

ADVANCED THERMODYNAMICS

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THE COURSE TO BE discussed here is Engineering 510 "Advanced Thermodynamics," which is a "core" course in the College of Engineering at Notre Dame. The only prerequisite is one semester of undergraduate thermodynamics, so that engineering graduate students of all disciplines can qualify for the course. The course is required for graduate chemical engineers and is often taken as an elective by engineers of other disciplines. The latter group of students generally

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has a one-semester background from, say, Holman¹ or Reynolds and Perkins,² while the chemical engineers are more thoroughly schooled in undergraduate thermodynamics, usually having two semesters of formal study, covering both physical and chemical thermodynamics, as well as additional exposure in "material and energy balances" and in physical chemistry.

The challenge is to present a course that will substantially enlighten and expand the knowledge of the chemical engineers, while at the same time will provide a strong, fundamental unit of thermodynamics for the non-chemical engineers, who may compose as much as one-half of the class. That thermodynamics, a discipline based on a few fundamental laws and their application, is taught at the graduate level to chemical engineers is probably an honest reflection of the fact that chemical engineers, despite their background, accept their bachelor's degree with a foundation in

thermodynamics that can be shaken without excessive effort.

The discussion that follows maps out the material covered in the course in its chronological appearance. The objective is to stress the aspects of the course that are given the most emphasis during the semester as well as to give a sense of the continuity of the topics treated. The several sections that follow form a rough syllabus of the course, covering approximately 14 weeks, or 42 meetings.

1. Review of Concepts (2 weeks)

Before starting a formal presentation of thermodynamics in a "postulational" manner, a review of the traditional "inductive" thermodynamics is performed. To make this review attractive, it is presented in a historical context, much in the spirit of Tisza,³ starting with Galileo and Torricelli, presenting the caloric theory and its shortcomings, continuing with the contributions of Carnot, Kelvin, Mayer, Joule, and finishing with the resolution of thermodynamics into its laws which occurred in the middle of the nineteenth century. Besides providing a review of this "thermodynamics of cycles," these initial lectures are designed to show the student that the difficulties that were encountered in the development of thermodynamics, historically speaking, are the same difficulties that trouble the contemporary student of thermodynamics. Besides treating the laws of thermodynamics and their function, lectures are presented on the concepts of reversibility and irreversibility, and the temperature concept and its measurement.

2. The Postulational Development of Thermodynamics (5 weeks)

The only text required for this course is Callen.⁴ Lectures structured about the first seven chapters of Callen are employed with the following philosophy: Take away the "laws" of thermodynamics from the student and develop a self-con-



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sistent, self-contained mathematically structured discipline which can be shown to provide the user with analytical tools equivalent to the "laws." One drawback to inductive thermodynamics is that the laws evolving from it are based on experimental observation (specifically, "thought" experiments), and the tendency of students is to develop "rules-of-thumb" which are not completely general. Consequently, the use of these rules-of-thumb can often lead to difficulties, much in the way paradoxes, or apparent contradictions, arose in the historical development of thermodynamics. A primary function of this development is to demonstrate that postulational thermodynamics is applicable to any thermodynamic problem, including those from which inductive thermodynamics evolved. Key points of emphasis in this section are:

- The informational content of thermodynamic fundamental relationships and the equations of state that come from them. The roles of the Euler and Gibbs-Duhem equations in providing the link between equations of state and fundamental relationships are detailed. The fact that one observes an incomplete set of equations of state in the laboratory is used to demonstrate the need for a basis, or reference, for the family of thermodynamic energy functions (internal energy, enthalpy, etc.).
- The equivalence of the extremum principles for entropy and internal energy and their extension by Legendre transformation to non-isolated systems. The Gibbs minimum principle for systems at some given (P_o, T_o) is used later as the starting point for handling complex chemical systems. (See Section 3.)

- The Jacobian transformations in concert with the Maxwell relations, presented as a system for handling the expression of process derivatives in terms of measurable quantities such as specific heat at constant pressure C_p , isothermal compressibility κ_T , and the coefficient of thermal expansion α , i. e., the three independent derivatives of the P-T basis.

The utility of the third point above can be accentuated by having the student demonstrate his capability at developing an H-S diagram for some substance, or at least the necessary formalism to do so. Generating formulae for isobars and isotherms in H-S space is fairly straightforward, but deriving a formula for the coexistence curve of, say, the saturated vapor is a bit more opposing (Denbigh⁵ has a related problem in which an expression for the specific heat at coexistence for a phase is desired.):

$$\left(\frac{\partial h}{\partial s}\right)_{\text{sat. vap.}} = \text{slope of saturated vapor locus in H-S space}$$

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP \quad (2-1)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP \quad (2-2)$$

Along the coexistence curve, the Clausius-Clapeyron equation states

$$dP = \left(\frac{\Delta h}{T\Delta v}\right) dT \quad (2-3)$$

and so

$$\left(\frac{\partial h}{\partial s}\right)_{\text{sat. vap.}} = \frac{TC_p + v(1-T\alpha)(\Delta h/\Delta v)}{C_p - v\alpha(\Delta h/\Delta v)} \quad (2-4)$$

since

$$\left(\frac{\partial h}{\partial T}\right)_P = C_p, \quad \left(\frac{\partial h}{\partial P}\right)_T = v(1-T\alpha), \quad \left(\frac{\partial s}{\partial T}\right)_P = C_p/T, \quad \left(\frac{\partial s}{\partial P}\right)_T = -v\alpha,$$

and where C_p , α , v are evaluated for the saturated vapor phase, and Δh and Δv are the enthalpy and volume changes upon vaporization respectively.

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Mastery of thermodynamic manipulations for pure substances, such as Jacobian transformations and Maxwell relations, is essential to developing confidently the complex expressions that are required, e.g., to describe mixtures (See Sec-

tion 6) while a firm basis of the thermodynamic extremum principles is necessary to realize the stability criteria for pure and multicomponent systems (See Section 5).

3. The Application of the Gibbs Minimum Principle to Complex Chemical Equilibria (2 weeks).

Zeleznik and Gordon⁶ have applied the Gibbs minimum principle to a general system of p phases and m species at some fixed (P_0, T_0) , and it is my experience that incorporation of their derivation into the course provides a quick, powerful method for the student to set up a complex chemical equilibria problem in a form amenable to computer solution. The derivation is lengthy and only the results will be presented here with accompanying comments.

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For the reacting system above, one solves the following set of equations:

$$\sum_i \sum_\alpha a_{ij} N_i^\alpha - b_j^0 = 0 \quad j = 1, \dots, l \quad \text{for elements} \quad (3-1)$$

$$\sum_i \sum_\alpha A_{ir} \mu_i^\alpha = 0 \quad r = 1, \dots, mp-l \quad \text{for } mp-l \text{ independent reactions} \quad (3-2)$$

where a_{ji} is a chemical subscript for element j in species i , α is the phase superscript, N_i is moles of species i , b_j^0 is the total number of gram-atoms of element j in the system, and A_{ir} is a stoichiometric coefficient for reaction r . The problem thus becomes mp equations in mp unknowns, namely, the set $\{N_i^\alpha\}$ $i = 1, \dots, m; \alpha = 1, \dots, p$. Each member of Equation (3-2) is called a reaction affinity.

If the reaction mechanism is unknown (or unspecified) the problem enlarges somewhat as Equation (3-2) is replaced by

$$\mu_i^\alpha + \sum_j \lambda_j a_{ij} = 0 \quad \text{for } i = 1, \dots, m; \alpha = 1, \dots, p \quad (3-3)$$

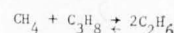
The problem is now $(mp+l)$ equations in $(mp+l)$ unknowns, namely $\{N_i^\alpha\}$ as before, and $[\lambda_j]$, $j = 1, \dots, l$, which are a set of Lagrangian multipliers introduced in applying the Gibbs minimum principle.

An important point brought out by this approach is the equivalence of problems, with and without a reaction mechanism, as the final equi-

librium state does not depend on the choice of a particular mechanism but rather on the choice of permissible species in the system. Elimination of $[\lambda_j]$ from Equation (3-3) will yield Equation (3-2), i. e., a possible set of reactions.

There are several difficulties inherent in adopting the Zeleznik-Gordon treatment directly for instructional purposes:

- Charge must be treated as an "extra" element, to be electroneutralized rather than conserved. Furthermore, free electrons are a species as well as a charge. The definition of species becomes "any entity for which the concentration at equilibrium is desired."
- In phase equilibria problems, where there are no reactions, conservation of elements, Equation (3-1), can either provide too many or too few constraints. One must replace Equation (3-1) with a set of equations conserving species rather than elements. If one has a problem in which only some of the species are reacting and some are not, and they have common elements, the statement of the problem becomes even more complicated. It is not satisfactory to consider all reactions permissible by stoichiometry as some will have rates so slow as to be disregarded. For example, in the phase equilibria of a natural gas system containing CH_4 , C_2H_6 , and C_3H_8 , it is of no interest to consider the possible reaction:



In other words, good judgment must be exercised in applying the Zeleznik-Gordon scheme.

- A traditional way of describing a m -component vapor-liquid phase equilibria problem is (See p. 47 of Reference 9, e.g.):
 $m + 2$ equations:

$$\mu_i^g = \mu_i^l \quad i = 1, \dots, m$$

$$P^g = P^g(v^g, T, \{y_i\})$$

$$P^l = P^l(v^l, T, \{x_i\})$$

$m + 2$ unknowns:

$$(T, v^g, v^l, y_1, y_2, \dots, y_{m-1})$$

The demonstration of the equivalence of this problem to that of Zeleznik and Gordon is made intricate by the fact that the Zeleznik-Gordon scheme, by virtue of solving for $\{N_i^\alpha\}$, suggests a batch process with finite phases, while the above problem makes no specification of phase size. The comparison of the two descriptions is presented in the course.

4. The Phase Rule (1 week).

The phase rule, written as

$$F = C - P + 2 \quad (4-1)$$

or

$$F = C - P + 2 - R, \quad (4-2)$$

where R is restrictions is one of these rules-of-thumb that most students feel they understand

by the time they reach the graduate level. Because this is often not the case, I generally start with an example complicated enough to produce a myriad of answers for the degrees of freedom f , and then backtrack, beginning at the beginning. Rather than deriving the rule as given above, I state the phase rule as:

“the number of degrees of freedom in the intensive phase variables = the number of independent intensive phase variables—the number of restrictions”

For example, consider the 3-component, 3-phase system (solid-liquid-vapor) where the components will be specified as A, B, C. The independent intensive variables are 12 in number

$$T^S, P^S, x_A^S, x_B^S, x_C^S, T^L, P^L, x_A^L, x_B^L, x_C^L, T^G, P^G, x_A^G, x_B^G, x_C^G$$

and the restrictions are 10:

$$\begin{aligned} T^S &= T^L = T^G \\ P^S &= P^L = P^G \\ \mu_i^S &= \mu_i^L = \mu_i^G, \quad i = A, B, C \end{aligned}$$

Thus $f = 2$, as can be readily obtained from Equation (4-1). The difficulty arises interpreting R in Equation (4-2). Consider the restrictions:

$$1) P = P_0$$

and

$$2) x_B^G = x_C^G = 0$$

In the first, logic dictates that f reduce to 1, and the form of analysis suggested introduces

$$P^S = P^L = P^G = P_0$$

or

$$f = 12 - 11 = 1$$

The restrictions (2) above do not affect f as there occurs a “balance”:

x_A^G, x_B^G are removed from the independent intensive variables and $\mu_A^G = \mu_A^L$ and $\mu_B^G = \mu_B^L$ can be removed from the restrictions. Thus the problem is

$$f = 10 - 9 = 1$$

Experience has shown that this detailed approach increases the student's confidence.

Since the phase rule makes no specification concerning the size of the phases (indeed, they could be considered infinite), the effect of “Batching” or, in a flow process, the setting of flow rates to a vessel can require careful examination. For example, consider the single (liquid) phase esterification reaction of ethyl alcohol and acetic acid at fixed T_0, P_0 . If one applies the phase rule Equation (4-2) directly

$$f = 4 - 1 + 2 - R$$

where $R = 3$: $P = P_0$, $T = T_0$, and 1 reaction ($mp-l = 1$), or $f = 2$. But one recognizes that if one batches the system identically each time,

i. e., fixes $[N_i] = [N_{i0}]$, one gets the same equilibrium composition in the vessel. Thus, the batching constitutes 2 restrictions. It can be seen by noticing that

$$x_i = \frac{N_{i0} - \Delta N_i}{\sum_i N_i}$$

for reactants and

$$x_i = \frac{N_{i0} + \Delta N_i}{\sum_i N_i}$$

where, in this particular case, EQUATION, as moles are conserved. Thus, e. g.,

$$x_i = a_i - z \quad (\text{reactants})$$

$$x_i = a_i + z \quad (\text{products})$$

and the single variable z replaces the 3 independent variables of the set $[x_i]$ ($\sum x_i = 1$), and batching in this case constitutes 2 restrictions.

Furthermore, the quantity ($mp-l$) used to denote reactions in the Zeleznik-Gordon scheme is really more general than that. One should consider it as representing the number of independent affinities, including those which describe a phase transformation:

$$\mu_i^\alpha - \mu_i^\beta = 0 \quad \text{for species } i \text{ and phases } \alpha \text{ and } \beta$$

Care must be taken not to count such a transformation twice, once as a reaction (transformation) in the set ($mp-l$) and once as a chemical equilibrium. For example, consider a vapor-liquid equilibrium between $\text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8, \text{CO}_2$, typical of a natural gas mixture prototype. For this system, $mp-l = 8-3 = 5$, yet common sense suggests 4 phase equilibria. The fifth “reaction” is the one cited in (2) of Section 3. The point here is not only should that reaction possibility be discarded but also that $mp-l$ includes that 4 chemical equilibria, i. e., phase transformations.

Applications relating to how many variables in a real process must be specified to produce a unique experiment (i. e., reproducible) can assume many forms and can be both interesting and challenging.

5. Stability Phenomena (2 weeks).

A brief introduction to phase stability (thermal and mechanical) and diffusional stability is presented. Phase stability is discussed in many texts, e. g., Callen,⁴ and can be demonstrated easily with the van der Waals equation. Some mention is made in passing of the fact that the

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occurrence of a van der Waals "loop" in the region of coexistence is a manifestation of the approximate nature of the equation of state.⁷

Diffusional stability, or immiscibility phenomena, is presented in a manner abstracted from Prigogine and Defay.⁸ Margules solution models, starting with the "regular," are adequate to demonstrate a broad spectrum of possible immiscibility behavior. Prausnitz's discussion of the subject⁹ is a good complement to this topic.

6. Thermodynamics of Mixtures (2 weeks, or whatever time remains).

Obviously, two weeks is not enough to do any justice to the practical aspects of the thermodynamics of mixtures, such as the fugacity and activity concepts. Often, these few lectures are given in a qualitative way to provide an overview of what is presently relevant in chemical thermodynamics. This is generally all that the non-chemical engineers will desire while the chemical engineers have refuge in a second course for which this course is a prerequisite. The second course is a course in phase equilibria and uses Prausnitz⁹ as a text. It will not be discussed here.

In closing, it is satisfying to note that Equation (3.1-8)—(3.1-14) and Equation (3.4-9)—

(3.4-17) of Prausnitz,⁹ equations for the properties of mixtures with independent variables (P,T) and (V,T) relative to an ideal gas basis (T = T, P = 1 atm absolute), are derivable by students of the core course without recourse to the work of Beattie.¹⁰ □

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