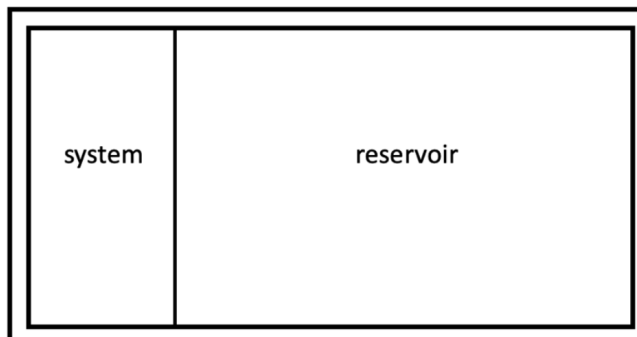


## C: Practical Variations of the 2nd Law

Again, we isolate a composite system comprising two compartments. For the present purposes, one compartment is our system of interest and the other is a "reservoir" (as shown in the figure below). The reservoir is an extremely large bath, such that any interaction with the system involves changes in the reservoir that are so tiny by comparison that they are reversible. Two cases are of particular interest. In one, thermal contact allows the reservoir to control the temperature of the system, while the system's volume and contents are fixed. We call this an **NVT system**. In the other, thermal and mechanical contact allows the reservoir to control the temperature and pressure of the system, while the system's contents are fixed. We call this an **NPT system**.



An isolated composite system (with its rigid, impermeable and insulating boundaries represented by double lines according to convention) comprising our system of interest in contact with a "reservoir".

### NVT systems

NVT conditions are maintained by perfect thermal contact with a reservoir at temperature  $T^r$ , so  $T = T^r$ , and by rigid and impermeable boundaries so  $dV, dN_i = 0$ . This system's only degree of freedom is heat exchange between the compartments.

Because the composite system is isolated, we know that

$$0 = d(E + E^r) \quad (\text{C1})$$

and that

$$0 < \frac{d(S + S^r)}{dt} \quad (\text{C2})$$

approaching equilibrium and

$$0 = d(S + S^r) \quad \text{and} \quad 0 > d^2(S + S^r) \quad (\text{C3})$$

at equilibrium. The key to making use of this information is to realize that, due to its huge size, the changes in the reservoir are reversible and therefore

$$dE^r = T^r dS^r = T dS^r \quad (\text{C4})$$

By replacing  $dE^r$  in Equation C1 and then  $dS^r$  in Equations C2 and C3, we arrive at

$$0 < \frac{d(S - E/T)}{dt} \quad (\text{C5})$$

approaching equilibrium and

$$0 = d(S - E/T) \quad \text{and} \quad 0 > d^2(S - E/T) \quad (\text{C6})$$

at equilibrium. Since  $T > 0$ , we can multiply through without a change the direction of the inequalities and obtain

$$0 < \frac{d(TS - E)}{dt} \quad (\text{C7})$$

approaching equilibrium and

$$0 = d(TS - E) \quad \text{and} \quad 0 > d^2(TS - E) \quad (\text{C8})$$

at equilibrium. Thus, for an NVT system, the Helmholtz free energy,  $F = E - TS$ , decreases with time

$$\frac{dF}{dt} < 0 \quad (\text{C9})$$

until it reaches a minimum

$$dF = 0 \quad \text{and} \quad d^2F > 0 \quad (\text{C10})$$

at equilibrium.

## NPT systems

NPT conditions are maintained by perfect thermal and mechanical contact with a reservoir at temperature  $T^r$  and pressure  $P^r$ , so  $T = T^r$  and  $P = P^r$ , and by impermeable boundaries so  $dN_i = 0$ .

Because the composite system is isolated, we know that

$$0 = d(E + E^r) \quad (\text{C11})$$

$$0 = d(V + V^r) \quad (\text{C12})$$

as well as that

$$0 < \frac{d(S + S^r)}{dt} \quad (\text{C13})$$

approaching equilibrium and

$$0 = d(S + S^r) \quad \text{and} \quad 0 > d^2(S + S^r) \quad (\text{C14})$$

at equilibrium. Again, the key to making use of this information is to realize that, due to its huge size, the changes in the reservoir are reversible and therefore

$$\begin{aligned} dE^r &= -P^r dV^r + T^r dS^r \\ &= +P dV + T dS^r \end{aligned} \quad (\text{C15})$$

Using Equation C12 and the fact that  $P$  is constant, we obtain

$$dE^r = d(PV) + T dS^r \quad (\text{C16})$$

By substituting for  $E^r$  in Equation C11 and then for  $S^r$  in Equations C13 and C14, we arrive at

$$0 < \frac{d(S - (E + PV)/T)}{dt} \quad (\text{C17})$$

approaching equilibrium and

$$0 = d(S - (E + PV)/T) \quad \text{and} \quad 0 > d^2(S - (E + PV)/T) \quad (\text{C18})$$

at equilibrium. Since  $T > 0$ , we can multiply through without change the direction of inequalities and obtain

$$0 < d(TS - E + PV)/dt \quad (\text{C19})$$

approaching equilibrium and

$$0 = d(TS - E + PV) \quad \text{and} \quad 0 > d^2(TS - E + PV) \quad (\text{C20})$$

at equilibrium. Thus, for an NVT system, the Gibbs free energy,  $G = E + PV - TS$ , decreases with time

$$\frac{dG}{dt} < 0 \quad (\text{C21})$$

until it reaches a minimum

$$dG = 0 \quad \text{and} \quad d^2G > 0 \quad (\text{C22})$$

at equilibrium.

## In summary

We have found extremum conditions for equilibrium in three types of systems:

System	Constants	2 <sup>nd</sup> Law
isolated	$E, V, \{n_i\}$	$S \uparrow$ to a max
thermal contact only	$T, V, \{n_i\}$	$F \downarrow$ to a min
thermal & mechanical contact only	$T, P, \{n_i\}$	$G \downarrow$ to a min

All equilibrium states are stable, i.e., perturbations and fluctuations regress in return to the extremum condition.

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