1s) from FeOOH/AlOOH	710.6 [8]
711.0	Fe (2p _{3/2}) from Fe ₂ O ₄ /Fe ₂ O ₃	711.3 [8]
711.0	Fe (2p _{3/2}) from FeOOH	711.8 [8]

TABLE III. Effect of Barrel's temperature on surface profile of wood particles.

Extruder's Barrel Temperature	Elemental Composition		O/C Atomic Ratio	Analysis of C _{1s} Peaks (%)				OH Index (HI)
	O %	C %		C ₁	C ₂	C ₃	C ₄	
Unextruded	31.85	68.15	0.47	39.75	51.20	8.46	0.58	1.00
130	3.36	96.64	0.03	95.27	3.04	1.69	0.00	0.06
140	5.47	94.53	0.06	92.61	5.26	2.12	0.00	0.10
160	2.39	97.61	0.02	96.90	3.10	0.00	0.00	0.06
180	5.05	94.95	0.05	95.24	4.76	0.00	0.00	0.09

II. GENERAL APPRAISAL

Polymer Surface

Thermodynamics of polymer surface, polymer films, and polymer emulsion is spread over a wide range of microscopic descriptions related to the thermodynamic criteria, thermodynamic stability and determination of thermodynamical parameters⁵³. Determination of the minimum film temperature of polymer emulsions and polymer films is one of the crucial considerations that involves high precision tools and advanced techniques. Protzman et al⁵⁴ have reported to develop an advanced tool for measurement of the minimum film temperature (MFT) of polymer emulsion. The apparatus consisted of a metal bar along which a temperature gradient could be maintained. Recessed channels were provided in which emulsion samples were spread and allowed to dry. Eight thermocouple stations along the bar were connected to a continuous recorder. Following drying of the film, the minimum temperature at which a continuous film formed was determined. Testing of the tools on one emulsion examined under a variety of conditions and on samples of varying composition demonstrated the reliability, versatility, and utility of the tools. However their investigation did not employ any numerical approximation towards the variation of temperature gradient so as to compute the minimum film temperature.

On the other hand temperature monitoring for the control of a convex molten polymer sheet and surrounding cooling air flows are highly demanded for improving both the productivity and quality of the polymer sheet products. The accurate measurement of temperature is preferably desired when molten polymer changes its phases. An intrusive thermometer such as a thermocouple finds difficulty because a molten polymer, blown out from a ring die, is extremely thin. Also temperature measurement with an infrared camera is not applicable since the polymer film is lightly transparent for the infrared radiation and the intensity of infrared radiation from the polymer film is too weak. In a relevant consideration, Kawaguchi et al⁵⁵ proposed a method for non-intrusive temperature measurement with the quantitative interferometer

in conjunction with direct cylindrical computer tomography, and discussed its feasibility for measuring the temperature distribution on a convex surface without any model prediction for the computation. In order to understand the thermodynamic behavior of polymeric as well as composite surfaces placed in an infra-red laser field, Nikitin et al⁵⁶ considered the numerical methods for calculating the surface temperature (T_s) of polymers upon exposure to infra-red laser radiation during modification, pyrolysis, ablation and ignition process. They showed that it was necessary to calculate the values of T_s for polymers using different analytical expression after estimating the value of the dimensionless parameter as shown by the mathematical equation, $u = \mu [\alpha t_e]^{1/2}$; where μ -absorption coefficient for the laser radiation, α - thermal diffusivity, and t_e is the radiation exposure time. Under these conditions, they achieved the smallest calculation error and took into account the volume absorption of the radiation.

Further the thermodynamics of polymer gear contact surface is known to be a high order phenomenon that results in local softening and increased surface wear⁵⁷⁻⁵⁸. K. Mao⁵⁹ discussed a detailed analysis of the heat partition between gear teeth and the flash temperature for polymer composite gear. The intensity distribution and velocity of each source changed as meshing proceeded. A numerical approach was adopted using finite element method so as to investigate it successfully. Assuming the coefficient of friction, the intensity of surface heat source due to friction was given by $Q = \mu p V_s$ where V_s relative sliding velocity. Based on the heat generation a basic mathematical equation was developed which governed the transfer of heat in the gear teeth surface. To obtain the heat transfer and the flash temperature of the meshing teeth, the teeth were divided into elements. Two dimensions were used assuming that heat and temperature were uniformly distributed along the tooth face width. The increase in internal energy per unit width was given by the expression,

$$\Delta E_i = \rho.C.\Delta V. \Delta T$$

$$\text{or } \Delta E_i = \rho.C.\Delta x\Delta y/2 [T_1^{t+\Delta t} - T_1^t]$$

Where ΔV -volume of the element, T_1 -the temperature at node 1, ΔT -increase in temperature, C -specific heat, and ρ -specific gravity. The heat conducted into volume from the lower surface may be given by the expression,

$$E_b = k (\Delta x\Delta T/\Delta y).\Delta t$$

Where k -thermal conductivity and the was approximated as given below

$$E_b = k [\Delta x (T_2^t - T_1^t)/\Delta y] \Delta t$$

Finally, the heat input from the upper surface was computed such as

$$E_t = Q_s \Delta x.\Delta t$$

where Δx - area of the element, and Q_s heat input per unit area into element. On combining the above relation resulted into following;

$$T_1^{t+\Delta t} = T_1^t + 2 [K \Delta t/\Delta y^2 (T_2^t - T_1^t) + (2\Delta t/\rho C \Delta x.\Delta y).Q_s]$$

$$T_1^{t+\Delta t} = A - BQ_s$$

Where, $A = T_1^t + 2 K\Delta t/\Delta y^2 (T_2^t - T_1^t)$

$B = - 2\Delta t/\rho C \Delta x\Delta y$

and K = thermal diffusivity ($k/\rho c, m^2/s$).

In order to establish the temperature at any of these nodal points within the body using the following equation as governing one, i.e.

$$\Delta^2 T / \Delta y^2 = 1 / K (\Delta T / \Delta t)$$

Finite difference were used to approximate differential increments in the temperature and space coordinates. Smaller the finite increments, more closely the true temperature distribution would be approached. Therefore,

$$\Delta^2 T / \Delta y^2 = 1 / \Delta y^2 (T_{i+1}^t + T_{i-1}^t - 2T_i^t)$$

Understanding the thermodynamic behavior of thin polymer films comprising polymer blends and co-polymers is really a typical task for surface experts⁶⁰⁻⁷⁴. Lang et al⁷⁵ studied the size and interface effects on kinetic and thermodynamic properties of thin polymer film at given temperature. Their approaches were based on free volume model and size dependent function for mean square molecules in polymer film at glass transition temperature. The predictions were in agreement with experimental measurement of polystyrene and poly butadiene chemical. According to their observation the thermal expansion coefficient $\beta (T, D)$ could decrease or increase with decreasing film thickness 'D' due to the influence of free surface, film/substrate interface interaction, strength and confinement effect, compared to the corresponding polymer bulk properties. In practical application, $V_f (T, \infty)$ was also correlated to the thermal expansion coefficient $\beta (T, \infty)$ of the substance by the following equation as given below;

$$\begin{aligned} \Rightarrow \beta (T, \infty) &\propto V_f (T, \infty) \\ \Rightarrow \beta (T, D) / \beta (T, \infty) &= V_f (T, D) / V_f (T, \infty) \\ \Rightarrow \beta (T, D) / \beta (T, \infty) &= \exp [3(\alpha-1)/(D/D_0 - 1)]. \end{aligned}$$

Considering a mathematical relationship of $\exp (-x) \approx 1-x$ where x is small enough, as the first-order approximation, the equation was simplified as

$$\begin{aligned} \eta (T, D) / \eta (T, \infty) &= 1 - 20 (\alpha - 1) D_0 / D, \\ \gamma (T, D) / \gamma (T, \infty) &= 1 - (\alpha - 1) D_0 / D, \\ \beta (T, D) / \beta (T, \infty) &= 1 + 3 (\alpha - 1) D_0 / D, \end{aligned}$$

In terms of these numerical models for thin films with strong interaction at the film substrate interface, $\eta (D)$ function increased, but $\beta (D)$ function decreased with D. While for free thin films supported by substrate with weak interface interaction can be achieved. The predicted result were consistent with available results of polystyrene and polybutadiene thin films.

III. SURFACE CHEMICALS

Interaction of surface chemical species (especially in liquid and gas phases) with a surface system is learnt to be one of the most critical situations in relation to the influence of temperature and pressure⁷⁶. The physical mechanism and DFT based description for the thermodynamics of surfaces and the kinetics of surface adsorption substantiate this phenomenon⁷⁷. Further, it is widely recognized that surface phenomenon adversely results into the atmospheric pollution caused due to the release of severe chemical specimens. These information help in undertaking the combined thermodynamic and structural characteristics of the interacting chemical species. In some cases both the isothermal compressibility and the isosteric heat of adsorption are deeply involved⁷⁸. Again, the thermodynamics of metal-chemical system, polymer-emulsion

system, ceramic-laser system and solution-vapor (gas) system is in many ways anomalous in their thermodynamic behavior. Different researchers have opined different routes for their mathematical investigations and precise analysis through their tentative numerical approach. For example, in the case of additive-metal surface system⁷⁹, the reaction rate is proportional to the power of additive concentration as given by the following relation,

$$\text{Reaction rate} = K [C]^n;$$

Where K - rate constant, C - additive concentration and n - order of reaction. The rate constant for such reaction is temperature dependent and is typically known as Arrhenius Equation, the expression for which is given in the following way;

$$K = A \exp (-E_A / RT);$$

Where A - temperature independent constant, E_A - activation energy, R - gas law constant and T - temperature in Kelvin. In a recent model study conducted on growth kinetics of nitrated layer in a binary Fe-N system, J Rataski⁸⁰ presented the methodical description of the layer development subjected to a continuous evolution concerned with a growing amount of empirical data. In his hypothesis the model involved the parabolic laws of the phase growth given by the equation, $\Delta t_i = K_i \sqrt{\tau}$; where Δt_i - thickness of the i^{th} phase in n-layer film after time τ of the reaction and K_i - kinetic growth parameter of i^{th} phase so-called parabolic growth constant. Further the distribution of the adsorbing/diffusing component concentration in a given phase was determined by making use of Karkaldi's equation according to which,

$$C_i (t, \tau) = A_i + B_i \operatorname{erf} [t_i / 2 \sqrt{D_i} t]$$

Where $C_i (t, \tau)$ is the concentration of the adsorbing/diffusing components in the i^{th} phase, D_i is the diffusion/adsorption coefficient of the adsorbing component in the i^{th} phase, and A_i and B_i are the constant referring to the initial and boundary conditions. It is evident that the concentration of the diffusing component is the function of $(t_i / 2 \sqrt{D_i} t)$. On observing the displacement of an interphase boundary they obtained the expression such that,

$$\begin{aligned} C(t, \tau) &= \frac{1}{2} \{ 1 + \operatorname{erf} (t / 2 \sqrt{D} \tau) \} = \text{constant} \\ &\text{and } t / 2 \sqrt{D} \tau = \text{constant} \end{aligned}$$

On applying the constant values of concentration for the boundaries of given phase $C_{i, i-1}$ and $C_{i, i+1}$ following the phase equilibrium diagram they obtained,

$$C_{i, i-1} (t, \tau) = \frac{1}{2} \{ 1 + \operatorname{erf} (t_{i, i-1} / 2 \sqrt{D} \tau) \} = \text{constant}$$

$$C_{i, i+1} (t, \tau) = \frac{1}{2} \{ 1 + \operatorname{erf} (t_{i, i+1} / 2 \sqrt{D} \tau) \} = \text{constant}$$

Then for the possible growth of a given phase,

$$\begin{aligned} \Rightarrow C_{i, i+1} - C_{i, i-1} &= \Delta C_i = \text{constant} \\ \Rightarrow \Delta t_i / 2 \sqrt{D_i} \tau &= \text{constant} \\ \Rightarrow \Delta t_i / 2 \sqrt{D_i} \tau &= k_i \\ \Rightarrow \Delta t_i^2 &= k_i^2, 4 D_i \tau \end{aligned}$$

The probable growth constant (k_i) depends on the value of the diffusion coefficient of the diffusing component in the i -th layers (D_i) and the value of concentration (ΔC_i) on interphase boundaries.

Therefore, $k_i^2 = \{ \Delta t_i (\Delta C_i) D_i \}$

On generalizing equation for n-phase layer and assuming that the growth speed of a given phase is influenced by the remaining phase such that,

$$k_i^2 = \phi (D_1, \dots, D_n, \Delta C_1, \Delta C_2, \dots, \Delta C_n, T)$$

The explicit form of the expression in above equation, enabled them to the detailed description of the kinetics for the phase growth in a multiphase system.

Surface Adsorption

Surface atoms are very different from atoms in the bulk. The fewer neighbors of the surface cause it to have a very different and anisotropic chemical environment compared with the bulk. The thermodynamics of the surface is most likely to be quite different from the thermodynamic properties of the bulk. Often certain atoms in multi-component systems selectively accumulate on the surface as a result of these properties and impart rather different surface properties compared with the bulk. The balance of energies at the surface is the reason why small drops are curved and why liquid interfaces may rise when placed in capillaries. Surface thermodynamic functions can also be computed accordingly. Consider a large crystalline solid containing a total of N atoms, which is bounded by surface planes. One can determine various thermodynamic properties by including a term that accounts for excesses from the surface properties. Let E_o , S_o be the energy and entropy of the solid per atom respectively. Also E_s = specific surface energy (energy per unit area);

$$E = NE_o + \alpha E_s$$

Where N = Number of atoms in the solid;

E = total energy of the solid and

αA = surface area

Similarly for entropy, the total entropy is given by the expression;

$$S = NS_o + \alpha S_s$$

Now the total free energy is given by

$$G = NG_o + \alpha G_s$$

Surface work constant;

$$A_s = E_s - TS_s$$

And Surface free energy;

$$G_s = H_s - TS_s$$

Understanding of the complex behavior of atoms and molecules at surfaces e.g. adsorption/desorption, chemical reactions, etc., involves detailed knowledge of both macroscopic and microscopic processes that take place. It also depends upon certain critical parameters like temperature and pressure. These understanding can be accomplished through the combination of (i) microscopic theories, i.e., density-functional theory (DFT) electronic structure calculations and (ii) macroscopic phenomenological approaches, e.g. lattice gas and Monte Carlo schemes as well⁸¹⁻⁸². Hilding et al reported the isosteric heats of adsorption, q_{st} , for butane on multiwalled carbon nanotubes (MWNTs) over a range of surface loadings at temperatures below the normal boiling point. Butane is a non-spherical, non-polar molecule that may exhibit different orientations in multi-layer adsorption. The morphology of our MWNTs is such that only surface adsorption or capillary condensation can occur: no interstitial sites between nanotubes are available to butane. For these nanotubes, exterior surface adsorption is the principal mechanism measured by gravimetric analysis as the internal pores are only a small volume fraction of the total solid volume. The isosteric heat of adsorption varied with the surface coverage, θ , defined as the ratio of adsorbed butane to the MWNT butane monolayer

capacity. The initial heat of adsorption was in the region ~22-26 kJ/mol, which is approximately $1/3$ lower than the corresponding value for various graphite-butane systems. At $\theta = 1$, q_{st} displays a minima (13.5-15.9 kJ/mol). The isosteric heat of adsorption approaches the butane heat of condensation for $\theta > 2.5$, suggesting that the surface film is similar to a bulk phase. The isosteric heat of adsorption of butane on MWNTs can be related to the morphology of the MWNTs. The higher heats of adsorption at low coverage are likely related to the presence of surface defects. The minima in q_{st} near the monolayer coverage relates to a high self-association of butane. At high loadings, the butane surface film is similar to a bulk phase⁸³.

The adsorption and decomposition of H_2S on the Ge (100) surface is investigated. H_2S is a simple sulfur containing molecule that eventually decomposes to yield hydrogen gas and deposits sulfur on the germanium surface. The surface reactions of H_2S are investigated by ultraviolet photoelectron spectroscopy, Auger electron spectroscopy, and temperature programmed desorption. Room temperature exposure of H_2S to Ge(100) results in dissociative adsorption which can be followed easily by ultraviolet photoelectron spectroscopy. Warming the H_2S exposed surface results in some molecular desorption and further decomposition of the adsorbed species. At saturation, 0.25 ML of H_2S decomposes generating 0.5 ML of atomic hydrogen. Above the hydrogen desorption temperature some etching of the germanium surface is observed by sulfur. The etch product, GeS, is subsequently observed in temperature programmed desorption experiments. Exposure of H_2S to the Ge surface at elevated temperatures leads to higher sulfur coverages. A sulfur coverage approaching 0.5 ML can be deposited at the higher exposure temperatures⁸⁴.

Wang et al⁸⁵ made extensive investigation on the application of zeolite (MCM-22) for basic dye removal from waste water. Further, thermodynamic studies for adsorption kinetics of photo assisted fenton catalyst were conducted by Hsueh et al⁸⁶ as an alternative technology in order to treat dye effects discharged from dyestuff manufacturing. Andreev et al⁸⁷ developed the formula for surface composition of solid solution Al-Me (Zn, Sn, In) that was derived from the Gibbs equation. Using the first principle data of Al and X_{Me} surface emerges, the value of adsorption X_{Me}/N_{Me} , and surface enrichment of alloy X_{Me}/N_{Me} versus concentration in the bulk of alloy N_{Me} were calculated. The phenomena of ultra-high rate of atomic diffusion within surface layer at room temperature and high solubility of tin (Sn) were discussed in terms of thermodynamic vacancy model. The thermodynamic approach to the description of surface segregation required equilibrium to exist between the bulk (b) and surface (s) of the alloy. The surface layer was viewed as a top monolayer of a low-index face (hkl) of a crystal. This equilibrium was described by Gibbs's adsorption equation for a binary solution as given by

$$\mu \Gamma \Delta \sigma = -\Gamma_1 \Delta \mu_1 - \Gamma_2 \Delta \mu_2$$

The transfer of atoms of each sort 1 and sort 2 from the bulk to the adsorbed surface state was accompanied by the respective changes in the chemical potential given by

$$\Delta \mu_1 = \mu_1(s) - \mu_1(b)$$

$$\text{and } \Delta \mu_2 = \mu_2(s) - \mu_2(b)$$

They considered the sort 1 atoms be surface active and the sort 2 atoms be inactive. Then the changes in the chemical potentials upon formation of a layer enriched the sort 1 and sort 2 atoms were $\Delta \mu_1 > 0$ and $\Delta \mu_2 < 0$ respectively. In other words the decrease in the surface energy due to adsorption of component 1 was $\Delta \sigma_1 = \Gamma_1 \Delta \mu_1$ and the increased surface energy due to desorption was $\Delta \sigma_2 = \Gamma_2 \Delta \mu_1$. The small change in the surface energy was given by the equation;

$$\Delta \sigma = \Delta \sigma_1 + \Delta \sigma_2 = -\Gamma_1 \Delta \mu_1 + \Gamma_2 \Delta \mu_2 \text{ (for } \Delta \sigma_2 = -\Delta \sigma_1)$$

Therefore, $\Gamma_1 [\mu_1(s) - \mu_1(b)] = \Gamma_2 [\mu_2(s) - \mu_2(b)]$

Where $\mu_1(b)$ and $\mu_2(b)$ were defined as for no ideal solutions such that

$$\mu_1(b) = \mu_1^0(b) + RT \ln a_1$$

$$\text{and } \mu_2(b) = \mu_2^0(b) + RT \ln a_2$$

Where $\mu_1^0(b)$ and $\mu_2^0(b)$ were the standard chemical potential of the same complex. However in terms of thermodynamic vacancy model of the surface layer, a relationship existed between the Gibbs Surface Free Energy and the vacancy concentration $N_{v(s)}$ in the surface layers of the alloy as given by the equation;

$$\Delta G_s = -RT \ln N_{v(s)}$$

Since adsorption and advanced oxidation process are the most common approach for removing hazardous and environmentally undesirable chemicals. It is also one of the most widely used methods for the removal of pollutants from water and improves high treatment efficiency. The adsorption process transfers pollutants or contaminants from one phase to another phase. Hsueh et al.⁸⁶ established the adsorption standard for free energy change (ΔG^0) as calculated and given below;

$$\Delta G^0 = -RT \ln K_0$$

Where R - universal gas constant (1.987 cal/deg mol) and T - temperature in Kelvin. The average standard enthalpy change (ΔH^0) was obtained from Van't Hoff equation as given below

$$\ln K_0(T_3) - \ln K_0(T_1) = \Delta H^0 / R (1/T_3 - 1/T_1)$$

Where T_3 and T_1 - two different temperatures. The standard entropy change therefore can be obtained by the following equation given by

$$\Delta S^0 = (\Delta G^0 - \Delta H^0) / T$$

The positive value of the standard enthalpy change suggested that interaction of RB5 when adsorbed by FeAA-25 was endothermic. The negative adsorption standard free energy changes and positive standard entropy changes indicated that the adsorption reaction was in fact a spontaneous process.

TABLE IV. Thermodynamic data for Me (Zn, Sn, and In) and calculated values of the surface concentration X_{Me} and surface enrichment X_{Me}/N_{Me} .

Values	Zn	Sn	In
$\Delta G (T = 0K) (J/mol)$	37146	37339	32998
$I_m (J/mol)$	7200	7080	3270
$T_m (^\circ C)$	420	232	156
$\Delta G (T = 298 K) J/mol$	34049	33162	30729
Mol. Frac. X_{Me}	0.53	0.47	0.71
X_{Me}/N_{Me}	126.3	203.2	298.6

TABLE V. Occurring temperature of worn defects related to the transition temperature of PMMA and PMMI.

Polymer materials	Transition Temp. ($^\circ C$)	Annealing Temp. and time	Worms occurring temperature ($^\circ C$)
PMMA	120	120 $^\circ C$ -15 min	99
PMMA	140	150 $^\circ C$ - 15 min.	122
PMMA	170	150 $^\circ C$ - 4 h	129
PMMI	140	120 $^\circ C$ -15 min	117

TABLE VI. Thermodynamic Values for adsorption of RBS on Fe AA-25.

Thermodynamic constant	Temperature (K)		
	288	303	318
k_0	5.339	5.378	5.705
$\Delta G^0 (X1000 \text{ cal mol}^{-1})$	-0.959	-1.013	-1.100
$\Delta H^0 (X1000 \text{ cal mol}^{-1})$	0.402	0.402	0.402
$\Delta S^0 (\text{cal mol}^{-1} K^{-1})$	4.724	4.670	4.724

IV. SOLID SURFACES

The nature and dynamics of solid surface and surface contacts often govern heat transfer in multiphase systems. Physical scale, time scale, and intermolecular forces all affect basic mechanisms of transport between the multiphase medium and a submerged surface. Parameters in one or more of these domains can be the determining factor for transfer rate and efficiency, depending on the specific application. Research results for systems as diverse as fluidized particles and condensing liquids can be investigated so as to illustrate this significance. Specifically, it is shown that for heat transfer to/from surfaces submerged in bubbling fluidized beds, parameters in time domain are most important. In the case of condensation, it is shown that substantial enhancement of heat transfer coefficient can be obtained by controlling parameters in the domain of surface free energies⁸⁸. Thermodynamics of contact zones and interfacial region influence the efficiency of surface operation and their utilization. The flow of heat and its distribution in the areas of surface operation invariably affect the mode of operation in the both synergistic as well as antagonistic way. Therefore, their computation at various stages of operations is highly desirable. *Sethuramiah* and *Rao*⁸⁹ described the thermodynamics of contact surfaces and made an attempt in order to develop an expression for estimating the rise in surface temperature. They presented a consistent set of equations for calculating this temperature and emphasized on the results for practical application. In actual situations the total heat flows into the two bodies and the resulting temperature rise was obtained by assuming that the average temperature over the area of contact was the same for body-I and body-II. Therefore considering the heat flowing into the two bodies, the average temperature rise was given by the expression;

$$1/\Delta\theta = 1/\Delta\theta_I + 1/\Delta\theta_{II}$$

where $\Delta\theta_I$ - average surface temperature rise in body-I and $\Delta\theta_{II}$ - average surface temperature rise in body-II. However, the average temperature at the contact surface was given by the following expression;

$$\text{Case-I for } Pe < 0.5; \quad \Delta\theta = 0.946 [ql/k_l] [1 + \beta]^{-1}$$

Case -II for $Pe > 0.5; \quad \Delta\theta = 0.75 [ql/k_l] Pe^{-1/2} [1 \pm \beta Pe]^{-1/2}$
where $\beta = k_{II}/k_I$ and $Pe = Peclt$ Number.

In another study conducted on the temperature dependence in photo emission from metal surfaces, Larsson et al [90] discussed that a simple theory of temperature

dependence of photo emission would be derived with a view to illustrate the main thermal effects. These proved to be the reduction in amplitudes of peaks due to hole state scattering and reduction in the matrix elements, and the shifting of surface state peaks which the authors attributed to narrowing of the band gap within which the surface state existed. Scattering of the escaping electron was relatively unimportant. In an another study of effects on surface temperature for coalescence and breakup of contact areas reported by Michael et al⁹¹, experimental observations were made of the apparent real area of contact and temperatures generated by friction in a dry-sliding system consisting of stationary polymer –coated steel balls loaded against a vibrating sapphire disk. Five different polymers were used in the original study at vibrating frequencies ranging from 100 to 200 Hz and amplitudes from 20 to 100 m. Surface temperature generated by friction were measured using infrared microscope. A photo macro/video technique was developed to view the fretting contact interface and measure the size and distribution of real areas of contact. The experiments revealed several complex patterns and unusual phenomena, significant surface temperature spikes corresponding to the occurrence of coalesced areas were observed. A general thermal model previously developed was used to theoretically predict the temperature corresponding to the experimental conditions. Using the changes in the apparent real area of contact as observed in the experiments, the theoretical model predicted surface temperature in close agreement with experimental values. The study was important since it illustrated the connection between areas of contact and surface temperature, a unknown key which influenced physical and chemical behavior in tribological processes. In a model prediction for surface temperature of roller and densification of iron powder during hot roll pressing reported by Chang et al⁹², it was recognized that the heat transfer coefficient between the iron powder and the roller surface was closely related with the rotating speed of roller. These results were quantitatively described by using a mathematical model which was derived based on the steady –state heat transfer during hot roll pressing.

However, for solids that do not dissolve in the contacting solution and whose surfaces contain fixed dissociable groups a rigorous thermodynamic treatment shows that when $m_i \gg m_{H^+}$ or m_{OH^-} , the expression $(\partial \ln m_{H^+} / \partial T)_{p,m_i} \Gamma_p = -\Delta h_p / RT^2$ describes the temperature dependence of potentiometric titration curves both at and away from the zero point of charge (ZPC), where m_{H^+} , m_{OH^-} , and m_i respectively are bulk concentrations of hydrogen ions, hydroxyl ions, and supporting electrolyte ions, $F\Gamma_p$ is the primary surface charge density, and Δh_p , the partial molar enthalpy of surface group protonation, is well defined physically and accessible via calorimetry. Consequently the necessary and sufficient condition for temperature congruence of potentiometric titration curves is that Δh_p does not depend on Γ_p at constant T , p , and m_i . An expression for the enthalpy of forming a diffuse double layer is forwarded that differs from the so-called field energy by a factor of $(1 + \partial \ln \epsilon / \partial \ln T)$, where ϵ is the dielectric constant of water. It follows therefrom that any contribution to Δh_p from the diffuse layer is insignificant. When the method of congruence plots is applied to titration

data on hematite and rutile it is found in common with other systems that the BET area per gram is about half the electrochemical surface area. The resultant inner region capacitances at 20 °C are 58 and 88 $\mu F cm^{-2}$, respectively⁹³.

Surface Radiation

Measurement and detection of surface heat and radiation balance is one of the most critical concern for surface experts. This involves surface radiation detector for sensing low energy ionizing radiation on the surface that includes a open window gas proportional counter provided with a compressible skirt surrounding the window in a detection chamber. The compressible skirt is preferably of open cell plastic foam, but may be made from a gas impermeable sheet formed in the shape of an accordion bellows⁹⁴. Horiba et al⁹⁵ performed an in-situ photoemission spectroscopy for well organized surfaces high quality epitaxial $La_{1-x} Sr_x MnO_3$ (LSMO) thin films to investigate the temperature changes in the electronic structure of LSMO for ferromagnetic metal LSMO. With $x=0.4$, spectral intensity of the e_g states near the Fermi-level significantly increased with decreased temperature from the detailed analysis of temperature dependence of the $Sr-3d$ core level. The possibility of phase separation derived from the spatial charge fluctuation was ruled out in LSMO thin films.

Most often it is advantageous to employ pyrometer to measure the temperature of a surface. However, reflected radiation originating from sources surrounding the surface of interest is inevitably included into the measurement process. Inclusion of this extraneous radiation component introduces erroneous result. Daniel et al⁹⁶ produced a report discussing the use of a multi-wavelength pyrometer in a laboratory experiment to measure the temperature of a beryllia ceramic tube surface heated by a propane torch flame while a copious amount of extraneous radiation produced by a quartz lamp was simultaneously reflected by the beryllia surface into the pyrometer. The multi-wavelength pyrometer successfully determines not only the temperature of the beryllia surface but also that of the quartz lamp filament.

Metal surfaces are known to be very sensitive to the irradiation of beam of varying nature. Whenever a metal surface is irradiated with a laser beam, electromagnetic radiation energy is converted into heat within the thin surface layer. The maximum surface temperature is the most important quantity which determines the processing of its result. The quantitative expressions for the maximum temperature have been provided by the literature for stationary cases. In practical cases, the moving beams are of better significance. In relation to the temperature effect on surfaces, ion beam plays vital role in the layer development at low energy fluence. The reason being, ion beam is an ideal heat source with a large cooling rate and yields a thick treated layer at low energy fluence.

A comparison study on intense pulsed electron, ion, and laser beams as a heat source for amorphous phase formation on metal surfaces was reported by Akamatsu et al⁹⁷ in which a temporal and spatial evolution of temperature in a pure titanium surface irradiated by the beam was calculated to estimate the cooling rate and the thickness of the treated layer.

The cooling rate increased with decreasing beam energy fluence. This resulted in a reduction in the thickness of the treated layer. Nakashima et al⁹⁸ studied the limiter surface temperature dependence on hydrogen recycling, and then molybdenum impurity production behavior was studied with optical spectroscopy during long pulse plasma discharge in TRIAM-1M. It was observed that the H α intensity critically depended on the limiter surface temperature. The surface temperature and the surface state were investigated with the IR spectroscopy by fitting the obtained spectrum with an assumption of Planck's blackbody radiation equation given by

$$L_{BB}(\gamma) = 2hc_0^2/\gamma^5 [\exp(hc_0/\gamma kT) - 1]$$

where h - Planck's constant, C_0 - velocity of light, k - Boltzmann coefficient, γ - wavelength. The observed spectrum indicated the much higher temperature T_s than the T_{bulk} determined with IR camera, although the absolute intensity was much lower than black body intensity of T_s . They adopted the analysis method reported by Reichle⁹⁹. The observed spectrum was considered to be combination of the low temperature component T_{bulk} from the main part and high temperature component T_{hot} from very small part i.e

$$L(T_s) \sim (1 - \epsilon) L_{BB}(T_{bulk}) + \epsilon L_{BB}(T_{hot})$$

where ϵ - the adjustable parameter to fit the intensity, which indicated to a fraction of the hotter emitter. Based on a fast numerical algorithm which allowed calculation of the induced temperature profile, Romer et al¹⁰⁰ computed the maximum surface temperature for stationary and moving laser beams in which two types of approximating functions were presented relating the scanning speed to the maximum surface temperature. Using dimensionless numbers, their results were applied to different materials. Yan et al¹⁰¹ found that some craters appeared on the irradiated surface that were melted under intense pulsed ion beam (IPB) irradiation. These craters with various size and morphologies limit the utilization of IPB as novel means of surface processing in some cases. The first kind of craters directly related to droplet from the ion source, and the other kind of craters is due to the non-equilibrium process of ultra fast quenching mechanism for the second kind of craters was proposed in this paper.

Surface Configuration

Thermodynamical change due to the change in surface-configuration of applied surfaces, starting from air to chemical liquids to high density amorphous and crystalline solids, can be investigated for value added surface species. At atomic scale, molecular scale, ionic scale and at lattice scale, the thermodynamic concept is very significant as far as the intrinsic characteristics of materials in condensed state is concerned. Being multi-functional in nature, these concepts help in understanding the infinitesimal changes in the bulk phase as well as in the surface system. The thermodynamic behavior of a chiral surface system (Cu-532) has also been investigated through local approach and the harmonic approximation with inter-atomic potential based on the embedded atom method¹⁰². The low coordination of the atoms dramatically affected the thermodynamics and vibrational dynamics of the states. The contribution of vibrational entropy to the thermodynamics of the surface system thus can be computed with the well esteemed vibrational density of

states¹⁰³. The effect of crystal temperature on the dissociation dynamics of nitrogen on a catalytic metal surface used was a non-adiabatic mechanism where the nitrogen crossed from the physisorption potential to a dissociative chemisorption potential. Within this framework the quantum dynamics was solved in three degree of freedom including surface vibrational excitation. In general, surface vibration promotes the dissociation. However, if the non-adiabatic coupling potential is peaked at restricted geometry, exciting surface vibrations can hinder dissociation. This effect can be maximized for the N₂/Fe mass ratio which leads to a negative temperature effect on the dissociation. For higher surface metal masses, this effect disappear (N₂/Ru) and even reverses to a positive temperature effect for the N₂/Re mass ratio¹⁰⁴. In a recent investigation for understanding the effect of temperature on metal-oxide nano structure, Zhou et al¹⁰⁵ studied the temperature effect on the Cu₂O morphology by oxidizing Cu (100) thin films at the temperature ranging from 350°C to 1000°C. They demonstrated that different morphologies of oxide nanostructures can be achieved by modifying the oxidation temperature. Quasi-one-dimensional Cu₂O structures, with aspect ratio as large as 40:1 were formed at the oxidation temperature of 600°C. The *in-situ* observation data on the elongation of Cu₂O islands agreed well with the energetic calculations based on the balance between surface and interface energies and the elastic stress relaxation in three dimensional islands. Further, for investigating the difference in metallic film growth modes on perfect and defective oxide substrate, Fuks et al¹⁰⁶ combined *ab-initio* B3LYP periodic calculations on the slab models of corresponding Me/MgO (001) interface (Me=Ag, Cu) with thermodynamic theory of solid solutions. The change of bonding tendencies between the metal and atoms in the vicinity of the defect-free versus defected substrate influenced the thermodynamic conditions and morphology of the forming monolayer. F_s center on the MgO (001) surface strongly enhances metal adhesion to the oxide substrate. Copper is bound more strongly than silver on both regular and defective MgO (001) surfaces, whereas Ag possess both larger covalence over the surface F_s center as well as higher ability to form dense clusters on perfect MgO (001) surface than Cu. The surface F_s centers tendency towards metal aggregation lead to the formation of disordered 2D metallic film. Thermal atom diffraction from a densely packed metal surface was observed for the first time by Boato et al¹⁰⁷ using a supersonic beam and a low temperature Ag (111) crystal face. For He-Ag, the intensity of the (1,0) diffraction peak was about 2x10⁻³ times that of the specular beam, while for H₂-Ag it was about 3x10⁻² times that of the specular beam. Solid state compound phase formation was investigated between thin metal films (Cu, Ir, Pt, Re, Y, Yb, and Zr) and SiO₂ substrate using Rutherford Backscattering Spectroscopy (RBS) and X-ray diffraction (XRD) techniques. The thin film couples were annealed for time periods ranging from 30 minutes to 3 hours between 320^o and 900^oC. It was found that Y, Yb, and Zr reacted with SiO₂ whereas Cu, Ir, Pt, Re, and Mo did not. Heats of reaction were calculated for all possible combination of silicate and metal-oxide reaction products. Comparing with experimental results obtained from this study and the

literature showed in all case the metal SiO₂ reaction only take place when the calculated heat of reaction was negative¹⁰⁸. These investigations however, did not involve any rigorous numerical approaches so as to compute the thermodynamical values.

V. RESULTS AND DISCUSSIONS

Studies on thermodynamic behavior of metallic, ceramic, polymeric and many other applied surfaces have been conducted by a large number of researchers as depicted in the varying paragraphs of previous sections. The reason being, these studies are heavily used in integrated circuits, electronic probes, bio sensors, chemical sensors, coating materials, and many other viable circumstances. With a view to improve the techno-economic profile of applied surfaces and develop chemical functionalities on to the substrate materials, thermodynamic behavior of surface systems stipulates mutual understanding for mathematical models and numerical approaches. This in return, cause to procure numerous research gaps and inconsistency in the interpretation as well.

One of the typical gaps observed in these models is the occurrence of the defects. During processing defects also occur on the surface of chemical layer or polymeric layer. These defects closely links to the transition temperature¹⁰⁹. These defects appear under particular thermal condition and the situation when the polymeric surface requires coating of a thin organic layer. Therefore the kinetics of the defects can also be correlated to the transition temperature of the substrate material. Another gap witnesses the absence of interpretation for entropy and heat of adsorption as well as heat of desorption for the adsorbibg/desorbing chemical species.

With the limited volume of the literature search, it has been observed that the thermodynamics of the surface films requires a multi-stages investigation for a well defined applied surfaces and related chemical species. During these studies the authors have recognized a wide spectrum of research gaps that do not suffice the data source so as to predict the most appropriate numerical approach (model) for the surface functionalization of applied surfaces (Fe-particle) resembling the situation of metal-chemical surface systems. Therefore, it is highly desirable to compute and compile the data source for the basic information with the comprehensive source of models that involve many crucial situations under the speculation of the following facts discussed below;

1. Transport of chemical species in bulk liquid phase.
2. Reactivity of metal surfaces and chemical species.
3. Adsorption of chemical species on to the substrate
4. Chemical reaction of chemical species with substrate.
5. Formation of surface compounds during the reactions.
6. Dissociation of surface compounds into small fractions.
7. Transport of the chemical fractions and surface diffusion.
8. Creation of the complex mixtures and multi-layer films.
9. Isolation of sub-layer (solvent-fractionated) film specimens.

VI. CONCLUSION

It is concluded that marked inconsistencies in the model predictions for thermodynamic properties of applied surfaces spreads over the literatures. Such an incoherent and

inconsistent behavior can be overcome with the unanimous approaches for computing the thermodynamic parameters of varying surface systems. The factors that cause these inconveniences severely can be rectified to some formidable level thereby employing a common algorithm. The same has marked scopes for improvement in the surface as well as bulk system. Further it is speculated that an appropriate approach can be put forward for the computation of thermodynamic properties of surfaces that should be unified in nature and hold good for a wide range of study.

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