

project is an application of the tubing bomb reactor extensively used in coal research to study kinetics of eastern oil shale hydroliquefaction. Modeling of a cross-flow reactor is part of an overall program of a gas-liquid-solid reactor study including the H-Coal ebullated-bed reactor. The solution of equations using computer codes has been applied to the Graetz problem for circular tubes and parallel plates. He has generated dimensionless temperatures and Nusselt numbers in agreement with the extensive tubulations of Shah and London. Many problems involving transport phenomena will be amenable to solution by computer codes.

The main emphasis of Ed Moorhead's research deals with electrochemical studies of oxidation and reduction at conducting and semiconducting electrode surfaces, and includes: investigating the kinetic effects of surface and solution catalysis (and photocatalysis), studies of mass transport to various electrode geometries, development of new or improved electronic measuring techniques (including relaxation methods), measurement of ppb-level trace metals, and application of in-lab mini/micro computers for data acquisition and analysis. He has recently developed (with NSF support) the electromagnetically driven transverse oscillating resonant electrode ("TORE") wire for electrode process studies. The vibrating wire (50 micron dia.) presents some challenging problems in cylindrical diffusion which are presently being addressed using finite element analysis.

Bill Conger's main interest in recent years has been the use of the second law of thermodynamics to analyze the energy inefficiencies in chemical process flow sheets. In addition he is interested in process simulations. He has combined these interests to analyze proposed hydrogen production schemes and coal gasification processes. Presently he is interested in using the second law analysis in determining design alternatives.

Jonathan Berman has several areas of interest. Among them are studies on diffusive and reactive transport of oxygen in red blood cells and on membrane blood oxygenators. He is presently working on theoretical and experimental studies to investigate the assumption normally made that the internal contents of the red blood cell are in instantaneous equilibrium with the local plasma surroundings. His work on membrane oxygenators centers around efforts to enhance the relatively inefficient mass transfer process which results from the separation of the two phases involved. He

is working on theoretical solutions consisting of coupled asymptotic and numerical analyses and on experimental verification of these solutions for particular oxygenator configurations.

The above are examples of the interests of some of our faculty showing the strong emphasis of the department in the pollution and energy areas.

#### FUTURE DIRECTIONS

We are faced with many of the same problems that confront other departments across the country. Our undergraduate population is growing rapidly, it is difficult to convince U.S. citizens to continue in graduate school, and financial support from the university is not what we would have it to be, to name just three. In spite of these problems we feel we are a dynamic growing department and our faculty is looking forward to what the next five years and beyond will bring. Being a very young department, we are experiencing growing pains; but maturing into a department that is recognized and respected by others in our profession has made it all worthwhile. □

## ChE letters

#### ALTERNATIVE APPROACH TO SELECTION OF REFERENCE STATES

Dear Sir:

The possibilities for selection of reference states for several thermodynamic functions are discussed in the article "Reference States and Relative Value of Internal Energy, Enthalpy, and Entropy" in the Spring, 1983 issue of Chemical Engineering Education by Professor A. G. Fredrickson. This letter is intended to suggest an alternative approach to that used in the article and some possible reinterpretation and extension. My points are:

1. The results of the article can be derived more satisfactorily from a starting point of simple closed system equations rather than the model used, which is applicable to complex open systems.
2. In discussion of an open system problem from Modell and Reid's classic text, unwarranted physical meaning is implied for the quantity total internal energy.
3. The discussion of reference states can be usefully expanded to include Gibbs and Helmholtz free energy, which are state functions of significantly different character from those treated in the article.

The article starts with mathematical statements of mass balance, first law, and second law applicable to ". . . open, moving and deforming, and unsteady state

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The *net* useful work or non-flow availability is then found as in Eqs. (6) and (7)  
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$$B \equiv \int_1^e PdV - (P_e \Delta V_{1e}) \quad (22)$$

$$= -[\Delta U_{1e} + P_e \Delta V_{1e} - T_e \Delta S_{1e} - \sum \mu_{i,e} \Delta n_{i,1e}]$$

which is the defining equation for non-flow availability found in Gibbs and elsewhere [4].

Now imagine a system that moves from an initial state (1), through isentropic (1→2), and isothermal (2→3) processes, into temperature and pressure equilibrium with its environment and then displaces its contents, wholly or in part into that environment, if need be through a semi-permeable membrane that allows transfer of the

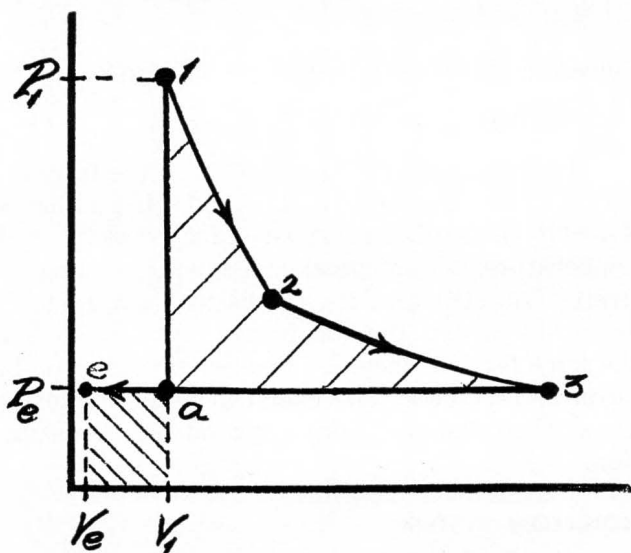


FIGURE 5

contents at its environmental potential or partial pressure. The process would appear as process 1-2-3-e in Fig. 5. The work of this process is the maximum work as given in Eq. (21), and is represented by the sum of area (1-2-3-a-1) and area  $P_e(V_e - V_1)$ . The net work of the process, or the non-flow availability, is according to Eq. (22), the maximum work minus  $P_e(V_e - V_1)$ , or simply the area (1-2-3-a-1), that is always *positive* definite.

It is interesting to note that Eq. (22) may also be written as

$$B = -(\Delta U_{1e} + P_e \Delta V_{13} - T_e \Delta S_{13}) \quad (23)$$

$$- (\Delta U_{3e} + P_e \Delta V_{3e} - T_e \Delta S_{3e} - \sum \mu_{i,e} \Delta n_{i(1e)})$$

The first bracket in Eq. (23) is exactly equal

to the area (1-2-3-a-1). Consequently, the second bracket must equal zero, or

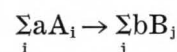
$$\Delta U_{3e} + P_e \Delta V_{3e} - T_e \Delta S_{3e} = \sum \mu_{i,e} \Delta n_{i,1e} \quad (24)$$

Therefore

$$B_{1e} = -(\Delta U_{13} + P_e \Delta V_{13} - T_e \Delta S_{13}) \quad (25)$$

where state (3) is isomolar with (1) but in equilibrium with the environment.

For reactive systems or materials that transform chemically before passing into the environmental state; for example



in equilibrium with an environment

$$B = -\sum_i (\Delta U_{13} + P_e \Delta V_{13} - T_e \Delta S_{13})_i - \sum_j (\Delta U_{3e} + P_e \Delta V_{3e} - T_e \Delta S_{3e})_j \quad (26)$$

where "i" refers to reactants, and "j" to products. State (3) is the reaction equilibrium state and state (e) is the environmental state. For the reasons given in Fig. 3 and 5, B remains positive definite. □

## REFERENCES

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2. Sussman, M. V., *Nature*, 256, 5514, 195-198 (1975).
3. Keenan, J. H., *Thermodynamics*, 1st MIT Press Ed: Cambridge, MA, 1970. Originally published by Wiley, New York, 1941.
4. Gibbs, J. W., *The Collected Works*, Volumes I, II, New York: Longmans, Green and Co., (1931).

## LETTER TO THE EDITOR

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systems . . .". Then some conclusions are derived about one's freedom to select reference states for internal energy, enthalpy, and entropy in terms of chemical compounds or chemical elements, with or without the possibility of chemical reaction. However, identical conclusions are easily derived from corresponding statements applicable to a simple closed system. Further the open system equations can only be obtained by derivation from the closed system relations. Thus the derivation of reference state constraints from the open system equations is not so much a **proof** as it is a **partial check** on the derivation(s) which led to the open system equations.

To illustrate the closed system approach, consider the familiar first law statement:

$$E_2 - E_1 = Q - W \quad (1)$$

As Kestin points out [1]:

“. . . The concept of energy is connected with **two different states of a single closed system** and a numerical value can only be ascribed to the difference  $E_2 - E_1$  between the energies in the two states, because only this difference, or its negative, can be measured by means of an adiabatic, irreversible process . . .”

Thus for any closed system, we may arbitrarily choose to assign an absolute numerical value to any one state of the system. Most often this is a numerical value of zero at a so-called reference state. Because of the requirement to satisfy equation #1, we have no more freedom of choice and corresponding absolute energy values are determined for all other possible states of our single closed system.

The conclusions about reference state selection reached in the article follow in a direct way from equation #1 and the corresponding second law statement. As one example, let us define a reference state for a single closed system to consist of a collection of sub-systems, each of which contains one pure element in some arbitrary state. If we assign a numerical value of zero to the energy of each sub-system, we have set the value of reference state energy equal to zero for the entire closed system. Clearly this choice of reference state is always available, regardless of what particular chemical compounds might be present, and further there is no constraint on what specific reference states we select for the individual pure elements. So this method of assigning absolute energy values is always acceptable in principle, whether or not chemical reactions are possible in a particular closed system. Similar results can be obtained in the case of entropy.

Not only is the closed system approach a simpler way to obtain information about acceptable reference states, but it also avoids possible misleading interpretations of total energy or entropy values. As Kestin points out [2]:

“. . . no physical meaning can be attached to the difference between the energies of **two different** systems, even if the two systems merely represent different masses of the same homogeneous system . . .”

In the CEE article, Professor Fredrickson uses the notions of total internal energy and total entropy in deriving reference state constraints. Then the results are applied to interpretation of a problem from the classic text by Modell and Reid [3]. The problem involves computation of heat transfer to the helium in a tank which will maintain total internal energy at a constant value despite the flow of gas from the tank. The comment is made that “. . . we cannot know how to adjust the heat transfer rate to the gas so that its absolute total internal energy remains constant as its mass changes . . .”. The implication of this and other remarks in the article is that there does exist a **unique** absolute energy value for any particular collection of matter, even though we cannot in principle determine what it is. But as discussed above, there is no one unique absolute internal energy for a particular system. We can assign absolute energy values, but the only unique values are for changes of state of a simple closed system. If we allow changes of system mass to occur, as in an open system, there is no physical meaning even to the numerical value of changes in the system (total) internal energy. By our freedom to select reference states, we can force an open system energy change to have whatever numerical

value we may desire. Even the notion of holding the energy of an open system constant has no physical meaning.

The lack of direct physical meaning for total internal energy does not invalidate the open system equation which contains such a term. Rather in that equation, the input, accumulation, and output terms in combination have the effect of making the open system balance equivalent to a closed system balance in disguise. The open system equation is valid, but the total energy term by itself has **no physical meaning**.

Finally, it can be noted that not all “state functions” are created equal. We commonly refer for example to internal energy, specific volume, and Gibbs free energy as state functions. But these are really not the same. The volume term, in common with pressure and temperature, is accepted as an inherently absolute quantity, except for choice of units. There is no issue of a reference state. Internal energy, however, can take on any desired numerical value at any one state. It is only changes of internal energy that must always be the same. Another such function is enthalpy. Clearly the product of two absolute quantities,  $PV$  is also an absolute quantity, and so the linear sum of internal energy and  $PV$  which we call enthalpy preserves the property that changes of enthalpy depend only on state changes and not upon choice(s) of reference state(s). Still a third kind of “state function” is exemplified by Gibbs free energy, defined as:

$$G = U + PV - TS \quad (2)$$

An arbitrary set of absolute values for  $G$  is determined by the selection of reference states for internal energy and entropy. But these absolute values do not behave in the same manner with respect to changes of state as do internal energy or entropy values. Comparing two different states, we have:

$$G_2 - G_1 = U_2 - U_1 + P_2 V_2 - P_1 V_1 - T_2 S_2 + T_1 S_1 \quad (3)$$

Clearly it is only in the case that  $T_2 = T_1$  that we can be assured that changes in  $G$  depend only on changes in state. In any other case, it is generally possible to affect the numerical value of the change in  $G$  by an arbitrary selection of the reference state(s) for entropy. Since we are always free to make such selection(s), and since no legitimate thermodynamic conclusion can be thereby affected, we conclude that Gibbs free energy is a third kind of state function. If the system is isothermal, free energy changes are unique. If the system is not isothermal, there is no physical meaning to the numerical value of free energy changes. This lack of meaning is a fact whether the system is open or closed.

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2. Ibid pp. 158-159.
3. M. Modell and R. C. Reid, “Thermodynamics and its Applications,” p. 141 (Englewood Cliffs, N.J.: Prentice-Hall, Inc., 1974).