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Thermodynamics of Steady States: "Resistance Change" Transitions in Steady-state Systems

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Some one-current steady-state systems showing a discontinuous change in flow resistance at a point of instability—forced vaporization of carbon tetrachloride, Bénard instability in a horizontal layer of fluid heated from below, Taylor instability in the Couette flow of a liquid between coaxial rotating cylinders—are analyzed from a thermodynamic point of view: the behavior of the rate of entropy production and of the local potential (thermokinetic potential) for the system at the point of instability is explored. A multi-current situation involving a flip-flop current *vs.* voltage relation for the flow of electric current across a porous charged membrane is also commented on briefly.

Continuing my studies[1-6] of the thermodynamics of steady-state systems, I examine here the thermodynamic properties of several one-current steady-state systems, each of which develops an instability in its flow behavior and undergoes a discontinuous change in flow resistance. The "resistance change" transition at a point of instability for a steady-state system is in some respects analogous[7-9] to a phase transition in a thermo-static system. I shall first briefly discuss the "resistance change" transition in general terms; and I shall then discuss specifically the forced vaporization of carbon tetrachloride, Bénard instability in a horizontal layer of fluid heated from below, and Taylor instability in the Couette flow of a liquid between coaxial rotating cylinders. Finally I shall comment briefly on a multi-current example showing a flip-flop current-voltage relation for the flow of electric current across a porous charged membrane.

1. General Considerations (One-current Situations). Consider a fluid in a state of thermo-static equilibrium characterized by the variables T_σ, P_σ, $\mu_\sigma^{(1)}, \cdots$—a fluid system in the equilibrium state σ, for short. Relabel the set of equilibrium state variables in the following fashion: $\{T_\sigma,\ P_\sigma,\ \mu_\sigma^{(1)}\cdots\} \equiv \{\sigma_1,\ \sigma_2,\ \sigma_3, \cdots\} \equiv \{\sigma_i\}$. By changing some of the boundary conditions, induce the steady flow of a current Y in the fluid system. Use the equilibrium state σ as a reference state; the current Y will then depend on the departure of variables of the type σ_i from their reference state values. For each state of steady current flow, the rate of entropy production $\theta \equiv \dot{S}$(system) $+\dot{S}$(surroundings) takes the form

$$\theta = Y\Omega \geq 0, \tag{1}$$

where Ω is the affinity[1] conjugate to the current Y; both Y and Ω measure, in a certain sense, the "distance" of the steady-flow state from the reference equilibrium state σ. In addition to the rate of entropy production, another thermodynamic concept, the local potential (also called the generalized entropy production or the thermokinetic potential[5,10,11])— first introduced by Glansdorff and Prigogine[7,12,13]— is of use in discussing "resistance change" transitions. When the Pfaffian differential form (for a one-current situation)

$$\mathrm{d}F_\sigma = Y\mathrm{d}\Omega \tag{2}$$

is integrable under the given experimental conditions, the resulting quantity F_σ is the local potential:[5,7,10-13]

$$F_\sigma = \int Y\mathrm{d}\Omega = \int_0^Y Y(\partial\Omega/\partial Y)_\sigma \mathrm{d}Y. \tag{3}$$

The local potential F_σ (when it exists) is never negative, has a minimum at the point where $Y=0$, and satisfies the condition

$$0 < (\partial^2 F_\sigma/\partial\Omega^2)_\sigma|_{Y=0} = (\partial Y/\partial\Omega)_\sigma|_{Y=0}. \tag{4}$$

Glansdorff and Prigogine[7,12,13] found the local potential concept to be very useful for discussing the temporal evolution of a system with fixed boundary conditions as it passed through a sequence of transient states toward some stable steady state. I discussed in an earlier paper[5] the role played by the local potential (thermokinetic potential) in thermodynamic analyses of *all steady state* situations. In this paper I am somewhat more interested in the behavior of the rate of entropy production at "resistance change" transitions than in the behavior of the local potential; I shall, however, keep both quantities in view.

Consider again a fluid system in the equilibrium state σ. By successive manipulations of the boundary conditions establish a series of steady-flow states in the system with monotonically increasing values of the current Y. Observe θ as Y increases. If the plot of θ *vs.* Y shows a jump or a kink — a point of discontinuity in θ or in $\partial\theta/\partial Y$ — we have a point of instability, a point at which the fluid system undergoes a "resistance change" transition. It is the thermodynamic properties of the fluid system at the point of instability that I intend to discuss — in macroscopic phenomenological terms.

Let $\partial\Omega/\partial Y$ be the (differential) flow resistance, let the subscript c refer to the point of instability, and let ΔZ be the jump in an arbitrary property Z at the point of instability, *i.e.* let $\Delta Z \equiv Z(Y_\mathrm{c}+0) - Z(Y_\mathrm{c}-0)$. We have then

$$\Delta\theta = Y_\mathrm{c}\Delta\Omega, \tag{5}$$

$$\Delta\partial\theta/\partial Y = \Delta\Omega + Y_\mathrm{c}\Delta\partial\Omega/\partial Y, \tag{6}$$

$$\Delta\partial^2\theta/\partial Y^2 = 2\Delta\partial\Omega/\partial Y + Y_\mathrm{c}\Delta\partial^2\Omega/\partial Y^2, \tag{7}$$

$$\Delta\partial^m\theta/\partial Y^m = m\Delta\partial^{m-1}\Omega/\partial Y^{m-1} + Y_\mathrm{c}\Delta\partial^m\Omega/\partial Y^m \quad (m = 2,\ 3,\ 4,\ \cdots). \tag{8}$$

In the canonical procedure, some parts of the boundary are maintained at the reference state values σ_i, and other parts are varied in condition so as to control the current Y. The partial derivatives in Eqs. 6—8

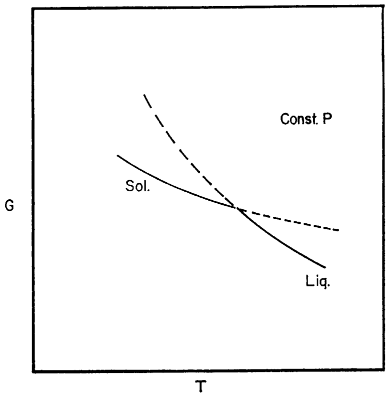

Fig. 1. Relative stability of the solid and liquid phases, at constant pressure, in a one-component system.

are thus at constant σ_{ξ} where appropriate.

"Resistance change" transitions in steady state systems are in some respects analogous[7–9] to thermostatic phase transitions where the phase with the lower Gibbs function value is the more stable one (see Fig. 1). Prigogine[7,8,12,13] considers the local potential F_σ to be the analog of the Gibbs function for "resistance change" transitions; for one-current steady-state situations there is no advantage in considering F_σ rather than θ, and I shall devote primary consideration to θ.

For stable steady states it is always true that[6,14]

$$\partial^2\theta/\partial Y^2 > 0, \quad \partial\Omega/\partial Y > 0; \tag{9}$$

and for "resistance change" transitions where both the upper ($Y > Y_c$) and lower ($Y < Y_c$) branches have metastable extensions beyond Y_c we anticipate that

$$\Delta\theta = 0, \quad \Delta\Omega = 0, \quad \Delta\partial\theta/\partial Y < 0, \tag{10}$$

i.e. we expect a kink in the θ *vs.* Y plot reflecting [Eq. 6] a discontinuous change in the flow resistance with $\Delta\partial\Omega/\partial Y < 0$: pipes spring leaks, vigorously rubbed paper tears, screwdrivers often shear the slotted heads of screws — in short, *processes usually take* the *path* of *least resistance*. If, however, the transition point is a point of intrinsic instability for one or both of the upper and lower branches, *i.e.* if one or both of the branches do not have metastable extensions beyond Y_c, then Eq. 10 must be modified — more about this later.

Rather than continuing in general terms, it will be better if we look at the special cases that we are interested in.

2. *Forced Vaporization of Carbon Tetrachloride.*

Consider a pure liquid in equilibrium with its vapor in a glass cell in a thermostat of temperature T. Let P_0 be the equilibrium vapor pressure of the liquid at temperature T. Reduce the pressure of the vapor to a pressure $P < P_0$, and establish a steady rate of vaporization of the liquid:

$$\text{liquid}(T, P_0) \rightarrow \text{vapor } (T, P). \tag{11}$$

The rate of entropy production for the forced vaporization process[15] is

$$\theta = -\dot{G}/T = \dot{\xi}[(\mu_{\text{liq}} - \mu_{\text{vap}})T^{-1}] = Y\Omega, \tag{12}$$

where $\dot{\xi}$ is the reaction velocity (amount vaporized per unit time) for Reaction 11 and I have neglected kinetic energy terms. Treating the vapor as an ideal gas $\{\mu_{\text{liq}} - \mu_{\text{vap}} = RT \ln (P_0/P)\}$ we have

$$\theta/R = \dot{\xi} \ln(P_0/P), \tag{13}$$

where R is the gas constant. Steady vaporization has been studied by Alty[15–17] and by Erikson;[15,18,19] nonsteady vaporization has been studied by Spangenberg and Rowland.[20]

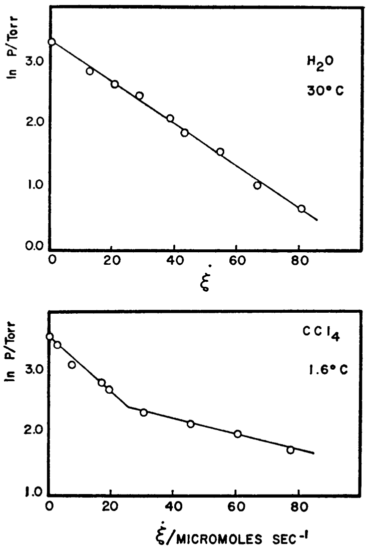

Fig. 2. Plots of $\ln P$ *versus* $\dot{\xi}$ for the steady forced vaporization of water at 30 °C and of carbon tetrachloride at 1.6 °C; P in Torr and $\dot{\xi}$ in μmol s^{-1}. Data of Alty and Nicoll.[17]

Figure 2 shows the data of Alty and Nicoll[17] for the steady forced vaporization of water and of carbon tetrachloride; the current is given in micromoles per second and the pressure is measured in Torr. There is clear evidence in the carbon tetrachloride data for a discontinuous change in flow resistance at $\dot{\xi}_c = 25$ μmol/s; the two flow regimes show the following behavior:

$$\ln P = \ln P_0 - A\dot{\xi}, \qquad (0 \leq \dot{\xi} \leq \dot{\xi}_c), \tag{14}$$

$$\ln P = \ln P_* - B\dot{\xi}, \qquad (\dot{\xi}_c \leq \dot{\xi}), \tag{15}$$

$$\theta/R = A\dot{\xi}^2, \quad F_\sigma/R = \frac{1}{2}A\dot{\xi}^2, \qquad (0 \leq \dot{\xi} \leq \dot{\xi}_c), \tag{16}$$

$$\theta/R = B\dot{\xi}^2 + (A-B)\dot{\xi}_c\dot{\xi},$$

$$F_\sigma/R = \frac{1}{2}B\dot{\xi}^2 + \frac{1}{2}(A-B)\dot{\xi}_c^2, \qquad (\dot{\xi}_c \leq \dot{\xi}), \tag{17}$$

where $-A$ and $-B$ are the slopes of the two line segments and P_* is the intercept on the line $\dot{\xi} = 0$ of the (extrapolated) line segment with slope $-B$. Values for A and B, in seconds per micromole, are $A = 0.045$, $B = 0.013$. Figure 3 is a graph of $10^6\theta/R$ *vs.* $\dot{\xi}$ for the carbon tetrachloride data, calculated from Eqs. 16 and 17 after insertion of the appropriate numerical values of A, B, and $\dot{\xi}_c$. The dashed and dotted curves are potential hysteresis curves extending the observed behavior into unstable regions. We see that at the

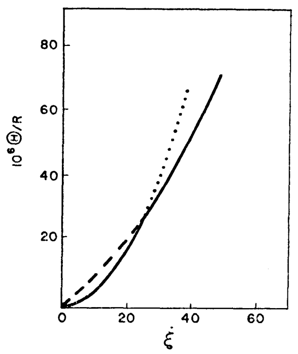

Fig. 3. Plot of $10^6\theta/R$ *versus* $\dot\xi$ for the steady forced vaporization of carbon tetrachloride at 1.6 °C. Data af Alty and Nicoll.[17]

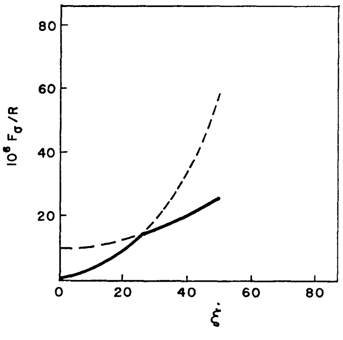

Fig. 4. Plot of $10^6F_\sigma/R$ *versus* $\dot\xi$ for the steady forced vaporiization of carbon tetrachloride at 1.6 °C. Data of Alty and Nicoll.[17]

transition point

$$\Delta\{\partial(\theta/R)/\partial\dot\xi\}_T = (B-A)\dot\xi_c < 0, \tag{18}$$

i.e. the discontinuous change is to a configuration of lower rate of entropy production.

Figure 4 shows that the behavior of the local potential F_σ at the transition point is somewhat similar to the behavior of θ: the branch with the lower value of F_σ is the more stable. In the case of F_σ, however, the metastable extension of the upper branch does not go through the origin of coordinates.[7]

In the carbon tetrachloride case, for fixed T, we have the transition point values θ_c, $\dot\xi_c$, P_c; if we repeat the experiment at another value of T we produce a new set of transition point values. In general then the thermodynamic data are the values of T, θ_c, $\dot\xi_c$, and P_c at the transition point (for a given apparatus configuration); and, from a thermodynamic point of view, we are interested in derivatives of the type $d\theta_c/d\dot\xi_c$, $d\dot\xi_c/dT$, $dP_c/d\dot\xi_c$, *etc.* Whereas in the somewhat analogous case of a phase transition in a thermo-static system we have the Clapeyron equation ($dP/dT = \Delta S/\Delta V$) to help us out in determining the slope of the phase coexistence line, in the present case we have no such useful general result.

2.1 Expectations and Queries: For the steady forced vaporization of carbon tetrachloride we have

$$\Delta\partial^2(\theta/R)/\partial\dot\xi^2 = 2(B-A) < 0, \tag{19}$$

$$\Delta\partial^n(\theta/R)/\partial\dot\xi^n = 0 \quad (n = 3, 4, 5, \cdots). \tag{20}$$

Equations 20 are consequences of the linear form of the given current-affinity relation; they, therefore, cannot be expected to have any *general* validity. Relation 19 will merit further investigation; is it generally true that

$$\Delta\partial^2\theta/\partial Y^2 < 0\,? \tag{21}$$

The physics of the steady forced vaporization process supplies us with some reasonable expectations concerning the behavior of the transition point variables. If the dominant feature of the transition point is the temperature gradient in the liquid in the vicinity of the liquid-vapor interface, then, since the heat of vaporization is a decreasing function of the temperature, we expect to find that

$$d\dot\xi_c/dT > 0, \tag{22}$$

to establish the same sort of temperature gradient at a higher temperature we have to pump off the vapor faster because the heat of vaporization now has a lower value. Note that

$$\frac{d(\theta_c/R)}{dT} = \frac{d\dot\xi_c}{dT}(\ln P_0 - \ln P_c) + \dot\xi_c\left(\frac{d\ln P_0}{dT} - \frac{d\ln P_c}{dT}\right). \tag{23}$$

Now we expect the coefficient A in Eq. 14 to be a decreasing function of temperature,[15,18,19,21] so, given Eq. 22, $d\ln P_c/dT$ should be positive. It is conceivable, then, that $d\ln P_c/dT$ might be large enough to make the right hand side of Eq. 23 vanish, leading to the result that, for a given liquid and a given apparatus configuration,

$$\theta_c = \text{const.} \tag{24}$$

Relation 24 would imply, for this type of experiment, an intrinsic limit to the rate of entropy production that the initial liquid configuration could support; in order to pass beyond the critical rate of entropy production, the liquid would have to change its configuration. An observation analogous to this is that small droplets of liquid have an intrinsic limit (at low to moderate pressures) to the degree of superheat that they can sustain.[22]

If Relation 24 were found to hold, then it would follow that for forced vaporization

$$d\theta_c/dY_c = 0 \tag{25}$$

and, consequently, that

$$d\Omega_c/dY_c = -\Omega_c/Y_c < 0. \tag{26}$$

It is hard to see how Relation 26 could possibly be true, and in section 3 I show that it is very unlikely the Relation 24 can hold true.

The carbon tetrachloride data in Fig. 2 clearly show a "resistance change" transition; the studies of Spangenberg and Rowland[20] indicate that such behavior should regularly occur in forced vaporization experiments; yet the data for water in Fig. 2 and other published results of forced vaporization experiments[15,16,18,19] do not clearly show evidence of "resistance change" transitions. What controls the presence or absence of such transitions? I shall discuss this matter at the end of the section on Bénard instability, but, to anticipate that discussion, what we need in forced vaporization experiments are a closer spacing of points in the $\ln P$ *vs.* $\dot{\xi}$ plots and more attention given to the depth of the liquid layer as an experimental parameter.

3. Bénard Instability. Sandwich a thin layer of fluid between two heat reservoirs (a, b) of temperatures T_a and T_b, with reservoir a above and b below the layer of fluid. By making $T_b \neq T_a$ we can generate a steady flow of heat through the fluid layer from one reservoir to the other. Characterize a reference thermo-static equilibrium state of the fluid by the variables T_a, P_a. Make T_b progressively larger than T_a. A sequence of states of steady heat flow results which ultimately shows an instability: thermal expansion causes the fluid to be less dense at the bottom of the layer than at the top — the layer becomes "top heavy;" eventually conductive heat flow gives way to convective heat flow. The sudden onset of a pattern of convective heat flow is referred to as the Bénard instability;[23,24] it is another example of a "resistance change" transition.

Let $T_b > T_a$ and let $\dot{Q}$ be the rate of influx of heat to the upper reservoir (reservoir a); take state a (T_a, P_a) as the reference state, then

$$\theta = Y\Omega = \dot{Q}\left(\frac{1}{T_a}-\frac{1}{T_b}\right) = \dot{Q}(T_b-T_a)/T_aT_b, \tag{27}$$

$$(\partial\Omega/\partial Y)_{T_a} = (1/T_b)^2[\partial(T_b-T_a)/\partial\dot{Q}]_{T_a}. \tag{28}$$

Schmidt and Milverton[25] immersed two circular brass plates, a fixed distance apart, into a tank of water. They passed a steady electric current I through a resistor of resistance ω affixed to the underside of the lower plate. If f is the fraction of the electrical energy dissipated per unit time by the resistor that passes directly from the lower plate to the upper one through the intervening layer of water, then

$$\dot{Q} = f\omega I^2, \tag{29}$$

$$\theta = \dot{Q}\left(\frac{1}{T_a}-\frac{1}{T_b}\right) = \frac{f\omega I^2(T_b-T_a)}{T_aT_b}, \tag{30}$$

$$T_0^2\theta/f\omega = I^2(T_b-T_a)(T_0^2/T_aT_b), \tag{31}$$

where T_0 is an additional reference temperature introduced for computational convenience. Figure 5 is a plot of $(T_b-T_a)(T_0^2/T_aT_b)$ *vs.* I^2, with T_0=291 K, of the data listed for Experiment 4 in the paper of Schmidt and Milverton;[25] the distance of separation between the plates was 5.5 mm. There is again clear evidence for a "resistance change" transition, and a plot of $T_0^2\theta/f\omega$ *vs.* I^2 would be qualitatively of the same shape as that of Fig. 3: at the point of transition the configuration of lower rate of entropy production is the more stable, and Relations 9, 10, and 21 are valid. Similarly a plot of $T_0^2F_\sigma/f\omega$ *vs.* I^2 would be qualitatively of the same shape as that of Fig. 4.

In the case of Bénard instability the thermodynamic variables characterizing the transition point are θ_c, $\dot{Q}_c$, $(T_a^{-1}-T_b^{-1})_c$ or $(T_b-T_a)_c$, T_a, and P_a (depending on the experimental setup, P_a may or may not be an independent variable). We are again interested in quantitites such as $\partial\theta_c/\partial\dot{Q}_c$, $\partial\Omega_c/\partial Y_c$, $\partial\dot{Q}_c/\partial T_a$, *etc.* We get some help from hydrodynamic stability theory[23] in this case. The (dimensionless) Rayleigh number $R_\#$ is defined to be

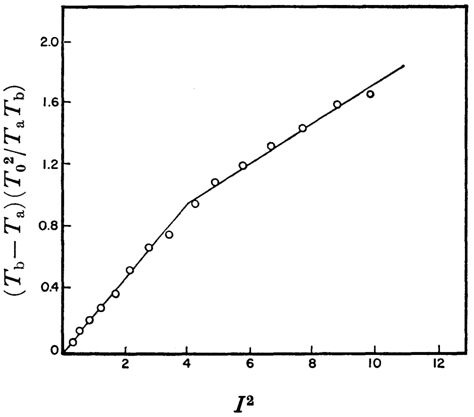

Fig. 5. Plot of $(T_b-T_a)(T_0^2/T_aT_b)$ *versus* I^2, with T_0=291 K. Data of Schmidt and Milverton.[25]

$$R_\# = g\alpha(T_b-T_a)\lambda^3/\kappa\nu, \tag{32}$$

where g is the gravitational acceleration, λ is the thickness of the fluid layer, and α, κ, and ν are the coefficients of volume expansion, thermometric conductivity, and kinematic viscosity, respectively. Stability theory[23] shows that at the point of Bénard instability

$$R_{\#c} = 1708. \tag{33}$$

In the conductive heat flow regime $\dot{Q}=D(T_b-T_a)\times\kappa\rho C_V/\lambda$, where D is the area through which the heat current flows, ρ is the density of the fluid, and C_V is the specific heat of the fluid; consequently

$$\theta_c \approx D(1708\nu/g\alpha T_a)^2(\kappa^3\rho C_V/\lambda^7), \tag{34}$$

where I have set $T_aT_b \approx T_a^2$. Since ν, α, κ, ρ, and C_V are all functions of the reference temperature T_a, the rate of entropy production θ_c for a given fluid with fixed values of D and λ, is apt to be a complicated function of T_a; and a relation such as Eq. 24 is not apt to be satisfied.

3.1 Forced Vaporization Reconsidered: With respect to the hydrodynamic stability of a layer of liquid, heating from below and cooling from above are much the same thing. The instability in the forced vaporization of carbon tetrachloride should thus be of the same nature as the Bénard instability, and the sensitivity of the Bénard instability to the thickness of the fluid layer [Eq. 32] indicates the advisability of treating the depth of the vaporizing liquid as an experimental variable in the forced vaporization case. (The forced vaporization problem is a more complicated one than the Bénard problem in that the temperature gradient in the vaporizing liquid has a complicated 3-dimensional structure[20] whereas the temperature gradient in the Bénard case is a simple 1-dimensional one.)

The data of Alty and Nicoll[17] displayed in Fig. 2 were all gathered in the same apparatus at the same fixed depth for the liquid layer. At the point of instability for the carbon tetrachloride the difference between the thermostat temperature T and the temperature T_s at the surface of the vaporizing liquid was $T-T_s$=7.5 K. If we assume the geometric factors of the two experiments displayed in Fig. 2 to be the same (same apparatus, same depth of liquid, same 3-dimensional structure for the thermal gradients) and if we scale the water data according to Eq. 33, relative to the carbon tetrachloride data, *i.e.* if we say that

$$[\alpha(T-T_{\mathrm{s}})/\kappa\nu]_{\mathrm{c},\,\mathrm{H_2O}} = [\alpha(T-T_{\mathrm{s}})/\kappa\nu]_{\mathrm{c},\,\mathrm{CCl_4}}, \qquad (35)$$

we find a predicted value of $T-T_{\mathrm{s}}\approx 59$ K at the point of instability for water under the given experimental conditions at 30 °C— such a value is far outside the range of experimental conditions displayed in Fig. 2.

In Alty's other experiments¹⁶⁾ and in Erikson's experiments^{18,19)} the depth of the liquid layer was an uncontrolled variable, so the resulting data were not gathered in such a way as to highlight the onset of Bénard-type instability. Note that Erikson did see evidence of convection currents in some of his experiments.¹⁸⁾ As I mentioned previously, what is needed in forced vaporization experiments is strict control of the depth-of-liquid variable — and a closer spacing of experimental points in plots of $\ln P$ *vs.* $\dot{\xi}$ (for a fixed depth of liquid). Also, as I mentioned in my discussion of Eq. 34, Relation 24 is unlikely to have any validity whatsoever.

4. Taylor Instability. Place a sample of liquid between two coaxial cylinders; put the device in thermal communication with a thermostat of temperature T, and rotate one of the cylinders at a constant angular velocity γ by exerting on it a torque N. (The case of simultaneous rotation of both cylinders is also of interest, but I do not consider it in this paper.) The simple Couette flow between the cylinders ultimately becomes unstable at $\gamma=\gamma_{\mathrm{c}}$, and toroidal Taylor vortices form at the point of instability^{24,26-28)}— another example of a "resistance change" transition. As in the previous case, the instability is correlated with the critical value of a dimensionless combination of fluid properties — the Taylor number.²⁶⁾

The rate of entropy production for a given angular velocity γ is

$$\theta = \gamma(N/T) = Y\Omega. \qquad (36)$$

To analyze the Taylor instability we need experimental data in the form of N *vs.* γ plots (plots of driving torque *versus* angular velocity) so as to be able to see discontinuities in N and/or $\partial N/\partial\gamma$ at $\gamma=\gamma_{\mathrm{c}}$. The usual experimental procedure,²⁶⁻²⁸⁾ however, is to measure the torque on the *stationary cylinder* as a function of the angular velocity γ. The measurements of Donnelly²⁸⁾ show a discontinuity in the torque on the stationary cylinder at γ_{c}, *i.e.* the fluid shows a discontinuous increase in apparent viscosity at the point of instability. What do these results imply concerning the variation of N with γ? Until we have some direct measurements or dependable calculations of the N, γ relationship, we cannot be sure of the implication; we can, however, explore some of the possibilities.

Suppose that the N, γ relation turns out to be similar in nature to the torque-on-the-stationary-cylinder, γ relation: suppose that $\Delta N\neq 0$, $\Delta\partial N/\partial\gamma>0$, and the configuration of *higher* rate of entropy production (and of higher local potential) is the more stable one beyond γ_{c}. What would be the thermodynamic implications of such a result? The idea here is to pursue the analogy to thermo-static phase transitions. If both phases have metastable regimes extending out beyond the transition point (Fig. 1, *e.g.*), then we are dealing with a problem of *relative stability* and the phase with the smaller Gibbs function value is the more stable. But it is also possible to have a phase transition point such that one of the phases reaches an *absolute limit of stability* at the transition point and has no metastable existence out beyond the transition point — the order-disorder transition in β-brass, for example.²⁹⁾ For "resistance change" transitions, then, where each configuration has a metastable extension beyond the point of instability (in one direction or the other) the question of relative stability is decided by having the configuration of lower rate of entropy production (or lower local potential) more stable (Fig. 3, *e.g.*). But if a given configuration approaches an inflection point in the θ, Y plot, *i.e.* $\partial^2\theta/\partial Y^2$ approaches zero, it approaches an intrinsic limit of stability [see Eq. 9]: at the point where $\partial^2\theta/\partial Y^2=0$ the configuration must change to some other stable configuration; it is no longer a question of relative stability but an absolute requirement for a change of configuration. Under such circumstances $\Delta\partial\Omega/\partial Y$ could just as well be positive as negative, and we could even have a discontinuity in Ω (and F_σ): $\Delta\Omega\neq 0$ ($\Delta F_\sigma\neq 0$). The requirement for such a point of intrinsic instability would be

$$0 = \partial^2\theta/\partial Y^2 = 2(\partial\Omega/\partial Y) + Y_{\mathrm{c}}(\partial^2\Omega/\partial Y^2), \qquad (37)$$

and we should have

$$Y_{\mathrm{c}} = -2(\partial\Omega/\partial Y)/(\partial^2\Omega/\partial Y^2) \qquad (38)$$

as $Y\to Y_{\mathrm{c}}-0$.

If the transition point is a point of intrinsic instability for both the upper ($Y>Y_{\mathrm{c}}$) and lower ($Y<Y_{\mathrm{c}}$) branches, we cannot say anything *a priori* about $\Delta\theta$ or $\Delta\partial\Omega/\partial Y$. If the transition point is a point of intrinsic instability for the lower branch and if the upper branch has a metastable extension below Y_{c}, then we can make the following observations relative to the transition point: i) it is not possible, under these circumstances, to have $\Delta\theta<0$ since the extension of the upper branch into the region $0\leq Y<Y_{\mathrm{c}}$ would be more stable (would have a lower θ value) than the experimental lower branch; ii) it is not possible to have $\Delta\theta=0$ and $\Delta\partial\theta/\partial Y>0$ for the same reason as in i)— the extension of the upper branch into the region $0\leq Y<Y_{\mathrm{c}}$ would be more stable than the experimental lower branch; iii) it is possible, but not likely, to have $\Delta\theta=0$ and $\Delta\partial\Omega/\partial Y<0$ — it is improbable to expect the lower branch to just "happen" to intersect the upper branch at the point of intrinsic instability; iv) it is possible, and likely, to have $\Delta\theta>0$ and either $\Delta\partial\Omega/\partial Y>0$ or $\Delta\partial\Omega/\partial Y<0$ — at the point of intrinsic instability it is highly probable that the lower branch will be some distance away from the upper branch, hence a jump discontinuity in θ (and in Ω) — and in F_σ — will occur, with no necessary restrinction on the sign of the change in slope $\Delta\partial\Omega/\partial Y$. Note that if $\Delta\partial\Omega/\partial Y>0$ then there *must* be a discontinuity in θ (and in Ω) — see Fig. 6.

If the N, γ relation for the Taylor instability proves to have $\Delta N\neq 0$ at $\gamma=\gamma_{\mathrm{c}}$ the most likely explanation

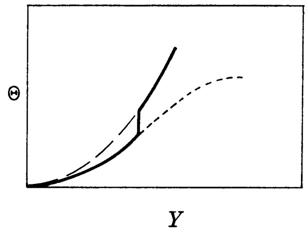

Fig. 6. Example: point of intrinsic instability with $\Delta\theta>0$ and $\Delta\partial\Omega/\Omega Y>0$.

will be that the transition point is a point of intrinsic instability for the lower branch. Points of intrinsic instability are special cases of the "bifurcations" and "catastrophes" discussed by Nicolis and Prigogine.[30)]

5. A Multi-current Situation — Flip-Flop Current vs. Voltage Relation. Interpose a sintered glass membrane between aqueous sodium chloride solutions of concentrations 0.01 and 0.1 M; place inert electrodes on opposite sides of the membrane and impose a voltage $\Delta\phi$ between the electrodes; exert an excess pressure ΔP on the more concentrated solution. Keep the concentration difference and the pressure difference across the membrane fixed and measure the electric current I induced by the impressed voltage $\Delta\phi$. (Maintain the entire system at a constant temperature T.)

Let subscript 1 indicate water and subscript 2 indicate sodium chloride, and let a single prime designate the more concentrated solution and a double prime designate the less concentrated solution. Then, if the experiment is conducted in a steady-state fashion, we have[31)]

$$T\theta = -(\dot{n}_1'\mu_1'+\dot{n}_2'\mu_2'+\dot{n}_1''\mu_1''+\dot{n}_2''\mu_2'') + I\Delta\phi, \tag{39}$$

and

$$\begin{aligned} T\theta &= \dot{n}_1'(\mu_1''-\mu_1') + \dot{n}_2'(\mu_2''-\mu_1') + I\Delta\phi \\ &= Y_1\Omega_1 T + Y_2\Omega_2 T + Y_3\Omega_3 T, \end{aligned} \tag{40}$$

since $\dot{n}_1'+\dot{n}_1''=0$ and $\dot{n}_2'+\dot{n}_2''=0$. If we treat the sodium chloride solutions as "ideal" we can say that

$$\begin{aligned} \mu_1'-\mu_1'' &= \int_{P''}^{P'} \overline{V}_1\,\mathrm{d}P + RT\ln(X_1'/X_1'') \\ &= \langle\overline{V}_1\rangle\Delta P + RT\ln(X_1'/X_1''), \end{aligned} \tag{41}$$

$$\begin{aligned} \mu_2'-\mu_2'' &= \int_{P''}^{P'} \overline{V}_2\,\mathrm{d}P + RT\ln(C_2'/C_2'') \\ &= \langle\overline{V}_2\rangle\Delta P + RT\ln(C_2'/C_2''), \end{aligned} \tag{42}$$

where X_i is the mole fraction, $\overline{V}_i$ the partial molar volume, $<\overline{V}_i>$ the average partial molar volume over the pressure interval ΔP, and C_i the concentration (moles per liter) of component i. Let $\dot{n}_1'<\overline{V}_1>+\dot{n}_2'<\overline{V}_2>\approx\dot{V}'$ and evaluate X_1'/X_1'' by setting molarities approximately equal to molalities. Impose the restriction on $\dot{n}_1'$ and $\dot{n}_2'$ that they keep the ratio n_1'/n_2' constant (*i.e.* constant C_2'). Upon substitution of the appropriate numerical values, we get

$$T\theta \approx -\dot{V}'\Delta P - 1.4\,\dot{n}_2'RT + I\Delta\phi. \tag{43}$$

Experiments measuring the current-voltage relationship for this type of experiment were carried out by H. Jahnke and reported on by Franck.[32)] Figure 7 shows the I *vs.* $\Delta\phi$ relation for various fixed pressure differences for one series of experiments carried out by Jahnke. The rather spectacular form of the I, $\Delta\phi$ relation is explained by Kobatake[8)] in the following way: "… under the external conditions studied here, the Poiseuille pressure flow transports fluid from the more concentrated to the less concentrated solution, while the electro-osmotic flow caused by the potential gradient tends to carry fluid in the opposite direction. With increasing $\Delta\phi$, the electro-osmotic flow becomes appreciable, outweighs the pressure flow, and eventually changes the direction of mass flow from negative to positive. Calculations show that this change of the direction of mass flow occurs discontinuously when $\Delta\phi$ reaches a certain value, when the pressure difference ΔP is larger than a critical value ΔP_c. Correspondingly, the average salt concentration in the membrane is lowered, *i.e.* the membrane is occupied with the less concentrated solution… The effect of this change in concentration in the membrane is reflected in the I *vs.* $\Delta\phi$ relationships depicted in [Fig. 7]."

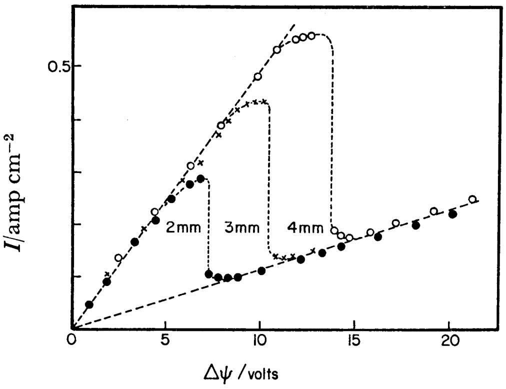

Fig. 7. Plots of I *versus* $\Delta\phi$ for the system of a sintered glass membrane and NaCl solutions of 0.01 and 0.1 M with various fixed pressure differences. Data of Jahnke as reported by Franck.[32)]

The results reported by Franck[32)] do not include data for $\dot{V}'$ and $\dot{n}_2'$ so we cannot actually calculate $T\theta$ for the experiment. It seems reasonable to expect, however, that at the critical value $\Delta\phi_c$ of the voltage $T\theta$ will actually show a discontinuous *decrease*. If such is indeed the case, it must be because the point $\Delta\phi=\Delta\phi_c$ is a point of intrinsic instability ($\partial^2\theta/\partial Y^2\rightarrow 0$) for *both* the upper ($\Delta\phi=\Delta\phi_c+0$) and lower ($\Delta\phi=\Delta\phi_c-0$) branches of the I *vs.* $\Delta\phi$ relation, *i.e. neither* branch has a metastable extension beyond the point $\Delta\phi=\Delta\phi_c$.

Kobatake[8)] has analyzed Jahnke's experiments in terms of the local potential:

$$TF_\sigma = T\int \textstyle\sum_i Y_i \mathrm{d}\Omega_i = \displaystyle\int_0^{\Delta\phi} I\mathrm{d}\Delta\phi + f(\Delta P, \Delta\mu_2). \tag{44}$$

By an elementary theorem of the calculus[33)] the integral in Eq. 44 is continuous at the point $\Delta\phi_c$, so TF_σ does not have a discontinuity at the flip-flop point.

6. Summary. I have considered the behavior of the rate of entropy production θ and the local potential F_σ for several one-current steady-state situations showing "resistance change" transitions — forced vaporization of carbon tetrachloride, Bénard instability, and Taylor instability. For these cases the behavior of the local potential is qualitatively similar to the behavior of the rate of entropy production. The complexity of the thermodynamic relations pertaining to the transition point depends upon whether the branches intersecting at the transition point have metastable extensions beyond that point. I also considered (briefly) a multi-current situation showing a flip-flop current-voltage relation at the transition point; here θ and F_σ seemingly show different kinds of behavior—F_σ is continuous at the transition point whereas θ appears to undergo a discontinuous change (it seems that *neither* of the branches intersecting at the transition point has a metastable extension beyond that point).

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