



Physical CHEMISTRY

An Indian Journal

Trade Science Inc.

Full Paper

PCAIJ, 5(2), 2010 [58-61]

Basic features of the young equation

Ahmed Kamel Helmy^{1*}, Eladio A.Ferreiro²

¹Universidad Nacional del Sur, B8000 Bahía Blanca (ARGENTINA)

²Consejo Nacional de Investigaciones Científicas y Técnicas, B8000 Bahía Blanca (ARGENTINA)

E-mail: akhelmi@criba.edu.ar

Received: 28th May, 2010 ; Accepted: 7th June, 2010

ABSTRACT

The young equation describes the equilibrium of three heterogeneous masses in contact and are homogeneous quite up to the separating interfaces, with respect to the density of energy, entropy and the chemical potential of the components (chemical species). The basic characteristics of the interfacial energy terms of the equation and their interrelations especially for the solid-water-vapour system are examined in detail. The solid-vapour interfacial energy, the introduction of surface pressure in the Young equation and their relation with monolayer coverage of adsorbate are considered in detail. The stability of the system and the conditions under which the equation is applied are emphasized.

© 2010 Trade Science Inc. - INDIA

KEYWORDS

Young equation;
Contact angles;
Solid-water-vapour system.

INTRODUCTION

Though almost two centuries have passed since the appearance of the Young equation^[1-3], many important properties of the equation have not been elucidated which lead to incorrect applications, doubtful results and conclusions.

Not only the equation is valuable in itself, defining relations between certain interfacial energies, but it is also a governing relation on other equations and formulas that contain a contact angle term such as the equations that describe capillarity and liquid flow through capillaries and beds; Washburn and similar formulas^[4-6]. In other words, the validity of the results obtained from such formulas depends on the fact that the systems involved obey the requirements of the Young equation to be mentioned below.

It is the purpose of this report to describe the basic features of the Young equation and the systems involved, with special emphasis on the solid-vapour system in an equilibrium unaffected by gravity.

THE YOUNG EQUATION

The Young equation was published first by Young without proof^[1-3] in (1805). Gibbs, 70 year later published similar equations for the same and different systems of heterogeneous substances at equilibrium. He treated in detail^[7] the thermodynamics of this equilibrium and the influence of surfaces of discontinuity between the phases under consideration. Basing on mechanical considerations (forces and vectors, see Figure 1) that the resultant of all forces exercised along the line at which the interfacial surfaces of discontinuity intersect is null,

he gave the same equation published by Young for the system of a solid (S) and two fluid masses (A and B) in which the solid is continuous at the line where it meets the two fluids. The condition of equilibrium as given by Gibbs is

$$\sigma_{AB} \cos \theta = \sigma_{BS} - \sigma_{AS}, \quad (1)$$

where the σ 's are interfacial tensions (energies).

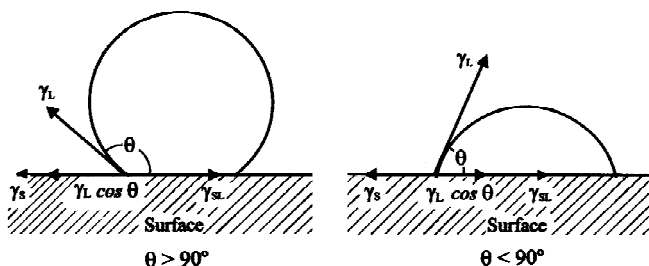


Figure 1 : Liquid-solid contact angles schematic diagram for $\theta < 90^\circ$ and $\theta > 90^\circ$. The Young equation when $\cos \theta$ is positive (as the directions of the vectors indicate): $\gamma_{sv} - \gamma_{sl} - \gamma_{lv} \cos \theta = 0$ and when $\cos \theta$ is negative is $\gamma_{sv} + \gamma_{lv} \cos \theta - \gamma_{sl} = 0$. Hence $\gamma_{lv} \cos \theta$ and γ_{sl} will have always a negative sign whether the angle is lower or greater than 90° .

He also gave similar relations when the line where the masses meet is at the edge of the solid. Thus at equilibrium

$$\sigma_{AB} \cos \alpha = \sigma_{BS} - \sigma_{AS}, \quad (2)$$

and

$$\sigma_{AB} \cos \beta = \sigma_{AS} - \sigma_{BS}, \quad (3)$$

which reduces to (1) when $\alpha + \beta = \pi$; where alpha and beta are the angles filled by the fluids A and B respectively.

More details about the systems under consideration follows.

THE SYSTEM

The system of application of the Young equation is that in which three homogeneous phases of matter meet at plane interfaces along a line. The interfaces therefore, are continuous, homogeneous and isotropic. These phases could be 3 fluids or two fluids and a solid. One of the fluids could be a gas as is the case of a solid-water-vapour system.

The temperature, pressure and chemical potentials must have values uniform throughout the phases so that there may be thermal, hydrostatic and physicochemical equilibrium. Also the interfaces must have no

components except such as belong to the bulk phases^[7,8].

The terms of the young equation

The Young equation for a solid-liquid-vapour system (SLV) reads

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta, \quad (4)$$

where γ_{sv} is the solid-vapour interfacial energy, γ_{sl} is the solid-liquid interfacial energy, γ_{lv} is the liquid vapour interfacial energy and θ is the liquid-solid contact angle.

Mathematical relations in general, contain variables and constants. In the SLV equilibrium system, γ_{sl} and $\gamma_{lv} \cos \theta$ are constants and independent of vapour pressure, hence γ_{sv} should have therefore a constant value. In other words eq. (4) is valid only for one value of vapour pressure. In order to identify such value we proceed as follows.

As all the γ 's in eq. (4) should represent energies of isotropic interfaces (uniform in properties) as is required by the theoretical treatment of heterogeneous masses in contact and in equilibrium^[7], the solid-vapour interface can only be isotropic at monolayer coverage. Above and below this coverage it loses its isotropic property since part of the solid surface would be bare below monolayer coverage and part of the surface would be covered with multilayers of water above monolayer coverage. Since γ_{sl} and $\gamma_{lv} \cos \theta$ are constant quantities, the Young equation is thus only valid for one value of γ_{sv} i.e. the solid-vapour interfacial energy at monolayer coverage. The difference $(\gamma_{sv} - \gamma_{sl})$ in the LHS of the Young equation represents therefore the energy difference between the solid-vapour and the solid-liquid isotropic interfaces.

The realization that there is an equilibrium adsorbed film on the solid surface was made by Bangham^[9]. This film is responsible for the lowering of the surface energy γ_s of the clean solid surface changing the clean surface to a surface covered with liquid molecules that are in equilibrium with the vapour phase i.e. the formation of a solid-vapour interface of lower energy. The difference between this two solid surface energies $(\gamma_s - \gamma'_{sv})$ is physically equivalent to a surface pressure^[10], thus

$$\gamma_s - \gamma'_{sv} = \pi, \quad (5)$$

where π is the surface pressure and can have values depending on the values of γ'_{sv} which depends in turn on the equilibrium vapour pressure.

Full Paper

Bangham did not distinguish between γ_{SV} of eq. (4) which is single valued, as shown above, and γ'_{SV} of eq. (5) considering that π and γ'_{SV} can have values that cover all the range of vapour pressure i.e. P/P_0 from (0 - 1), which is untrue as shown below.

The introduction of π in eq. (4) produces a Young equation that contains the surface energy of the clean surface γ_S in place of γ_{SV} :

$$\gamma_S - \gamma_{SL} = \gamma_{LV} \cos \theta + \pi. \quad (6)$$

The surface pressure in the young equation

Since γ_S in eq. (5) is a constant, the value of π depends on the value of γ'_{SV} . As shown above γ_{SV} is single valued and its value is fixed at the monolayer coverage, hence π in eq. (5) has the value of the surface pressure at monolayer coverage. This appears reasonable, since below monolayer coverage π is continually decreasing as the vapour pressure increases. Furthermore for equilibrium vapour pressures higher than that at monolayer coverage, the surface pressure does not exist as such, since the solid surface acquires layers of water arriving at a thick film at the saturation pressure^[6,11-13] and the solid-vapour interface is replaced by a solid-liquid interface. The system is then not the three phase system of the Young equation (4) in which a surface pressure exists. In films on liquid surfaces the surface pressure is equal to zero after monolayer coverages (^[3], p. 398).

The contact angle and the sign of $\gamma_{LV} \cos \theta$ term in the young equation

The sign of the $\gamma_{LV} \cos \theta$ term of the Young equation can be appreciated examining Figure 1 where two drops of liquid with two different contact angles are shown. The Young equation when $\cos \theta$ is positive is (as the direction of the vectors indicate):

$$\gamma_{SV} - \gamma_{SL} - \gamma_{LV} \cos \theta = 0,$$

and when $\cos \theta$ is negative is

$$\gamma_{SV} + \gamma_{LV} \cos \theta - \gamma_{SL} = 0,$$

hence $\gamma_{LV} \cos \theta$ and γ_{SL} will have always a negative sign whether the angle is $< 90^\circ$ or $> 90^\circ$.

With respect to the values of vapour pressure for contact angle determinations, in order that the solid-liquid system be in thermodynamic equilibrium, that is stable in time with no loss or gain of water to or from the vapour phase, the equilibrium vapour pressure should

be the same as that of the surface of the drop. The value of the vapour pressure P/P_0 of pure water of a drop is almost equal to 1 at 25 °C since a drop of water of radius of 10^{-5} cm has only a P/P_0 value 1 percent greater than that of a flat water surface as the Kelvin equation would indicate^[14].

It is worth mentioning that the contact angle in Young equation is an equilibrium angle (the SLV system is in a thermodynamic equilibrium). Contact angles determined under non equilibrium conditions (dependent on time) such as advancing and receding angles are not valid for use in the Young as well as in the equations mentioned earlier dependent on the Young equation.

It is worth mention that it is possible to obtain the value of a contact angle from the adsorption isotherm of powder samples through the use of the Gibbs adsorption integral^[6,11,19].

The relation between the terms of the young equation and the stability of the SLV system

The application of the Young equation is limited to the validity of certain relation between the energies of the interfaces in addition to the interfaces being isotropic. As appears from eq. (4), limiting our consideration to a solid-water-vapour system, γ_{SV} is greater in value than γ_{SL} since $\gamma_{LV} \cos \theta$ is always a positive quantity, as shown above. Since γ_{SL} is also a positive quantity, γ_{SV} is greater than γ_{LV} since $\cos \theta$ has values between zero and one. Also the value of γ_{SL} is between the values of γ_S and γ_{LV} ^[8]. Therefore $\gamma_{SL} > \gamma_{LV}$. The inequality $\gamma_{SV} > \gamma_{SL} > \gamma_{LV}$ follows then from the Young equation. Furthermore when

$$\gamma_{SV} > \gamma_{SL} + \gamma_{LV}$$

or

$$\gamma_{SV} < \gamma_{SL} + \gamma_{LV},$$

the discontinuities between the phases are difficult to realize (^[7], p. 258).

It is clear therefore that the Young equation and other relations containing contact angles cannot be applied to systems when the above inequalities exist and the values obtained would be of doubtful value^[4,6,13,15].

The surface energy of solids (γ_S)

Though the Young equation gives differences between interfacial energies and not the individual values

of the energies, the solid-water-vapour systems that obey the Young equation and have water adsorption isotherms of type I or II from which the monolayer of adsorbate and the vapour pressure at the monolayer coverage can be obtained^[16], average values of the solid surface energy can be calculated^[11]. The calculations are based on the combination of the Young equation with the pair interaction relation^[8]:

$$\gamma_s + \gamma_{LV} - k \gamma_{SL} = 0, \quad (7)$$

where k is an interaction parameter.

The results obtained by this method are of the right order of magnitude for quartz^[6], graphitized carbon^[18] and for several clay minerals^[17,19,20].

REFERENCES

- [1] T.Young; Phil.Trans., (1805).
- [2] Miscellaneous Works of the late Tomas Young; 3 volumes. Ed. Peacock. Murray, London (1855), republished by Thoemes Press, 1, 432, 418 (2003).
- [3] N.K.Adam; 'The Physics and Chemistry of Surfaces'. Oxford University Press, London, (1941).
- [4] A.Siebold, A.Wallizer, M.Nardin, M.G.Oppliger; J.Colloid Interface Sci., 186, 60 (1997).
- [5] M.Lazghab, K.Saleh, I.Pezron, P.Guigon, L.Komunjer; Powder Techn., 157, 79 (2005).
- [6] A.K.Helmy, S.G. de Bussetti, E.A.Ferreiro; Appl. Surf.Sci., 253, 6878 (2007).
- [7] J.W.Gibbs; 'The Collected Works', Oxford Univ. Press, London, 1, (1957).
- [8] E.A.Guggenheim; 'Thermodynamics', North Holland Publ. Co., Amsterdam, 221 (1959).
- [9] D.M.Bangham; Trans.Faraday Soc., 33, 805 (1937).
- [10] J.H.de Boer; 'The Dynamic Character of Adsorption'. The Clarendon Press, Oxford, (1953).
- [11] A.K.Helmy, E.A.Ferreiro; Physical Chemistry: An Indian Journal, (in press) (2010).
- [12] C.S.Brooks; J.Phys.Chem., 64, 532 (1960).
- [13] A.W.Adamson; J.Chem.Education, 44, 710 (1967).
- [14] J.A.V.Butler; Chemical Thermodynamics, McMillan and Co. Ltd., London, (1951).
- [15] T.H.Muster, C.A.Prestige, R.A.Hayes; Colloids Surf.A: Physicochem.Eng.Aspects, 176, 253 (2001).
- [16] A.K.Helmy; 'Relationship between Adsorbate Molecular Area and Monolayer Coverage', in: A.T.Hubbard (Ed.) Encyclopedia of Surface and Colloid Science, 2nd ed., Taylor & Francis, N.Y., 133 (2006).
- [17] A.K.Helmy, E.A.Ferreiro, S.G.de Bussetti; J.Colloid Interf.Sci., 285, 314 (2005).
- [18] A.K.Helmy, E.A.Ferreiro, S.G.de Bussetti; Appl.Surf.Sci., 235, 4966 (2007).
- [19] A.K.Helmy, S.G.de Bussetti; Appl.Surf.Sci., 255, 2920 (2008).
- [20] A.K.Helmy, S.G.de Bussetti, E.A.Ferreiro; Powder Technol., 171, 126 (2007).