Subscripts

a = activity basis
C, D, E, F = components
i = component i
x = mole fraction basis

Superscripts

B = bulk liquid
M = mixture
S = surface

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The Second Law. Caratheodory's Principle with Simplified Mathematics

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It is readily apparent that the phenomena of nature are for the most part irreversible. After a change takes place, such as the conduction of heat, diffusion, motion, or flow with friction, it is impossible to restore the initial conditions for both the system and its surroundings. The principle of Caratheodory takes as an axiom in the logical system, what is believed to be a law of nature, that is, the existence of irreversible phenomena. In its formal statement it uses the observed fact that a system can in any state be disturbed, or change spontaneously, in such a way that no adiabatic process can return it to its original condition. For example, a small amount of work performed on the system in the presence of friction produces an irreversible change. The previous state of the system can only be restored by removing heat, thereby effecting a net change of work into heat in the surroundings. The reverse of this process is not possible (the Kelvin statement of the second law). Rather than dwell upon the forbidden process, we choose to examine the original irreversible change. A state has been reached from which the return is impossible by an adiabatic process. The initial state is termed *adiabatically inaccessible* from the final state. Since any system in any state may be adiabatically isolated, and an arbitrarily small irreversible process may be executed, the adiabatically inaccessible states may be arbitrarily close to any state.

[A complete logical exposition would begin by definition of *state*, *process*, and *adiabatic*. Of these the most difficult is *adiabatic*. We will assume that a satisfactory definition has been made, such as *a process is adiabatic if the only external effects are work.*]

FORMAL DEVELOPMENT

Caratheodory's Principle: In the Neighborhood of Every State There are Adiabatically Inaccessible States

This is analogous to a statement which can be made about the real number system: in the neighborhood of every number there is a smaller number. We would like to be able to assign numbers to the states of a system which would rank them by adiabatic accessibility. With real numbers we have the property that if A is less than B, B is not less than A. The corresponding property for states of systems is taken as an auxiliary axiom.

Auxiliary Axiom 1: There are no pairs of states which are mutually inaccessible by adiabatic processes. (If state A is inaccessible from B, then B is not inaccessible from A.)

As a consequence of Caratheodory's principle and the auxiliary axiom, there appears to be a correspondence or similarity between the adiabatic accessibility of states and real numbers. We may define a ranking of states according to adiabatic accessibility in which a larger number is assigned to a more accessible state, starting with an arbitrarily chosen reference state. This ranking is the function called *entropy* in thermodynamics, but we will give it the name *rank* and the symbol R in this context to avoid prejudicing the case. A pair of states which are mutually accessible will have the same value of R. Every state has a rank and the values of R form a continuum. For any possible adiabatic process $dR \geqq 0$. For those processes for which $dR = 0$, the reverse process is possible.

In any physically possible adiabatic process, the sequence of states is always such that each R attained is greater than all previous values of R. This may continue only until a maximum of R is reached. The existence of a constraint on the system such that R has a maximum from which all permissible displacements $dR \leqq 0$, and when R is a continuous function of state variables this means that when R is at the maximum, $dR = 0$. A condition is reached which is called *equilibrium*, from which no change is possible as long as all the external constraints remain unchanged.

Let us examine the properties of R.

Definition: The rank R for a composite system is the sum of the R values of its parts. This has an interesting consequence. Since the only property required of R before this definition was that of order of the points, any monotonically increasing function of R would serve just as well as the original R. The requirement of additivity puts a severe restriction on the acceptable forms for a function of R. In order to display this, we need a mathematical theorem.

Theorem:

If

$$z = x + y \tag{1}$$

and

$$f(z) = f(x) + f(y) \tag{2}$$

Then

$$f(z) = az \tag{3}$$

where a = constant

Proof: Differentiate (2) with respect to x

$$f'(z)\frac{dz}{dx} = f'(x) = \text{independent of } y \tag{4}$$

Differentiate (2) with respect to y

$$f'(z)\frac{dz}{dy} = f'(y) = \text{independent of } x \tag{5}$$

INFORMATION RETRIEVAL

(*Continued from page 194*)

Axial dispersion of spheres fluidized with liquids, Kennedy, S. C., and R. H. Bretton, **A.I.Ch.E. Journal, 12,** No. 1, p. 24 (January, 1966).

Key Words: A. Dispersion-8,7, Solids-9, Diffusion-6, Classification-6, Spheres-9, Fluidized-0, Glass-9, Lead-9, Water-9, Glycol-9, Mathematical Model-10, Length-6, Bed-9, Concentration-7.

Abstract: Solids dispersion due to the simultaneous diffusion and classification of fluidized spheres has been investigated. The model developed permits calculations for the mean concentration of spheres of both sizes in a mixture of two sizes of fluidized spheres as a function of bed length. Glass and lead beads were used in the experiments.

The condensing of low pressure steam on vertical rows of horizontal copper and titanium tubes, Young, Edwin H., and Dale E. Briggs, **A.I.Ch.E. Journal, 12,** No. 1, p. 31 (January, 1966).

Key Words: A. Condensation-8, Steam-9, Tubes-9, Horizontal-0, Vertical-0, Copper-9, Titanium-9, Heat Transfer-8, Condensing Coefficient Correction Factor-8, 7, Velocity-6, Water-9.

Abstract: Heat transfer data are presented for condensing steam at 2 in. Hg absolute pressure on the outside of nine copper and nine titanium horizontal tubes in a vertical row. The condensing coefficient correction factor was maximum for the top titanium tube and was 46% higher than the correction factor for the top copper tube. The difference between the correction factors for titanium and copper tubes diminished with the number of tubes in a vertical row to 8% higher than the correction factor for copper tubes with six to nine tubes in a vertical row.

Flow and turbulence in a stirred tank, Cutter, Louis A., **A.I.Ch.E. Journal, 12,** No. 1, p. 35 (January, 1966).

Key Words A. Flow-8, Turbulence-8, Tank-9, Stirred-0, Baffles-10, Water-9, Momentum-8, Angular-0, Velocity-8.

Abstract: Photographic measurements have been made of the mean and fluctuating components of velocity of water in a fully baffled stirred tank. Equations have been developed to describe the flow of energy and the conservation of angular momentum in the impeller stream of a stirred tank with a radial flow impeller and vertical baffles. The equations derived are used with the photographic data on mean and fluctuating velocities to estimate the angular momentum at different radial sections of the tank and to calculate the flow of energy through these sections.

A two-way capillary viscometer, Tzentis, L. S., **A.I.Ch.E. Journal, 12,** No. 1, p. 45 (January, 1966).

Key Words: A. Viscometer-8,10, Capillary-0, Measurement-8, Shear-9, Bulk Velocity-9, Precision-8. B. Rheology-8,7, Polyacrylonitrile-9, Concentration-6.

Abstract: A two-way capillary viscometer for measuring shear rates from <0.01 to >1,000,000 sec.$^{-1}$ at pressure drops up to 1,000 lb./sq.in. has been designed. The special feature of this viscometer is the indirect automatic measurement of bulk velocity of the fluid sample in the capillary tube by means of a mercury manometer. A study of the rheology of polyacrylonitrile shows that the non-Newtonian behavior and elsaticity of PAN solution increases rapidly with concentration.

Free tear sheets of the information retrieval entries in this issue may be obtained by writing to the New York office.

(*Continued on page 198*)

Using (1) to evaluate $\frac{dz}{dx}$ and $\frac{dz}{dy}$, we get

$$f'(z) = f'(x) = \text{independent of } y$$

and

$$f'(z) = f'(y) = \text{independent of } x$$

Therefore $f'(z)$ is independent of x and y; hence it is independent of z.

Let

$$f'(z) = a$$

Then

$$f(z) = az + b$$

From (2)

$$az + b = ax + b + ay + b$$

$$a(x + y) + b = a(x + y) + 2b$$

$$b = 0$$

Hence

$$f(z) = az$$

Thus, if the function R is defined to be additive for composite systems, we can consider R to be fully defined except for a scale and a reference point.

Since R is a function of the state of the system, we may represent it mathematically as a function of any set of variables which define the state of the system. For example, with gaseous systems, there are two independent variables. Specification of two variables, that is, internal energy U and volume V, is enough to specify fully the state of the system. Mathematically

$$R = R(U, V)$$

Since R varies with the state of the system in a continuous manner we may write

$$dR = \left(\frac{dR}{dU}\right) dU + \left(\frac{dR}{dV}\right) dV$$

Consider an adiabatically enclosed system, in which two subsystems, designated 1 and 2, are in equilibrium, but do not exchange work. Their volumes will be constant. (In a more complex system, requiring more than two independent variables to specify the state, when the deformation variables are constant, the subsystems do not exchange work.)

The total energy of the system is constant.

$$dU = dU_1 + dU_2 = 0$$

$$dR = \frac{dR_1}{dU_1} dU_1 + \frac{dR_1}{dV_1} dV_1 + \frac{dR_2}{dU_2} dU_2 + \frac{dR_2}{dV_2} dV_2 = 0$$

$$dV_1 = dV_2 = 0$$

$$\left(\frac{dR_1}{dU_1} - \frac{dR_2}{dU_2}\right) dU_1 = 0$$

when $R(U, V)$ is continuous.

Since dU_1 may have an arbitrary value, we deduce that

$$\left(\frac{dR_1}{dU_1}\right)_{V_1} = \left(\frac{dR_2}{dU_2}\right)_{V_2}$$

Let

$$\varphi = \left(\frac{dR}{dU}\right)_V$$

Then we have

$$\varphi_1 = \varphi_2$$

A requirement for thermodynamic temperature is that in systems in equilibrium it have the same value. This requirement is met by $\varphi = \left(\frac{dR}{dU}\right)_V$. If it could be evaluated, it would have a fixed value for all systems in equilibrium, regardless of physical properties or the specific nature of the substance used to measure it (unlike the empirical temperature which depends on the particular thermometer).

For a reversible process

$$dR = \varphi dU + \left(\frac{dR}{dV}\right) dV$$

For the system under consideration

$$dU = dQ - pdV$$

$$dR = \varphi(dQ - pdV) + \left(\frac{dR}{dV}\right) dV$$

For an adiabatic reversible process we must have $dR = 0$; hence

$$\left(\frac{dR}{dV}\right) = \varphi p$$

$$dR = \varphi(dU + pdV) = \varphi dQ$$

If we consider now an irreversible process in which heat is transferred from one subsystem to another through a conductor of very small mass which makes negligible contribution to the thermodynamic properties, and in which all the irreversibility occurs, we have the following:

Change in subsystem 1

$$dR_1 = \varphi_1 dQ_1$$

Change in subsystem 2

$$dR_2 = \varphi_2 dQ_2$$

Overall, the process is adiabatic

$$dQ_2 + dQ_1 = 0$$

Hence

$$dR = dR_1 + dR_2 = (\varphi_1 - \varphi_2) dQ_1$$
$$dR > 0$$

Hence $(\varphi_1 - \varphi_2)$ and dQ_1 have the same sign. Heat is received by the system with the higher φ and leaves the system with the lower φ. To conform with traditional assignments of the concepts high and low to hot and cold, we will define thermodynamic temperature T by

$$T = 1/\varphi$$

If we now make the identification of R with entropy, we can summarize with

$$T = \left(\frac{dU}{dS}\right)_V$$

$$dU = TdS - pdV$$

Entropy is defined thus far with an unspecified scale and reference point. The scale is supplied by suitable definitions for heat units and for the temperature scale. The reference point remains arbitrary. The discussion of the thermodynamic temperature scale, and the techniques for making thermodynamic temperature observable, should follow here, but it is entirely conventional.

OTHER WORKS

While specific references to other discussions of the second law were omitted, claims for complete originality should not be inferred therefrom. In particular this discussion is inspired by the papers of Turner (*4*, *5*) and Buchdahl (*1*) and the textbook of Callen (*2*), while the present author accepts the responsibility for the way in which they are combined. The recent book by Giles (3) presents a complete axiomatic development along lines similar to those given here.

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On a Neglected Effect in Entrance Flow Analyses

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Dealy (*1*) has recently presented a discussion of analyses of the problem of laminar flow development in the entrance region of either a cylindrical tube or a parallel plane channel. He points out that at least twenty-five papers have appeared on the development of a parabolic profile from a uniform entry profile. He also points out that with only one exception these papers have all been based on equations of the boundary-layer type. His conclusions are that the boundary-layer analysis is invalid for small X and that the shape of the velocity profile is such as to make suspect stability analyses based on the boundary-layer equations. These conclusions are not questioned. However, the tenor of the note was entirely negative and it is possible that a reader could be led to the conclusion that only inaccurate results are obtained by use of the Prandtl boundary-layer equations. Such a conclusion would, for most purposes, be incorrect, since the boundary-layer equations yield results of remarkable accuracy except within one or two diameters or channel widths of the entrance. Some particular points which should be mentioned are:

1. The pressure drop and velocity distributions calculated from the boundary-layer solutions agree with all applicable published experimental measurements to within the accuracy of the