

A Course on

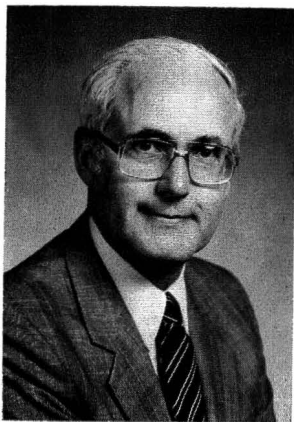
SURFACE PHENOMENA

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COLLOID AND SURFACE SCIENCE have been subjects of interest to scientists for many years. Within the last 20 years engineers have been paying more and more attention to this area of study. The more recent developments of the application of mathematical modelling and the gradual collection of numerical values for different surface properties have meant that colloid and surface science can be used to solve industrial problems. The combination of the fundamentals of surface phenomena with practical problems is what is unique about the graduate course offered in our department. The course is structured around a series of case problems encountered in the process illustrated in the flow diagram shown in Fig. 1. Here the engineer is faced with a multi-phase reactor, a phase separator, a vacuum distillation column, a solvent extraction process, a wastewater treatment facility and a coating process.



D. R. Woods is a graduate of Queen's University and the University of Wisconsin (Ph.D.). His teaching and research interests are in process analysis, and synthesis communication skills, cost estimation, separations, surface phenomena and developing problem solving skills. He is the author of "Financial Decision-Making in the Process Industry." He received the Ontario Confederation of University Faculty Association award for Outstanding Contribution to University Teaching.

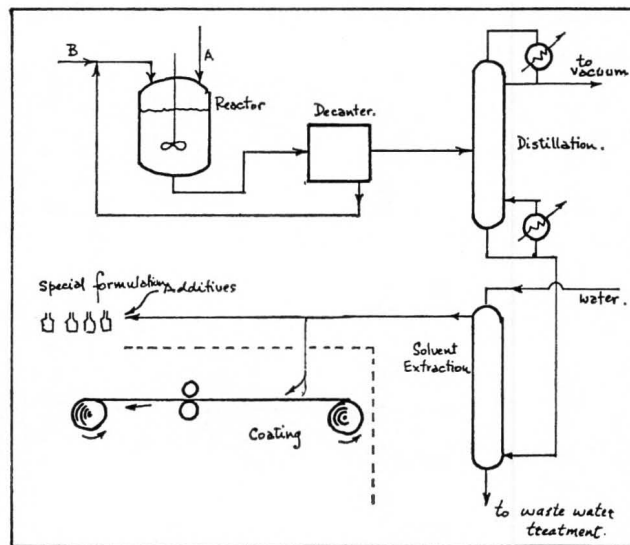


FIGURE 1. An imaginary process.

The course is divided into nine units and in each of the nine units students focus first on a case problem related to the process shown in Fig. 1 that is to be solved. The problems have been chosen carefully so as to require certain new knowledge in the area of surface phenomena. Once this knowledge has been acquired the practical calculations are then completed to solve particular case problems. Each unit ends by discussing other applications of the fundamental concepts of surface phenomena to practical problems of interest.

The first unit focusses more on what is a surface and a way of thinking about surfaces that forms the background for the rest of the text. The very thin thickness of the surface, the anisotropy of the surface and the force fields that a molecule experiences in the surface are the major themes in the first chapter. The basic idea that two-dimensional surface phenomena is but an extension of the familiar three-dimensional behaviour is the overall theme of the course. The identification of analogous two-dimensional surface properties to the familiar three dimensional

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surface properties is highlighted. These are illustrated in Table 1. Similarly, the analogous surface equations of change are tabulated and contrasted with their three dimensional bulk phase analogues. Practical problems are given to illustrate the application of these principles.

The next unit helps the student identify when surfaces should be important. Although much of the detail in this unit focusses on particle and polymer size characterization, the emphasis is on thinking about when surface phenomena will become important. The general guidelines are whenever the particles are less than a millimeter in diameter, whenever we encounter thin films, whenever a surface is broken to create sprays, emulsions or powders, whenever surfaces are bound together, whenever reactions occur at surfaces, and whenever we experience some unexplained behaviour.

The third unit focusses on the multiphase reactor and poses the question "How does one decide on the operating conditions within the reactor to generate a dispersion with a given characteristic size?" More specifically, "For the reactor in our process, the vessel is 2 m in diameter with a 0.7 m diameter, 6 bladed impeller. Full baffles are used. If the reactant mixture in our alkylation reactor is i-butane and 98% sulfuric acid, what should be the rotational speed of the impeller to give a volume to surface average drop size of 200 μm ? Assume the temperature is 20°C and that the holdup is 0.40." Since this problem involves the creation of an emulsion, surface phenomena should be important. To answer this question requires that we learn something about surface tension. The concept of a surface tension of a liquid is discussed as a thermodynamic reversible work required to increase the surface area by one unit, as a two-dimensional pressure in a mechanical energy balance and as the result of cutting the microscale bonds to create a surface. Methods of estimating the dispersion contribution of surface tension are given. Tables of data are provided. Measurement techniques are surveyed. Methods of estimating both the surface and interfacial tensions for fluids systems are given. The fundamental concepts introduced are:

a. Young-LaPlace equilibrium relationship between bulk phase pressures and surface tension:

For a single surface surface

$$p^{\text{II}} - p^{\text{I}} = \gamma \left[\frac{1}{r_1} + \frac{1}{r_2} \right]$$

TABLE 1
Analogous Properties in Bulk and Surface Phases

Concept	Bulk Phase	Surface Phase	
		Parallel to Surface	Perpendicular to Surface
Temperature	T	T ^o	
Pressure	P	γ , surface tension π , surface pressure	
Concentration	c	c ^o , surface concn. Γ , surface excess concentration	
Shape	NA	radii of curvature	
Chemical potential	u	u ^o	
Electrochemical potential	e	e ^o	
Charge	σ	σ^o	
Potential	ϕ	$\phi_{DL}^o X$	
Internal Energy	U	U ^o	
Entropy	S	S ^o	
Enthalpy	H	H ^o	
Gibbs Free Energy	G	G ^o	
Helmholtz Free Energy	A	A ^o	
Work functions		of cohesion of adhesion	
Force balance		θ , contact angle S, spreading coefft.	
Thermal conductivity	k	k ^o	k*
Electrical conductivity	K	K ^o	K*
Diffusivity	D	D ^o	D*
Elasticity, shear coefft.	G	G ^o	
dilational coefft.	ϵ	ϵ^o	
Viscosity, shear coefft.	μ	μ^o	
dilational coefft.	K	K ^{o*}	

b. For fluids whose intermolecular forces are based solely on physical forces (and no hydrogen bonding occurs), then

$$\gamma^d = \frac{1 A}{4(6 \pi h_0^2)}$$

or for close separations,

$$\gamma = \frac{1.2 A}{4 \pi y_0^2}$$

c. For two liquids

$$\gamma_{\text{II-III}} = \gamma_{\text{I-II}} + \gamma_{\text{I-III}} - 2\phi\sqrt{\gamma_{\text{III}} \gamma_{\text{II}}}$$

where

p = pressure

γ = surface tension

r = radius of curvature

A = Hamaker's constant

h = distance of separation between two layers

y = distance of separation between molecules

ϕ = Good and Elbing correction factor

Super- or subscripts

I = bulk phase I

II = bulk phase II

III = bulk phase III

d = dispersion component

The combination of the fundamentals of surface phenomena with practical problems is what is unique about the graduate course offered . . . it is structured around a series of case problems . . .

With this background in surface phenomena, the students then proceed to select the speed of rotation for the case problem: 2.4 rps. From this practical calculation the students then estimate what happens to the drop size distribution if the reacting mixture is discharged from the reactor at 5 m per s through an 8 cm diameter pipe. The answer to this is that the volume to surface average diameter decreases to 195 μm . Other variations on the theme would be to predict the drop size distribution coming from a pump that is pumping the material. These basic principles that have defined surface tension illustrate how the dispersion is now extended to other applications. These include bubble formation as required in an activated sludge reactor, flotation or liquid phase oxidation reactors; the diameter of sprays for drying in spray dryers, air pollution control equipment, jet scrubbers, ink jet printing and sprays of insecticides. All of these applications have considered only fluid-fluid surfaces. We add the definition of surface tension for solid systems at this stage and go on to illustrate how this information can be used to describe crushing and grinding circuits.

The case problem for Unit 4 is to select the correct material of construction for tower packing in a distillation tower. The case specifically is: in a column distilling benzene and n-heptane, can we use a teflon packing? Is this the correct choice? This case problem requires that we look at the interaction amongst three surfaces and introduce the idea of a contact angle and how it varies as a function of state properties and solid systems, especially the solid roughness. The concept is defined for a solid-liquid-liquid or a three-liquid system and Young's equation is introduced. The characteristics of contact angles depend upon advancing versus receding hysteresis effect, the inhomogeneities of the solid and the roughness ratio. The sensitivity of contact angle to the force fields in the immediate vicinity of the contact line, and the importance of the outermost adsorbed surface are illustrated. The concepts of critical surface tension for a solid and autophobicity are introduced. Methods of estimating the contact angle from surface tension data and correcting for

mutual solubility of the various phases are given. Finally, the relationship between work of cohesion, work of adhesion and spreading coefficient are given. This interaction is illustrated through the various possible conditions for engulfing, particle engulfing or complete engulfing of a particulate when it is at a moving boundary. The dynamic behaviour of contact line and the flow of slugs of material through capillaries and the wetting of a fluid in coating processes are described. The summary of the key equations including the definition of the capillary number are as follows.

Young's Equation:

$$\gamma_{I-II} \cos \theta = \gamma_{I-III,2} - \gamma_{I-III,1}$$

for gas-liquid-solid

$$\gamma_{I-II} \cos \theta = \gamma_{I-III} - \gamma_{II-III} - \pi_{III,2} + \pi_{II-III,1}$$

for liquid-liquid-solid

$$\begin{aligned} \gamma_{I-II} \cos \theta_{123} &= \gamma_{I-III} - \gamma_{II-III} - \pi_{III,2} - \pi_{III,1} \\ &\quad - \pi_{I-III,2} + \pi_{II-III,1} \end{aligned}$$

Cassie equation for inhomogeneous solid

$$\cos \theta = n_1 \cos \theta_1 + n_2 \cos \theta_2$$

Wenzel's result for rough surfaces

$$\gamma_{I-II} \cos \theta' = r(\gamma_{I-III} - \gamma_{II-III})$$

We defined advancing and receding angles in terms of an intrinsic angle θ_E

For low energy solids, Zisman defined a critical surface tension for a solid, γ_c , which indicated that a fluid with $\gamma_{I-II} < \gamma_c$ would spread over the solid, whereas if $\gamma_{I-II} > \gamma_c$, it will not spread.

For most high energy solids (with $\gamma_{I-II} > 100 \text{ mN}\cdot\text{m}^{-1}$), most liquids spread over these solids except autophobic liquids that will not because the bulk liquid cannot spread over its own adsorbed species.

The work of cohesion is $W_c \cong 2 \gamma_{II-V}$

The work of adhesion is $W_A = \gamma_{III} + \gamma_{I-II} - \gamma_{II-III}$

The spreading coefficient is $W_A - W_c$

For example

$$S_1 \cong \gamma_{II-III} - (\gamma_{I-III} + \gamma_{I-II})$$

The spreading coefficient can be used to predict engulfment or rejection. For dynamic behaviour, the flow through a capillary is given as

$$(\Delta P) D = 4n \gamma_{I-II} (\cos \phi_R - \cos \phi_A)$$

A significant dimensionless group is the Capil-

lary number defined as

$$Ca = \frac{V_{CL} \mu_{II}}{\gamma_{I-II}}$$

Based on this information we could use the critical surface tension and the surface of the material being distilled (in this case benzene and normal heptane) to show that this choice of teflon would give film instability and non-wetting of the packing would result. As in other chapters we extend the concept of contact angle to the design of condensers, and specifically promoting drop-wise condensation to the design of reboilers, boiling phenomena and to film breakup in a tube two-bundle of a nuclear reactor to prevent dry patch formation. This is also related to polymerization reactors, to oil spill cleanup and to detergency, and finally to tertiary oil recovery.

Table 2 leads off the case problem for Unit 5. This illustrates that for different distillation conditions we get strange behaviour. To understand this behaviour we lead into a study of how the surface tension varies as a function of temperature, pressure, concentration, applied electrical field, curvature and time. After this exploration (which includes the Krafft temperature, water, surfactant and co-surfactant systems, and the effect of electrolyte on surface tension behaviour), we can use this information to lead into Marangoni type instability analysis. We start with macro and micro generated flows based on a temperature difference and then move on to the same type of flows as based on concentration variation. The application is not only to this case problem of looking at surface tension positive and surface tension negative systems and their use in understanding distillation behaviour, but in the drying of paint films, the conditions for a solvent extraction column, the stability of thin films in heat

TABLE 2
Unexpected Behaviour

Location/ Operation	Device	Chemicals	Observation
Edmonton, distillation	30 sieve tray column	n-heptane toluene	plate efficiency abnormally high, floods easily
Glace Bay, distillation	12 m Pall ring packed tower	benzene cyclohexane with azeotrope as the distillate product	required HTU almost double what we expected

exchanger and wiped film evaporator systems and in gas adsorption. We have been fortunate enough to obtain films from Royal Dutch Shell, Dr. Harvey Palmer at the University of Rochester, Dr. J. C. Berg, the University of Washington and Dr. Keith Brimacombe, the University of British Columbia, that visually illustrate this behaviour.

The next unit presents the case problem of trying to design an adhering system that will bind a plastic to a metal. This introduces the attractive force between two surfaces of condensed media. The emphasis in the overview is on the microscopic, or Hamaker, approach—although references are made to the Lifschitz and Ninhan and Persegian methods of estimating the attractive force between two surfaces. Various methods of estimating the Hamaker constant and accommodating for the attractive forces between various configurations are illustrated. Worked case examples include the attractive force between drops of chlorobenzene in water and the same drops coated with a monolayer of surfactant. When it comes to the adhesion question the additional aspects of the viscosity and flowability of the adherent and the surface area of contact between the two surfaces is also important. The application of these ideas to the production of pellets is illustrated with case examples.

Unit 7 explores the possibility of foam fractionation as a technique to remove some of the emulsifier that gets into the waste water from our process. This leads to the concept of surface concentration, methods of defining it, modelling it and measuring it. Our emphasis is on the indirect mass balance and the indirect thermodynamic balance (Gibbs adsorption isotherm technique). The methods of estimating based on heats of immersion and calorimetry are discussed briefly as are the various models for relating surface concentration to bulk concentration. The case problem, namely the design of the waste treatment plant, is worked out. The ideas are extended to adsorption and mass transfer in a solvent extraction column and where the surfaces are contaminated with surfactant and to the adsorption of emulsifier on latex.

A very large unit is on surface charge and the stability of dispersions. Many problems can be used to illustrate this application although our initial focus is on the decanter design and coalescence. The description of surface charge parallels the description of surface concentration (the only

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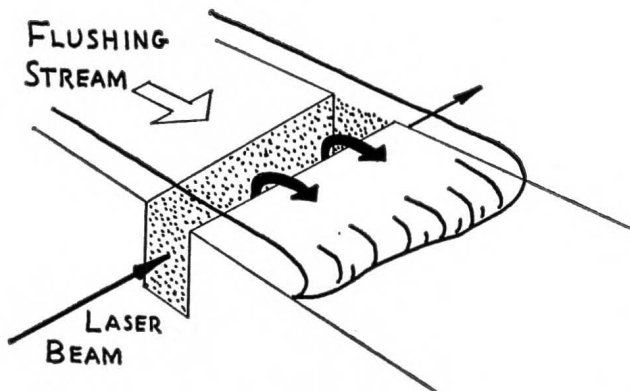


FIGURE 7. Experiment for study of removal of fluid from a cavity by an external stream.

that simulates a trapped contaminant. An external flushing flow is then initiated, which induces circulation within the cavity. A laser light shines down the cavity axis, and is received at the far end of the cavity. The intensity of the transmitted light is related to the amount of dye remaining in the cavity. In this way it is possible to measure the rate of removal of the contaminant, as a function of external flowrate, cavity geometry (aspect ratio), and viscosity of the trapped liquid.

This dual approach to research, in which theoretical and experimental studies proceed simultaneously, **but interactively**, is characteristic of our philosophy of research, and is proving to be quite successful.

Space does not permit a more complete discussion of our research program in this field. Suffice it to say that we are pursuing many of the questions raised in the discussion above, and that we anticipate that we will continue to carry on research in this field for some time to come. □

ACKNOWLEDGEMENT

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difference is that now we are accounting for the charged species rather than any species at the surface). The indirect mass balance and the indirect thermodynamic approaches (the Lippman equation) provide nice parallels between the two subjects. Details are given of the modelling of the electrochemical double layer with the emphasis on the effect of the variables, especially the potential determining ions, the indifferent electrolyte and the valence of the indifferent electrolyte on the double layer. The case problem is discussed and the emphasis then shifts to the DLVO theory which combines the material from Unit 6 with that of the current unit to yield the energy interaction curves. The dynamics of the stability of dispersions is discussed in the context of the von Smoluchowski equation for rapid coagulation and the use of the retardation factor, W , to account for slow coagulation. Models are also developed for orthokinetic coagulation. This section concludes with the design procedures for coagulation basins. Examples are worked for the case of coagulation of SBR latex and polystyrene latex. Other examples illustrated include ion exchange, froth flotation, electrostatic charging through pumping, deep bed filtration and corrosion product deposition in cooling circuits.

In the final unit in this course the stated case problem is to select a protective colloid (namely a polymer) that can be used in the suspension polymerization of PVC. This topic requires that we understand not only the adsorption of polymers to a surface but the configuration of the polymers once they are absorbed into the surface. The calculations introduced focus on the volume restriction and osmotic repulsion that occur when two surfaces containing polymers approach each other. This discussion of steric stabilization focuses mostly on suspension polymerization ap-

plications, although it could be used and extended to other topics.

This course has evolved over the past 10 years and has taken on more and more of the practical application flavour as data become available and as examples of the application are worked out. At the present time the course is offered both as a graduate course and as a technical elective for seniors. We find that the attractive features of this course are the practical applications, the demonstrations that can be given in class to illustrate the behaviour, and the research films that have been developed to illustrate the behaviour. □

REVIEW: REACTOR DESIGN

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good qualitative discussion of the many problems related to reactor analysis and design.

The book is divided into two parts. The first part, containing six chapters, is on Chemical Engineering Kinetics. The second part has eight chapters, and deals with the Analysis and Design of Chemical Reactors.

In the kinetics part, the first chapter is on homogeneous reaction kinetics, while the second deals with kinetics of heterogeneous catalytic reactions. In Chapter 2, the treatment of how Langmuir-Hinshelwood Hougen-Watson rate equations are derived, given a reaction mechanism, is presented well. Both chapters also contain methods for kinetic parameter estimation, which are usually not found in most texts. Chapter 3 is the longest one in the first part, and it treats the interaction of transport processes with reaction kinetics in a single catalyst pellet—essentially the effectiveness factor problem. It is a good and thorough chapter. Chapter 4 has a good account of gas-solid noncatalytic reactions. Catalyst deactivation, by poisoning and coking, is treated in Chapter 5. Gas-liquid reactions are covered in Chapter 6, where both the film and surface renewal models are discussed.

The second part of the book starts out with a short Chapter 7 on transport equations for reactors. The next three chapters treat the batch, plug-flow, and stirred-tank reactors, respectively. Chapter 11, on fixed-bed reactors, is the longest (130 pages) in the book, and is indeed comprehensive. One and two-dimensional pseudohomogeneous and heterogeneous models are discussed in detail, and correlations to estimate transport parameters for these models are also given.

Chapter 12 deals with non-ideal flow patterns, and also has a description of the more fundamental population balance models. Chapters 13 and 14 discuss the modeling of fluid-bed and multiphase reactors, respectively.

The collection of topics in the book is broader than in most other books available in the reaction engineering area, and this is a genuine strength. Nevertheless, there are omissions, some of which may also be cited. These include thermodynamics of chemical reactions (a weakness also in several other books in the area); experimental methods for measuring transport properties in pellets, and a comparison of measurements with predictions of several models that are discussed; metal catalyst deactivation by sintering. In a book of this type, it would have also been nice to see, at least for CSTRs, a more thorough treatment of steady state multiplicity for single and complex reactions, and of the complexities of transient behavior that are possible—but, of course, not everyone shares the same hobbies.

The preface suggests that the book can be used at both the undergraduate and graduate levels. However, in view of the general level and extent of treatment, I expect that it is appropriate and more likely to be used as a graduate text. Those engaged in practice will also find this to be a useful source of principles and design information, and with the extensive references provided, an excellent introduction to the research literature.

There are some 112 problems given at the end of chapters, and a solutions manual is available. □

SELECTED NUMERICAL METHODS AND COMPUTER PROGRAMS FOR CHEMICAL ENGINEERS

*By Huan-Yang Chang, Ira Earl Over
Sterling Swift Publishing Co.
Manchara, Texas 78562*

**Reviewed by
Charles A. Walker
Yale University**

Introductory courses in computer programming necessarily emphasize methods that are available for solving general classes of problems without going into detail on the applications of these methods to the subject matter of specific disciplines. Since students of any discipline usually study computer programming at the same time that they are being introduced to the fundamental