CHEMICAL ENGINEERING THERMODYNAMICS II (0905323)

01. EQUILIBRIUM AND STABILITY

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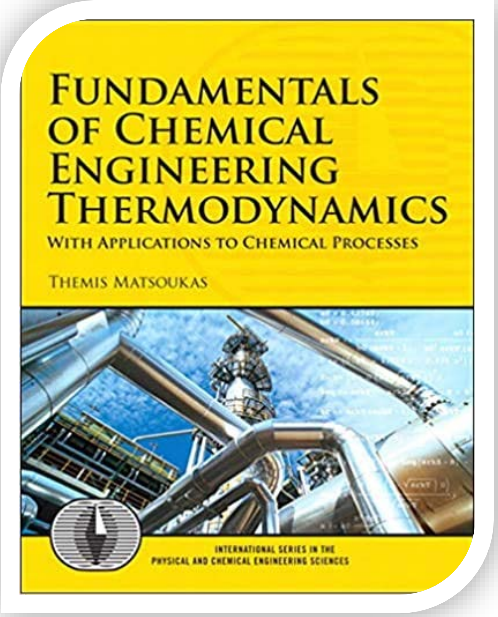
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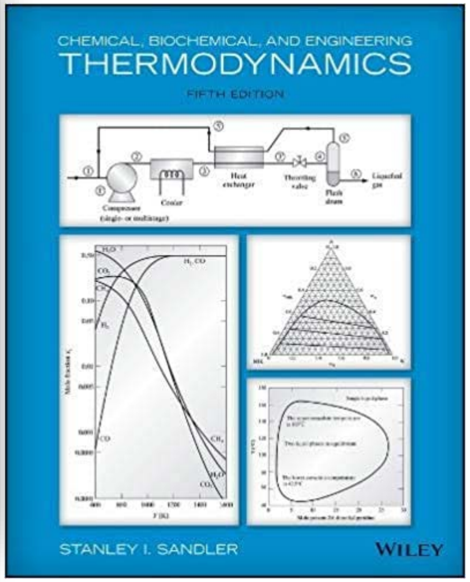
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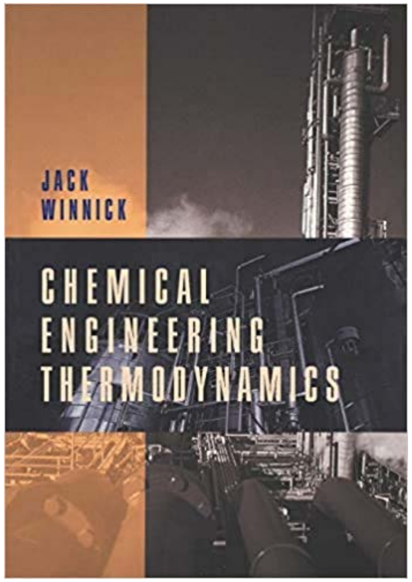
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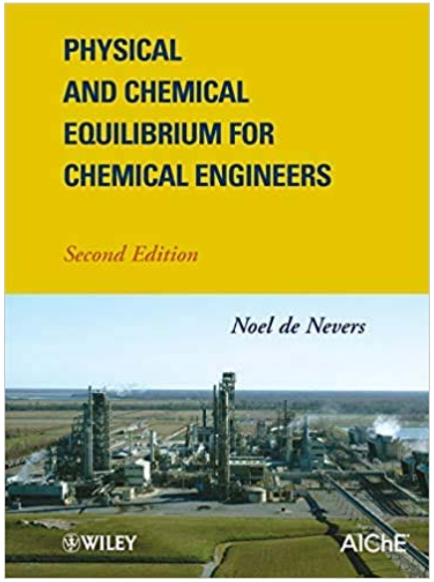
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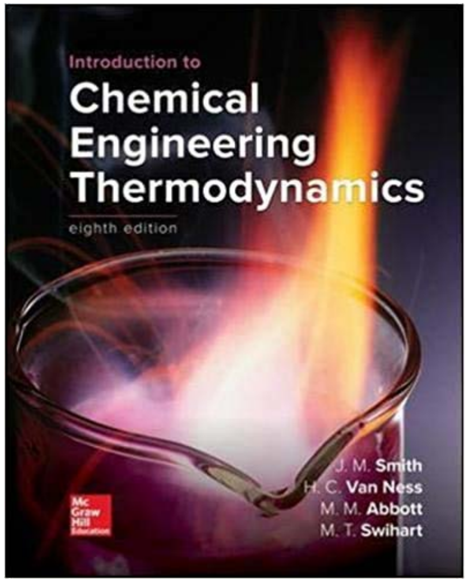
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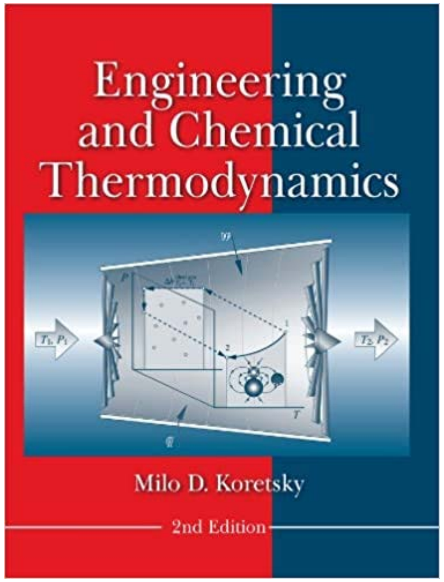
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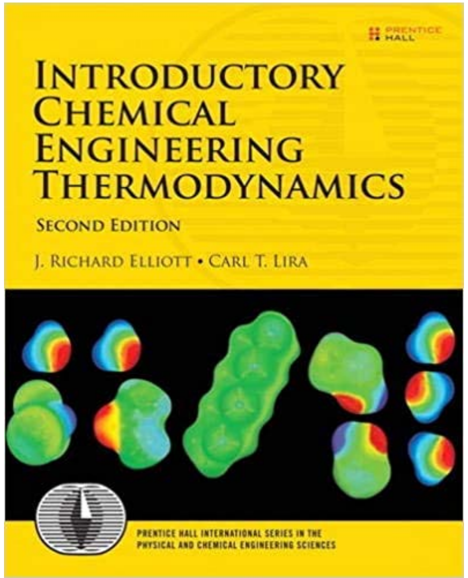
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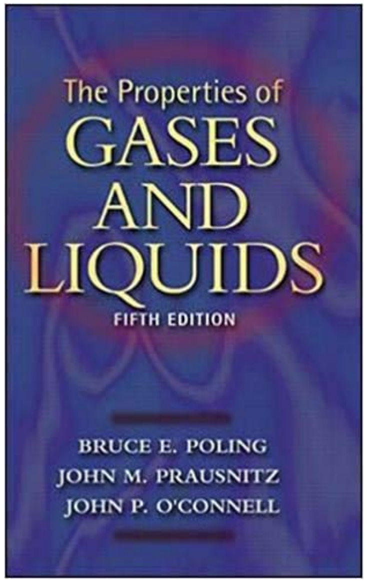
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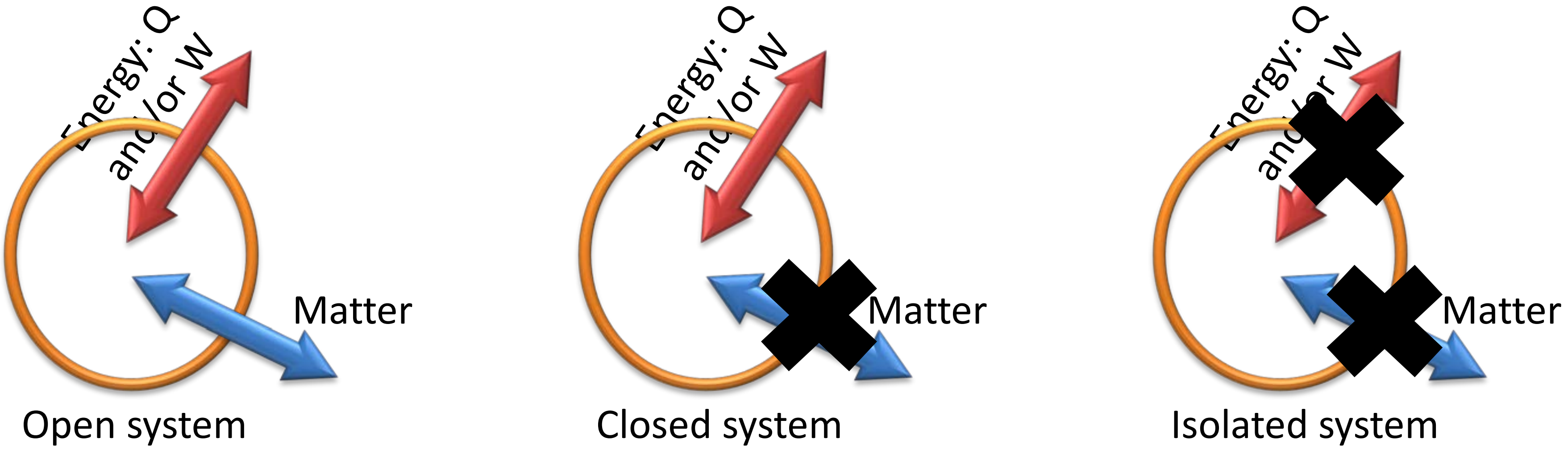
Outline

- Criterion for Equilibrium: Isolated System
- Entropy Function Behavior
- Equilibrium Conditions for Closed System: Constant (U, V)
- Stability Analysis
- Closed Systems at Constant (T, V)
- Closed Systems at Constant (P, T)
- Open Systems at Constant (P, T)
- Stability Criteria

Review

- Write down the first and second laws of thermodynamics analysis for an isolated system.
- What are the implications for the derivation you've just carried out?



Criterion for Equilibrium: Isolated System

- Start with energy and entropy balances for a closed system with:
  - Constant volume.
  - No heat exchanged between the system and its surroundings (adiabatic).

$$\frac{dU}{dt} = \dot{Q} - P\frac{dV}{dt}$$

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

$$\dot{S}_{gen} \geq 0$$

$$\Longrightarrow$$

$$\frac{dU}{dt} = 0 \Rightarrow U = \text{const.}$$

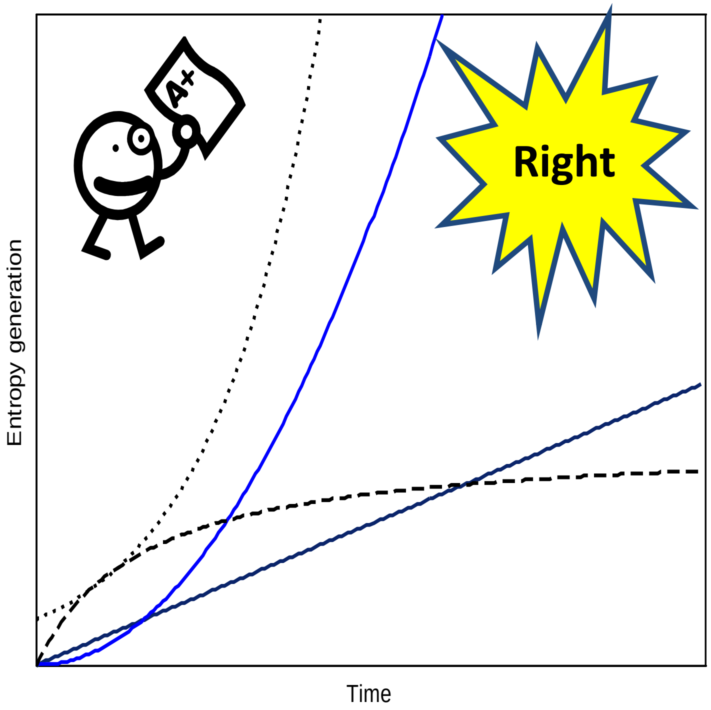
$$\frac{dS}{dt} = \dot{S}_{gen} \geq 0$$

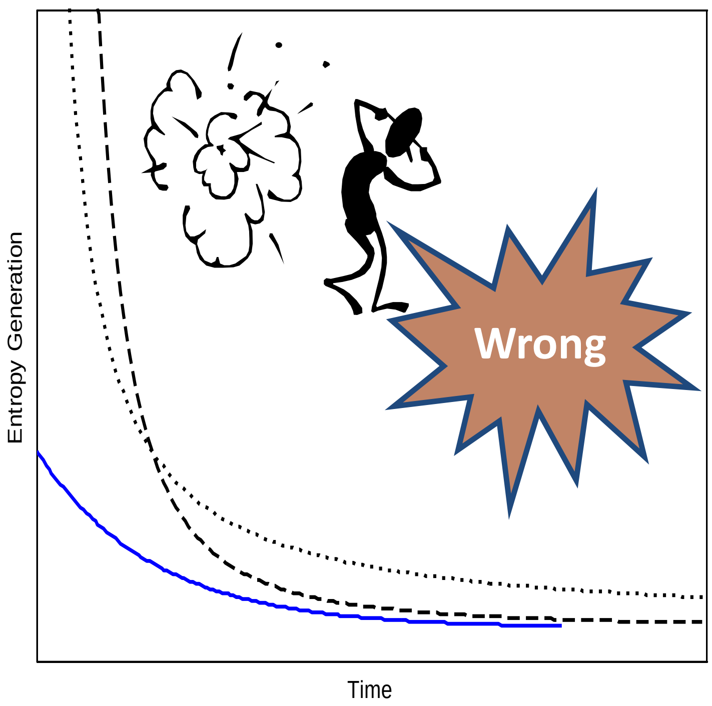
- At equilibrium in a closed system at constant *U* and *V:*

$$\left.\begin{aligned} S &= \text{maximum} \\ s &= \text{maximum} \end{aligned}\right\}$$

Entropy Function Behavior

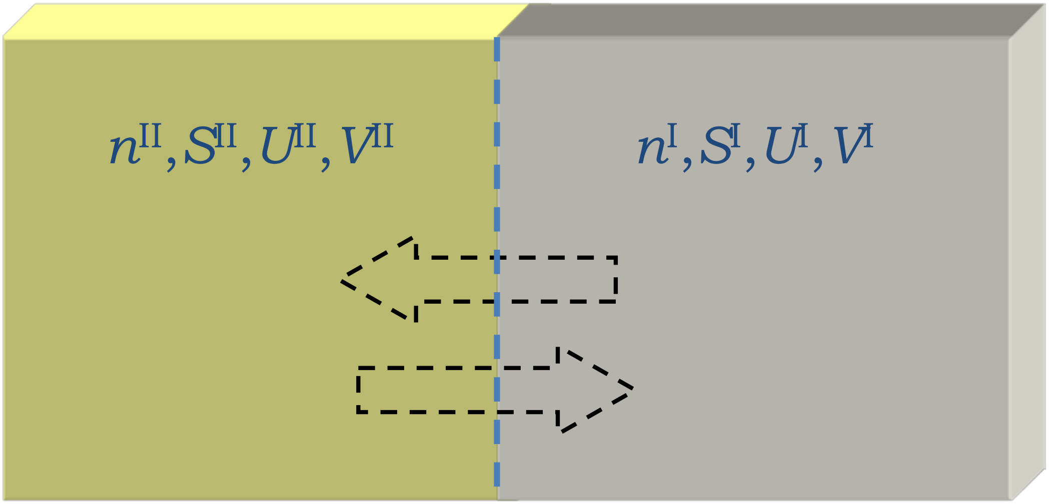
- The entropy function is monotonically increasing during the approach to equilibrium (entropy generation is always positive).





Equilibrium Conditions for Closed System: Constant (U, V)

- Single component, single phase closed adiabatic system with constant volume [constant (U, V)].
- Divide into two nonuniform subsystems by an imaginary boundary.
- Nonuniform may include different T and/or P initially.
- These two subsystems are open to flow of heat and mass across the internal boundary.



Balance Equations

- Overall material and energy balances, note that the total volume is the sum of the two subsystems' volumes:

$$n = n^{I} + n^{II} = \text{constant} \Rightarrow dn^{I} = -dn^{II}$$

$$U = U^{I} + U^{II} = \text{constant} \Rightarrow dU^{I} = -dU^{II}$$

$$V = V^{I} + V^{II} = \text{constant} \Rightarrow dV^{I} = -dV^{II}$$

$$S = S^{I} + S^{II}$$

- This is natural since the system is isolated from the surroundings. The loss in one subsystem must appear in the other as gain.

Mathematical Derivatives and Mapping to First Law

- Consider the entropy to be a function of (U, V, M). From the definition of partial and total derivatives:

$$dS^{I} = \left(\frac{\partial S^{I}}{\partial U^{I}}\right)_{V^{I},n^{I}} dU^{I} + \left(\frac{\partial S^{I}}{\partial V^{I}}\right)_{U^{I},n^{I}} dV^{I} + \left(\frac{\partial S^{I}}{\partial n^{I}}\right)_{U^{I},V^{I}} dn^{I}$$

$$dS^{II} = \left(\frac{\partial S^{II}}{\partial U^{II}}\right)_{V^{II},n^{II}} dU^{II} + \left(\frac{\partial S^{II}}{\partial V^{II}}\right)_{U^{II},n^{II}} dV^{II} + \left(\frac{\partial S^{II}}{\partial n^{II}}\right)_{U^{II},V^{II}} dn^{II}$$

- First law of thermodynamics for an open system:

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{g}{T} dn$$

- From the equality of the thermodynamic function and the energy balance for each subsystem we can write

$$dS^{I} = \frac{1}{T^{I}} dU^{I} + \frac{P^{I}}{T^{I}} dV^{I} - \frac{g^{I}}{T^{I}} dn^{I}$$

$$dS^{II} = \frac{1}{T^{II}} dU^{II} + \frac{P^{II}}{T^{II}} dV^{II} - \frac{g^{II}}{T^{II}} dn^{II}$$

$$dS = dS^{I} + dS^{II}$$

$$= \left(\frac{1}{T^{I}} - \frac{1}{T^{II}} \right) dU^{I} + \left(\frac{P^{I}}{T^{I}} - \frac{P^{II}}{T^{II}} \right) dV^{I} - \left(\frac{g^{I}}{T^{I}} - \frac{g^{II}}{T^{II}} \right) dn^{I}$$

Equilibrium Conditions

- S is a maximum, or dS = 0 for all system variations at constant (n,U,V).
- Consequently, the individual terms are zeros. Therefore, the equilibrium conditions are:

$$\frac{1}{T^{I}} = \frac{1}{T^{II}} \Rightarrow T^{I} = T^{II}$$

$$\frac{P^{I}}{T^{I}} = \frac{P^{II}}{T^{II}} \Rightarrow P^{I} = P^{II}$$

$$\frac{g^{I}}{T^{I}} = \frac{g^{II}}{T^{II}} \Rightarrow g^{I} = g^{II}$$

For a single-component, single-phase system, this implies that the composite system should be uniform!

ILLUSTRATION 7.1-2

Proving the Equality of Gibbs Energies for Vapor-Liquid Equilibrium

Use the information in the steam tables of Appendix A.III to show that Eq. 7.1-9c is satisfied at 100°C and 0.101 35 MPa.

SOLUTION

From the saturated steam temperature table, we have at 100°C and 0.101 35 MPa

$$\hat{H}^{\mathrm{L}} = 419.04 \text{ kJ/kg} \qquad \hat{H}^{\mathrm{V}} = 2676.1 \text{ kJ/kg}$$
$$\hat{S}^{\mathrm{L}} = 1.3069 \text{ kJ/(kg K)} \qquad \hat{S}^{\mathrm{V}} = 7.3549 \text{ kJ/(kg K)}$$

Since $\hat{G} = \hat{H} - T\hat{S}$, we have further that

$$\hat{G}^{\mathrm{L}} = 419.04 - 373.15 \times 1.3069 = -68.6 \text{ kJ/kg}$$

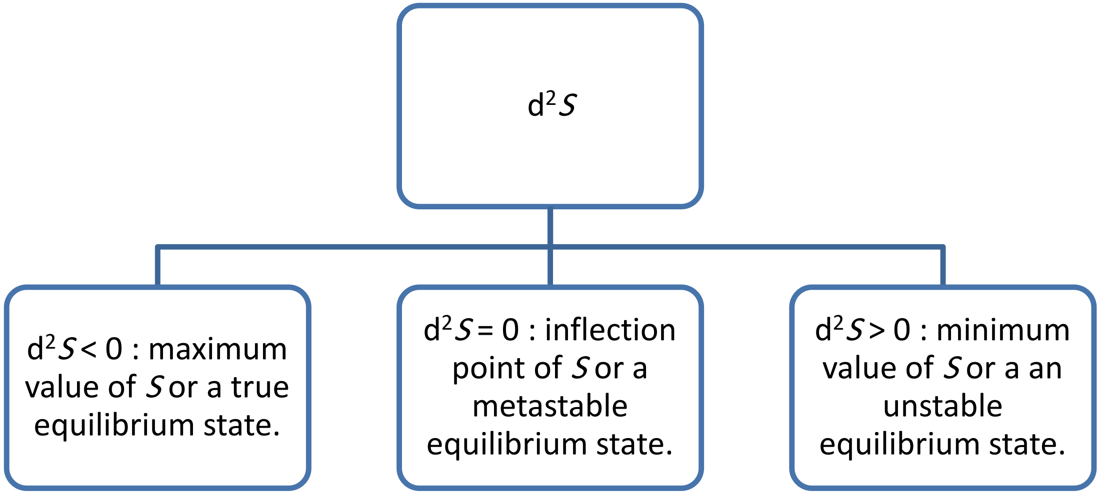
and

$$\hat{G}^{\mathrm{V}} = 2676.1 - 373.15 \times 7.3549 = -68.4 \text{ kJ/kg}$$

which, to the accuracy of the calculations here, confirms that $\hat{G}^{\mathrm{L}} = \hat{G}^{\mathrm{V}}$ (or, equivalently, that $\underline{G}^{\mathrm{L}} = \underline{G}^{\mathrm{V}}$) at this vapor-liquid phase equilibrium state. ■

Stability Analysis

- A stable equilibrium state will be established when *S* is a maximum. The first derivative is equal to zero.
- To check for maximum conditions, we have three possible values of the second derivative

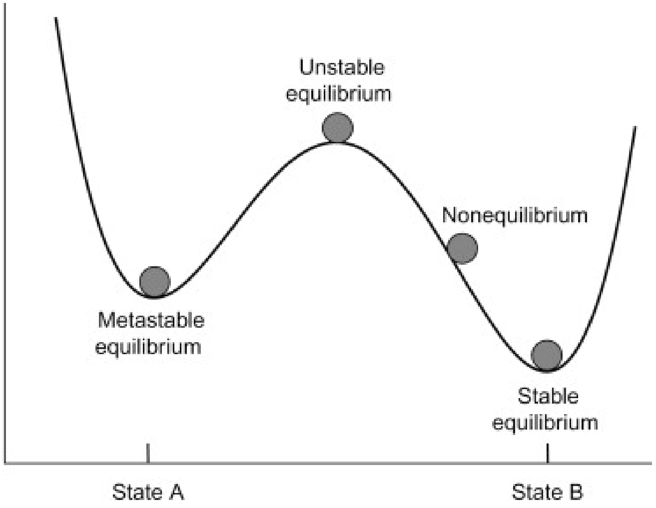


d^2S

$d^2S < 0$: maximum value of *S* or a true equilibrium state.

$d^2S = 0$: inflection point of *S* or a metastable equilibrium state.

$d^2S > 0$: minimum value of *S* or a an unstable equilibrium state.



Closed Systems at Constant (*T*, *V*)

- Suppose that we have a closed system such that it is:
  - Constant volume system.
  - The adiabatic assumption is relaxed i.e., there is heat exchange between the system and its surroundings to keep the system isothermal.
- Energy and entropy balances

$$\frac{dU}{dt} = \dot{Q}$$

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{gen} \geq 0$$

Eliminate the *Q* term between the energy and entropy balances and use the isothermal conditions.

$$TdS = d(TS)$$

$$\frac{d\left(U - TS\right)}{dt} = \frac{dA}{dt} = -T\dot{S}_{gen} \leq 0$$

Equilibrium Criterion

- Temperature is always positive, so is the entropy generation term. The negative of their product must be negative.

$$\frac{d\left(U - TS\right)}{dt} = \frac{dA}{dt} = -T\,\dot{S}_{gen} \leq 0$$

- Helmholtz energy must be a minimum at equilibrium.

$$\left.\begin{aligned} A &= U - TS = \text{minimum} \\ a &= u - Ts = \text{minimum} \end{aligned}\right\}$$

at equilibrium in a closed system at constant *T* and *V*

Closed Systems at Constant (*P*, *T*)

- Suppose that we have relaxed the assumptions of constant volume and adiabatic systems such that the system is:
  - Constant pressure (isobaric).
  - There is heat exchange between the system and its surroundings to keep the system isothermal.
- The energy and entropy balance equations for this system reduces to:

$$\frac{dU}{dt} = \dot{Q} - P\frac{dV}{dt} = \dot{Q} - \frac{d(PV)}{dt}$$

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{gen} \geq 0$$

Equilibrium Criterion for Closed Systems at Constant (*P*, *T*)

- Eliminate the *Q* term between the energy and entropy balances to obtain:

$$\frac{dU}{dt}+\frac{d(PV)}{dt}-\frac{d(TS)}{dt}=-T\dot{S}_{gen}$$

$$\frac{d\left(U+PV-TS\right)}{dt}=\frac{dG}{dt}=-T\dot{S}_{gen}\leq 0$$

- Temperature is always positive, so is the entropy generation term. The negative of their product must be negative.
- Gibbs energy must be a minimum at equilibrium.

$$\left.\begin{aligned} G&=H-TS=\text{minimum}\\ g&=h-Ts=\text{minimum}\end{aligned}\right\}$$

at equilibrium in a closed system at constant *T* and *P*

Open Systems at Constant (*P*, *T*)

- Suppose that we have
  - Constant pressure (isobaric) system, and
  - There is heat exchange between the system and its surroundings to keep the system isothermal.
  - There is an element of fluid moving with the velocity around it.
- The system is chosen such that there is no convected mass flow into or out of the system.
- Such an element of mass in a pure fluid is a system closed to the flow of mass.
- Consequently, it is treated exactly like closed systems discussed before depending on the constraints.

$$\left.\begin{aligned} G &= H - TS = \text{minimum} \\ g &= h - Ts = \text{minimum} \end{aligned}\right\}$$

at equilibrium in an open system at constant *T* and *P*

Stability Criteria

- Without mathematical derivation, the following pair of criterion must be satisfied to have a stable phase:
  - Heat capacity at a constant volume must be positive (**Thermal stability criterion**).

$$c_V = \left(\frac{\partial u}{\partial T}\right)_V > 0$$

  - Isothermal compressibility must be positive (**Mechanical stability criterion**).

$$\kappa_T = \frac{-1}{v}\left(\frac{\partial v}{\partial P}\right)_T > 0 \Rightarrow \left(\frac{\partial P}{\partial v}\right)_T < 0$$

Summary

- The derived equilibrium and stability criteria are valid for multicomponent systems.

System	Constraint	Equilibrium Criterion	Stability Criterion
Isolated, adiabatic, fixed boundary	Constant (U,V)	$S = \text{Max}$ $dS = 0$	$d^2S < 0$
Isothermal, closed, fixed boundary	Constant (T,V)	$A = \text{Min}$ $dA = 0$	$d^2A > 0$
Isothermal, isobaric, closed	Constant (T,P)	$G = \text{Min}$ $dG = 0$	$d^2G > 0$
Isothermal, isobaric, open moving with fluid velocity	Constant (T,P,m)	$G = \text{Min}$ $dG = 0$	$d^2G > 0$

Types of Equilibria and Equilibrium

- Three types of equilibria must be satisfied to have equilibrium established under all constraints
  - Thermal equilibrium

$$T^{I} = T^{II} = \cdots = T^{N}$$

  - Mechanical equilibrium

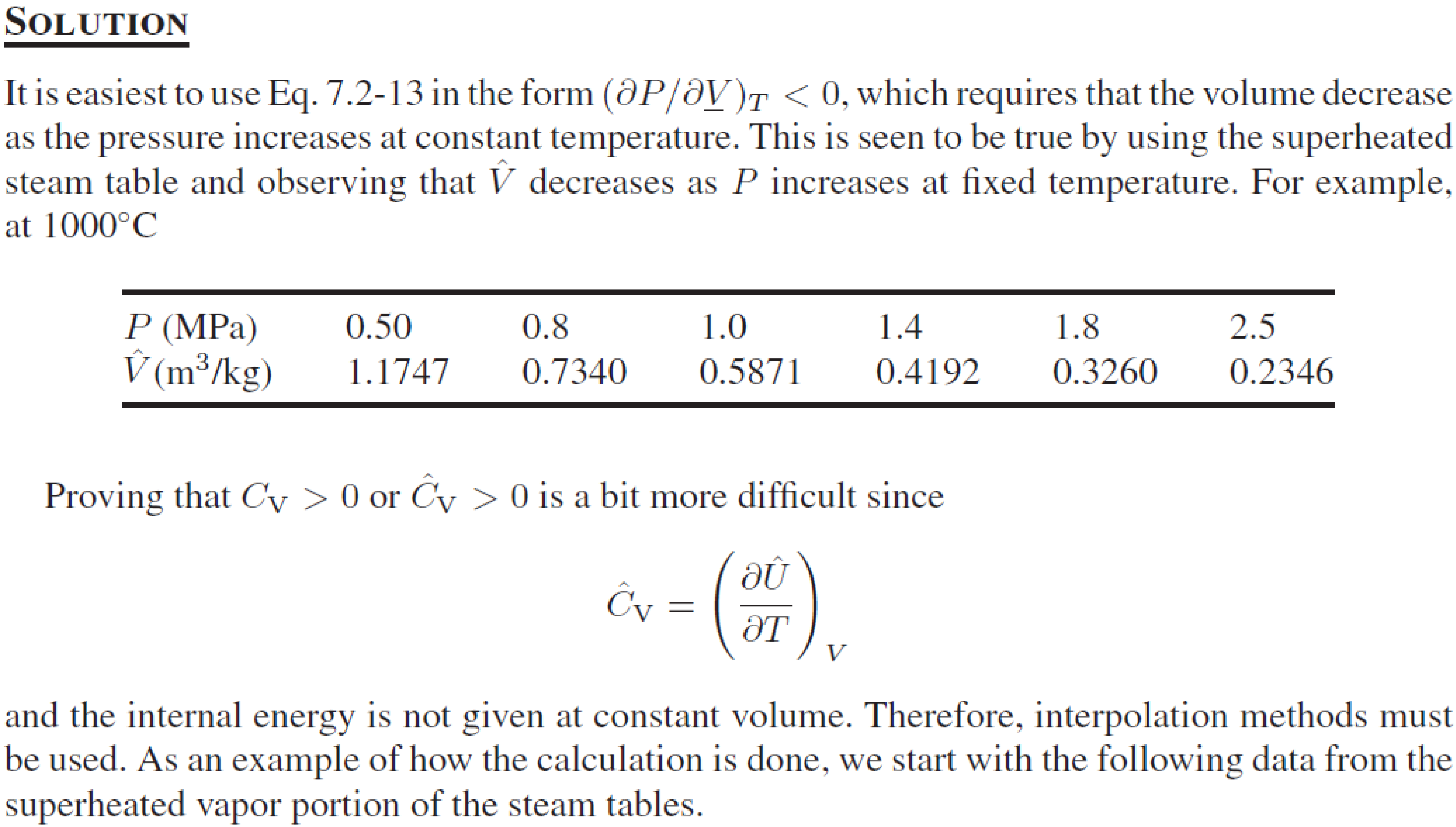
$$P^{I} = P^{II} = \cdots = P^{N}$$

  - Chemical equilibrium

$$g^{I} = g^{II} = \cdots = g^{N}$$

Illustration 7.2-1

Use Steam Tables to show that the stability conditions are satisfied for superheated steam.



SOLUTION

It is easiest to use Eq. 7.2-13 in the form $(\partial P/\partial \underline{V})_T < 0$, which requires that the volume decrease as the pressure increases at constant temperature. This is seen to be true by using the superheated steam table and observing that $\hat{V}$ decreases as P increases at fixed temperature. For example, at 1000°C

P (MPa)	0.50	0.8	1.0	1.4	1.8	2.5
$\hat{V}$ ($\mathrm{m^3/kg}$)	1.1747	0.7340	0.5871	0.4192	0.3260	0.2346

Proving that $C_V > 0$ or $\hat{C}_V > 0$ is a bit more difficult since

$$\hat{C}_V = \left(\frac{\partial \hat{U}}{\partial T}\right)_V$$

and the internal energy is not given at constant volume. Therefore, interpolation methods must be used. As an example of how the calculation is done, we start with the following data from the superheated vapor portion of the steam tables.

	$P = 1.80$ MPa		$P = 2.00$ MPa	
T (°C)	$\hat{V}$ (m^3/kg)	$\hat{U}$ (kJ/kg)	$\hat{V}$ (m^3/kg)	$\hat{U}$ (kJ/kg)
800	0.2742	3657.6	0.2467	3657.0
900	0.3001	3849.9	0.2700	3849.3
1000	0.3260	4048.5	0.2933	4048.0

To proceed, we need values of the internal energy at two different temperatures and the same specific volume. We will use $P = 2.00$ MPa and $T = 1000°\text{C}$ as one point; at these conditions $\hat{V} = 0.2933\ \text{m}^3/\text{kg}$ and $\hat{U} = 4048.0\ \text{kJ}/\text{kg}$. We now need to find the temperature at which $\hat{V} = 0.2933\ \text{m}^3/\text{kg}$ at $P = 1.80$ MPa. We use linear interpolation for this:

$$\frac{T - 800}{900 - 800} = \frac{\hat{V}(T, 1.80\ \text{MPa}) - \hat{V}(800°\text{C}, 1.80\ \text{MPa})}{\hat{V}(900°\text{C}, 1.80\ \text{MPa}) - \hat{V}(800°\text{C}, 1.80\ \text{MPa})} = \frac{0.2933 - 0.2742}{0.3001 - 0.2742}$$

so that $T = 873.75°\text{C}$. Next we need the internal energy $\hat{U}$ at $T = 873.75°\text{C}$ and $P = 1.80$ MPa (since at these conditions $\hat{V} = 0.2933\ \text{m}^3/\text{kg}$). Again using linear interpolation,

$$
\begin{aligned}
\frac{873.75-800}{900-800} &= \frac{\hat{U}(873.75^\circ\mathrm{C}, 1.80\ \mathrm{MPa}) - \hat{U}(800^\circ\mathrm{C}, 1.80\ \mathrm{MPa})}{\hat{U}(900^\circ\mathrm{C}, 1.80\ \mathrm{MPa}) - \hat{U}(800^\circ\mathrm{C}, 1.80\ \mathrm{MPa})} \\
&= \frac{\hat{U}(873.75^\circ\mathrm{C}, 1.80\ \mathrm{MPa}) - 3657.6}{3849.9 - 3657.6}
\end{aligned}
$$

we find that

$$\hat{U}(873.75^\circ\mathrm{C}, 1.80\ \mathrm{MPa}) = \hat{U}(873.75^\circ\mathrm{C}, 0.2933\ \mathrm{m}^3/\mathrm{kg}) = 3799.4\ \mathrm{kJ/kg}$$

Finally, replacing the derivative by a finite difference, and for the average temperature [i.e., $T = (1000 + 873.75)/2 = 936.9^\circ\mathrm{C}$], we have

$$
\begin{aligned}
&\hat{C}_\mathrm{V}(T = 936.9^\circ\mathrm{C}, \hat{V} = 0.2933\ \mathrm{m}^3/\mathrm{kg}) \\
&\qquad \approx \frac{\hat{U}(1000^\circ\mathrm{C}, 0.2933\ \mathrm{m}^3/\mathrm{kg}) - \hat{U}(873.75^\circ\mathrm{C}, 0.2933\ \mathrm{m}^3/\mathrm{kg})}{1000^\circ\mathrm{C} - 873.75^\circ\mathrm{C}} \\
&\qquad = \frac{4048.0 - 3799.4}{1000 - 873.75} = 1.969\ \frac{\mathrm{kJ}}{\mathrm{kg\ K}} > 0
\end{aligned}
$$

Similarly, we would find that $\hat{C}_\mathrm{V} > 0$ at all other conditions. ■

- This presentation is based in its majority on §7.1 and 7.2: Sandler, Stanley I. *Chemical, biochemical, and engineering thermodynamics*. John Wiley & Sons, 2017.