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Lecture 20: 11/1/07

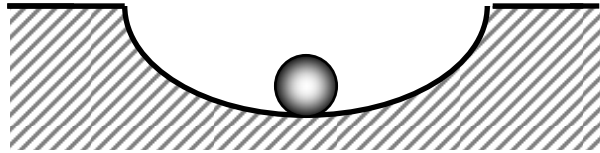
Introduction to Chemical  
Thermodynamics

# *Thermodynamic equilibrium*

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- Mechanical equilibrium
- Thermal equilibrium
- Chemical equilibrium

# Criterion for mechanical equilibrium



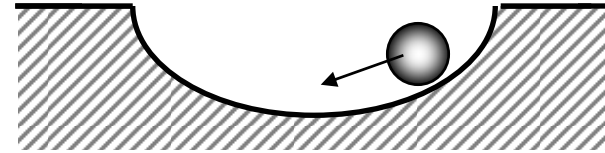
**Equilibrium**

**At equilibrium, PE is  
minimum**

$$d(PE) = 0$$

**On return to equilibrium**

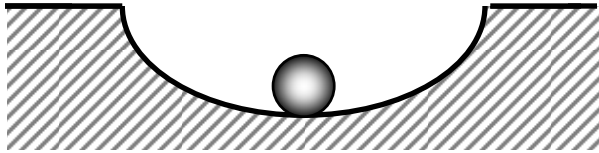
$$dPE < 0$$



**Approach to  
equilibrium**

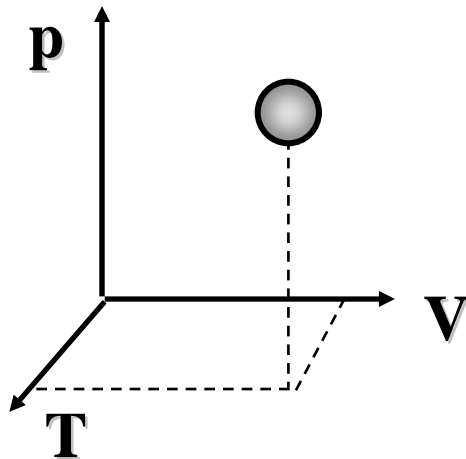
# *Stable equilibrium states*

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Mechanical Equilibrium

The equilibrium state is characterized by the minimization of the Potential Energy function.



Thermodynamic Equilibrium

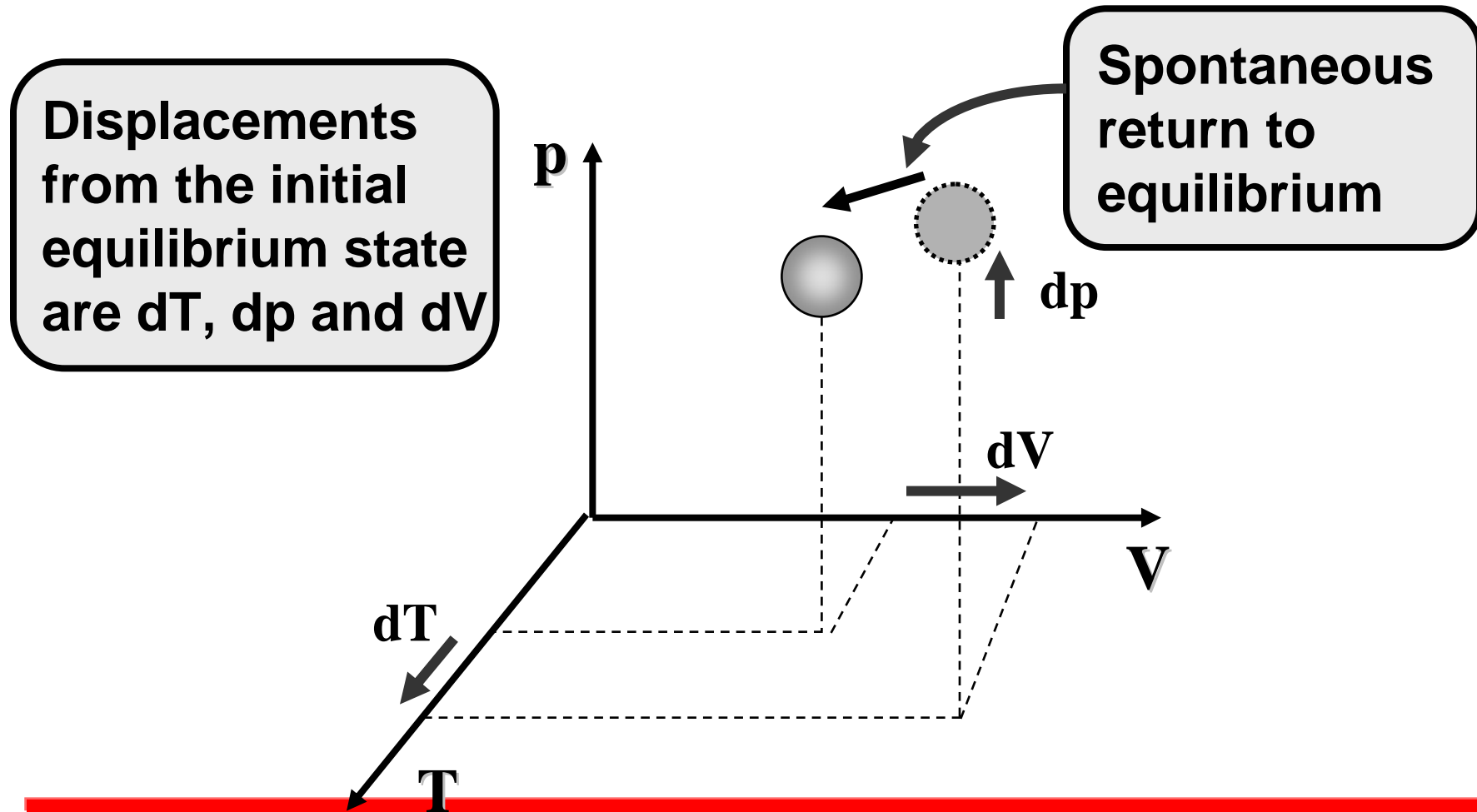
Thermodynamic equilibrium is likewise characterized by the minimization of a thermodynamic potential in approximately the same manner as with the gravitational potential.

# *Thermodynamic equilibrium*

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- Does the system have the ability for spontaneous change of state?
- When displaced from equilibrium, which way will changes occur thereafter?
- A state of equilibrium will have existed if the spontaneous tendency is for a return to the original equilibrium state.

# *The general criteria for thermodynamic equilibrium*



# *Types of displacements from equilibrium*

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- Constant volume,  $dV = 0$ , and constant temperature,  $dT = 0$
- Constant pressure,  $dP = 0$ , and constant temperature,  $dT = 0$

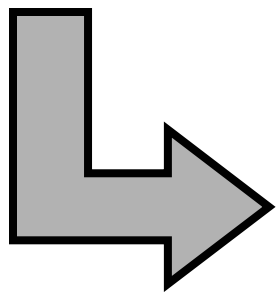
# *Constant volume and temperature*

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*displacements ( $dT = dV = 0$ )*

$$dU = \delta Q$$

$$dS = \frac{\delta Q}{T} + \sigma$$



$$dS = \frac{dU}{T} + \sigma$$

$$T\sigma = -d(U - TS)$$

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*Constant temperature and volume  
displacements ( $dT = dV = 0$ )*

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$$T \sigma = -d(U - TS)$$

**F = U-TS is the Helmholtz function.**

$$T \sigma = -dF$$

# *Constant temperature and volume displacements ( $dT = dV = 0$ )*

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**When T, V are constant during the displacement from equilibrium,**

$$-dF = T\sigma > 0$$

**T is fixed, and  
 $T > 0$  always**

**Entropy production,  
 $\sigma > 0$  always**

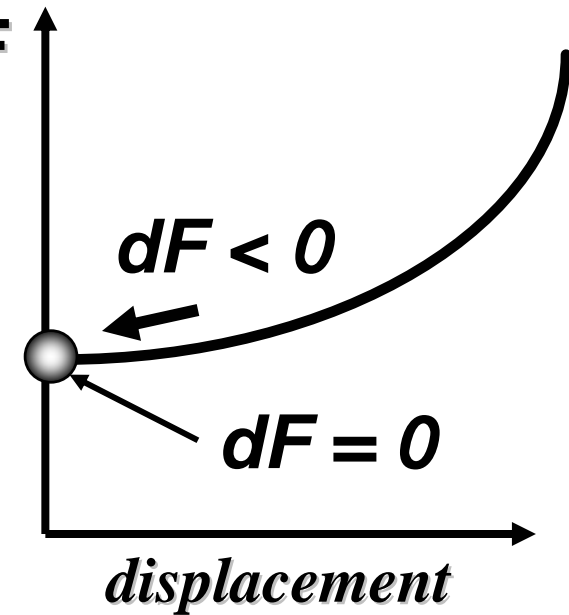
**Thus, on return to equilibrium  $dF < 0$ .**

# *The Helmholtz criterion for equilibrium*

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When  $dV = 0$  and  $dT = 0$ ,  
and  $dF < 0$ .

Thus, at equilibrium  
 **$dF = 0$**



***F is a minimum at equilibrium.***

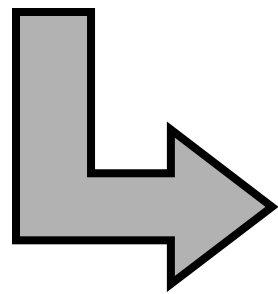
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# Constant temperature and pressure

*displacements* ( $dT = dp = 0$ )

$$dU = \delta Q - \delta W$$

$$dS = \frac{\delta Q}{T} + \sigma$$



$$dU = \delta Q - d(PV)$$

$$TdS = \delta Q + T\sigma$$

*Constant temperature and pressure  
displacements ( $dT = dp = 0$ )*

$$dU + d(PV) - Tds = -T\sigma < 0$$

$$d(U + PV - Ts) < 0$$

**G = H-TS is the Gibbs function.**

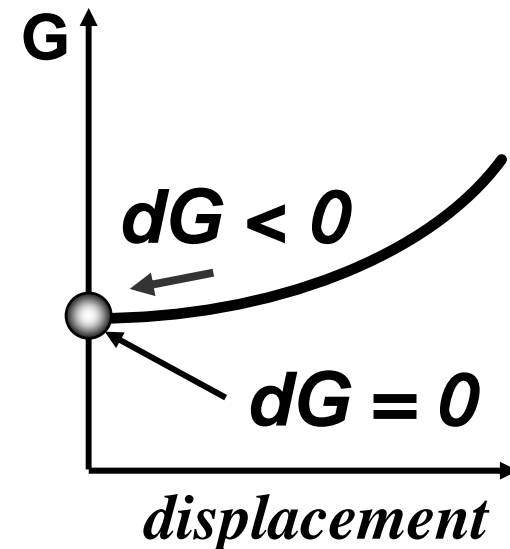
$$dG < 0$$

# The Gibbs criterion for equilibrium

When  $dp = 0$  and  $dT = 0$ ,  
and  $dG < 0$ ,

At equilibrium

$$dG = 0$$



**G is a minimum at equilibrium.**

# *The Gibbs Function*

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$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$dH = Tds + Vdp$$

$$dG = Vdp - SdT$$

**For a reversible, isothermal, isobaric process  
(T = Constant, p = Constant)**

$$\mathbf{dG = 0, G = Minimum}$$

# *Isolated system $dU=0$ , $dV=0$*

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- Consider an isolated system with  $dU=0$  and  $dV=0$
- If we consider a system that only performs PV work on its surroundings, we can write for any quasi-static (constantly in equilibrium) process:

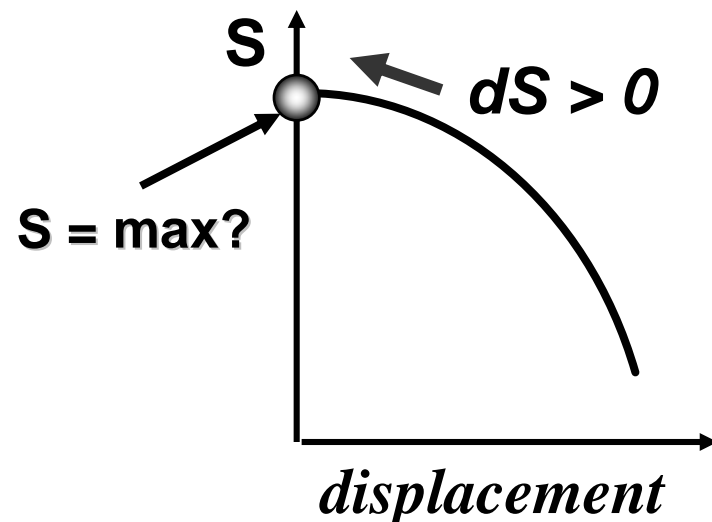
$$dS = \frac{dU}{T} + \frac{pdV}{T}$$

- Therefore, at equilibrium the entropy must be a maximum or a minimum:

$$dS = 0$$

# Entropy maximum principle

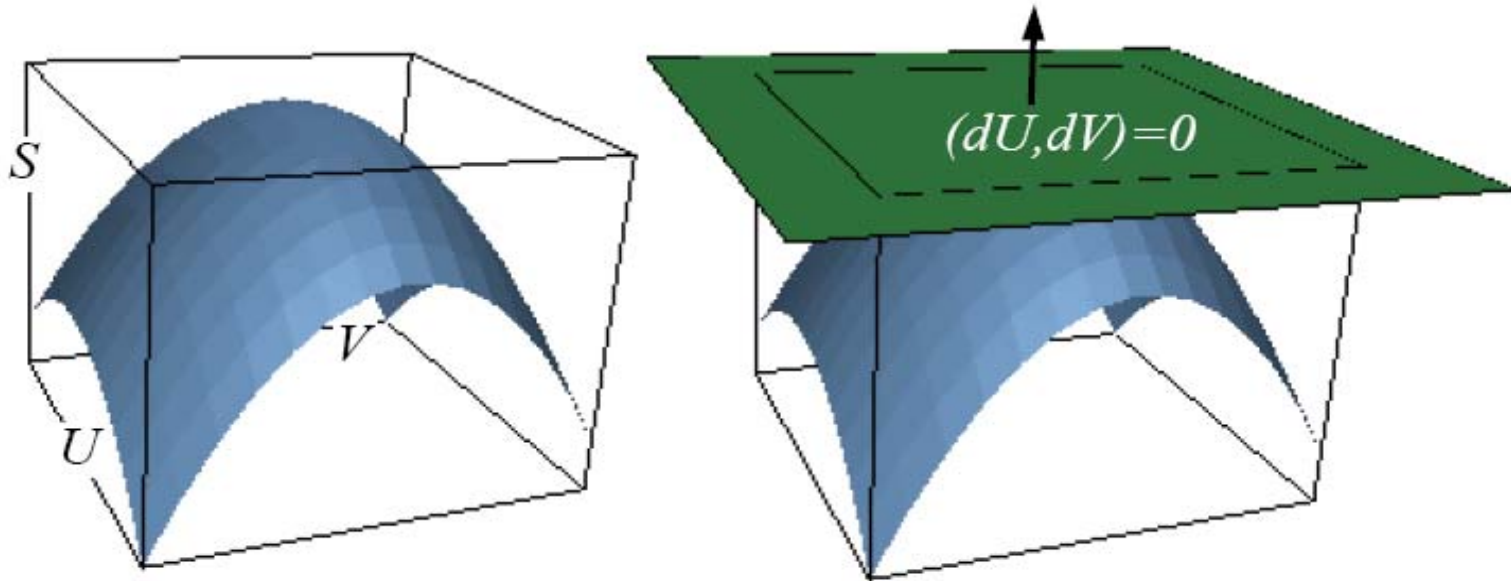
The equilibrium value of any unconstrained internal parameter is such as to maximize the entropy of the system for a given value of total internal energy.



$dS > 0$  on return to equilibrium  
 $dS = 0$  at equilibrium  
 $U = \text{Constant}$

# *Unconstrained equilibrium: maximum $S$*

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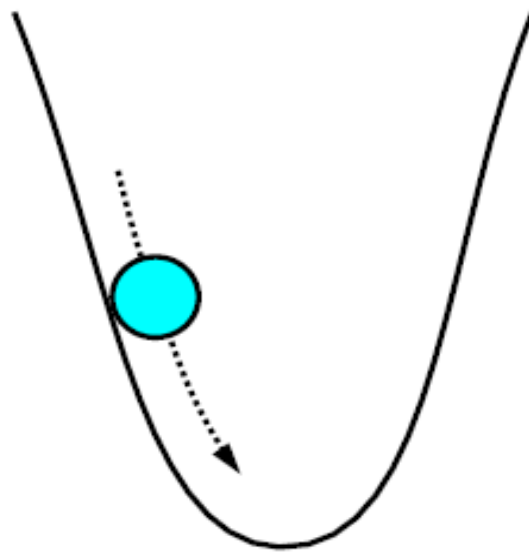


- Since entropy must always increase as a system approaches equilibrium, it must be maximum at equilibrium. On return to equilibrium:

$$dS \big|_{dU=0, dV=0} \geq 0$$

# *Unconstrained equilibrium: minimum U*

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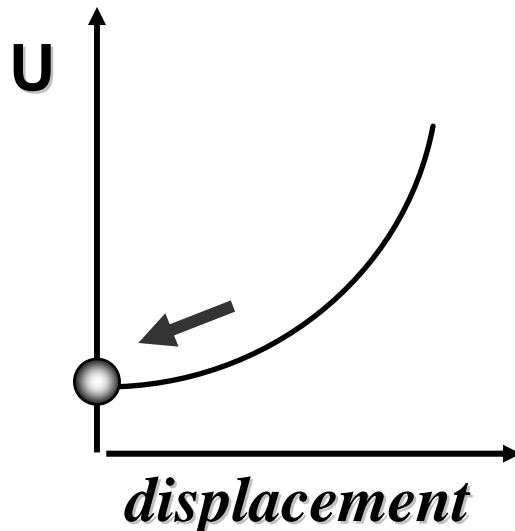


- Equilibrium can also be stated as follows:  $U$  is minimum at constant  $S$  and  $V$ . On return to equilibrium:

$$dU \Big|_{dS=0, dV=0} \leq 0$$

# The Energy minimum principle

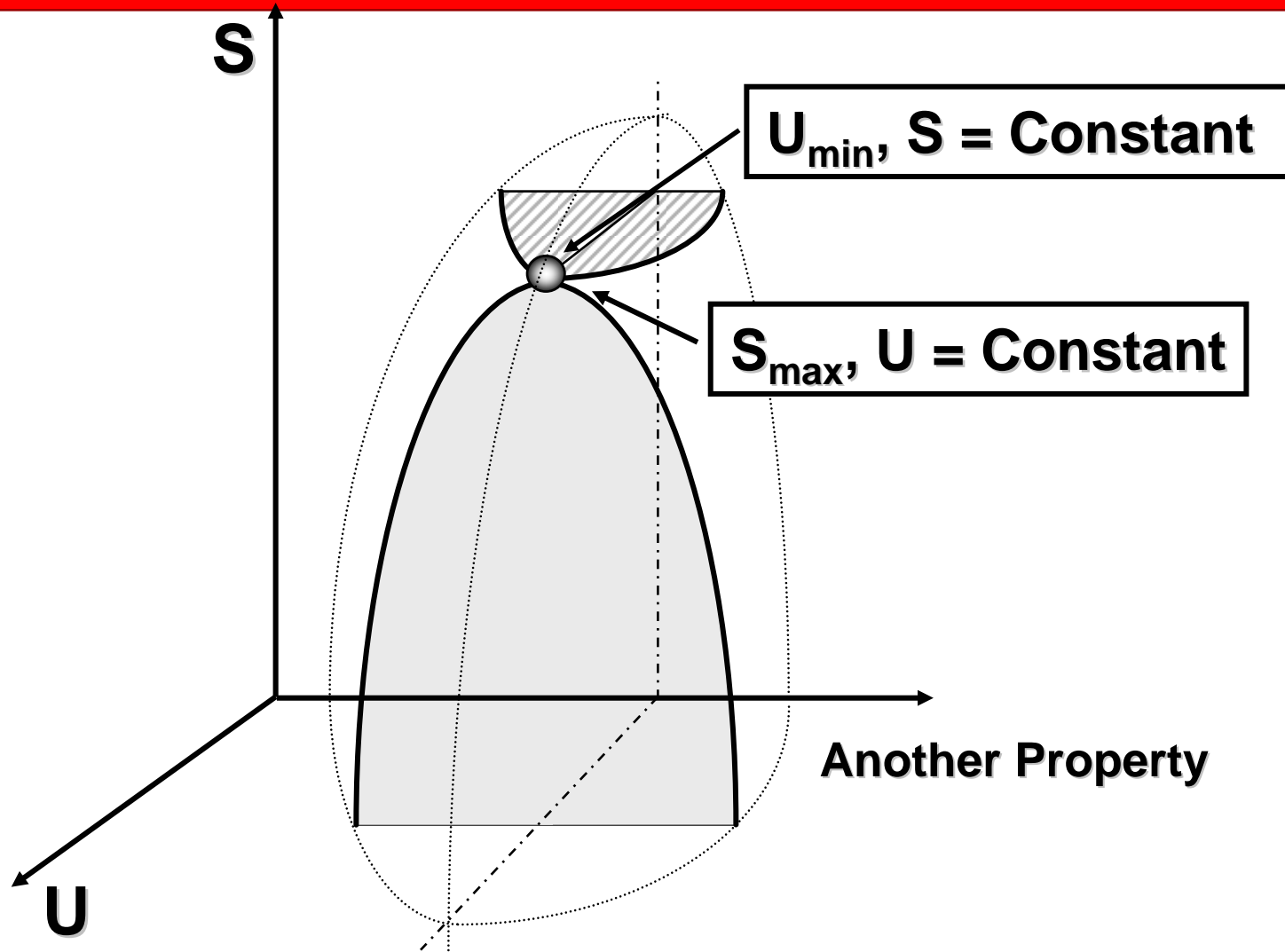
The equilibrium value of any unconstrained internal parameter is such as to minimize the energy for the given value of total entropy.



$dU < 0$  on return to equilibrium  
 $dU = 0$  at equilibrium  
 $S = \text{Constant}$

# *Energy and entropy principles*

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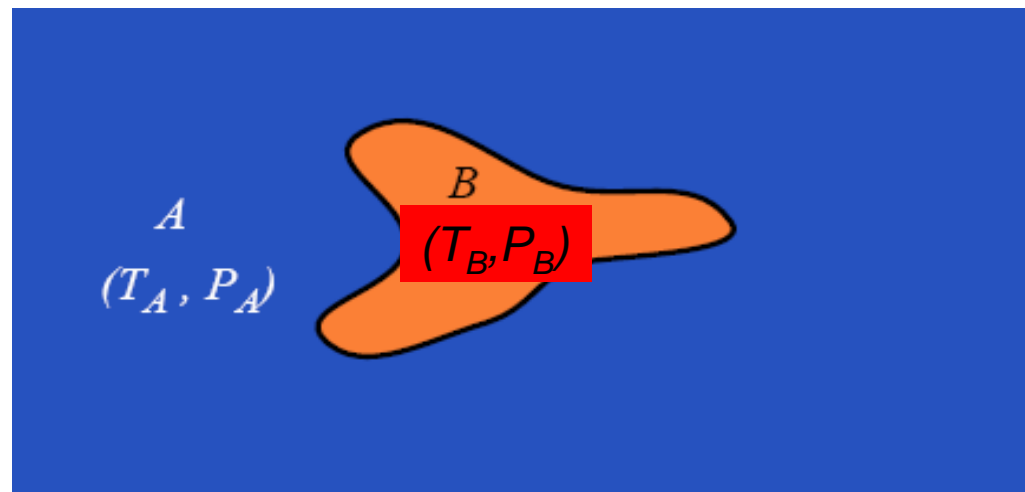


# *An example of an isolated system:*

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$$dU=0, dV=0$$

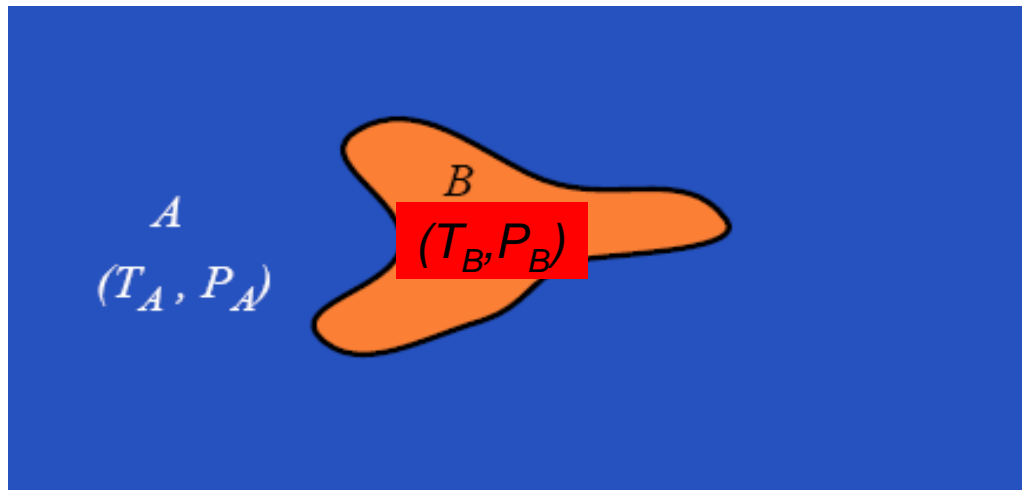
- Consider an isolated system with two separated regions at uniform (but potentially different pressures and temperatures)



# *Isolated system: $dU=0, dV=0$*

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- Suppose that there is a virtual change, i.e. any one of an infinite number of possible changes in the system such that  $\delta U=0$  and  $\delta V=0$ .

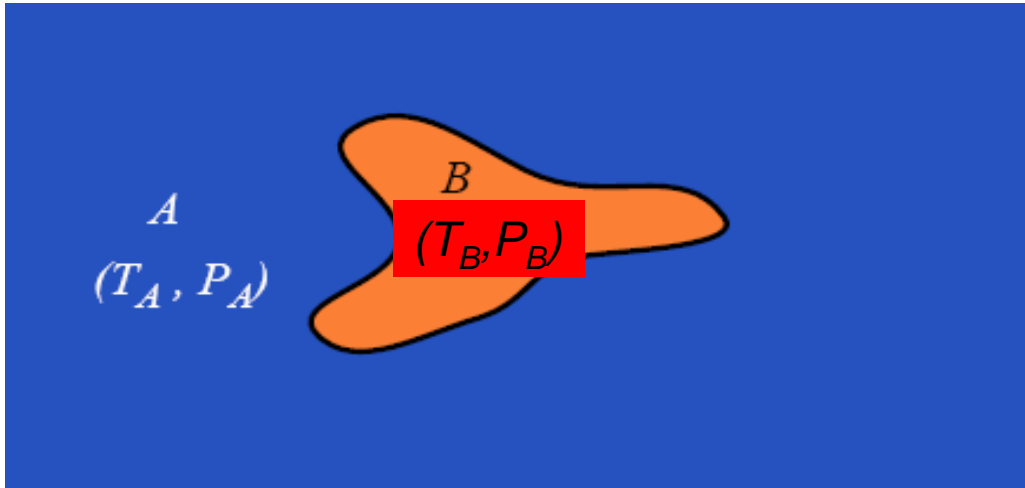


$$\delta U_A = -\delta U_B$$

$$\delta V_A = -\delta V_B$$

# Isolated system: $dU=0, dV=0$

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$$\delta U_A = -\delta U_B$$

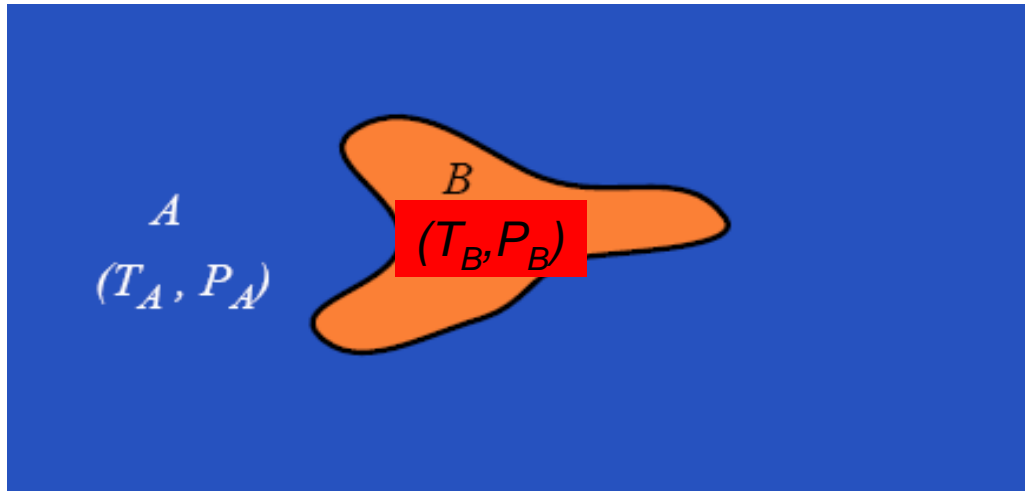
$$\delta V_A = -\delta V_B$$

- Then we can write:

$$\begin{aligned}\delta S^{\text{total}} &= \delta S_A + \delta S_B \\ &= \frac{1}{T_A}(\delta U_A + P_A \delta V_A) + \frac{1}{T_B}(\delta U_B + P_B \delta V_B) \\ &= \left(\frac{1}{T_A} - \frac{1}{T_B}\right) \delta U_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right) \delta V_A\end{aligned}$$

# Isolated system: $dU=0, dV=0$

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$$\delta U_A = -\delta U_B$$

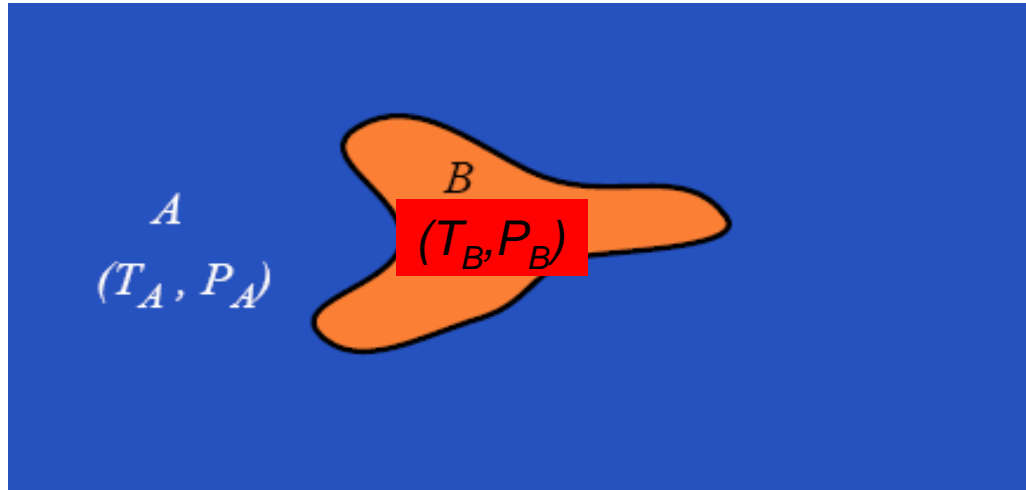
$$\delta V_A = -\delta V_B$$

$$\delta S^{\text{total}} = \left( \frac{1}{T_A} - \frac{1}{T_B} \right) \delta U_A + \left( \frac{P_A}{T_A} - \frac{P_B}{T_B} \right) \delta V_A$$

- Since  $\delta U_A$  is independent of  $\delta V_A$ , we can find a  $\delta S_{\text{total}} > 0$  unless:

# Isolated system: $dU=0, dV=0$

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$$\delta U_A = -\delta U_B$$

$$\delta V_A = -\delta V_B$$

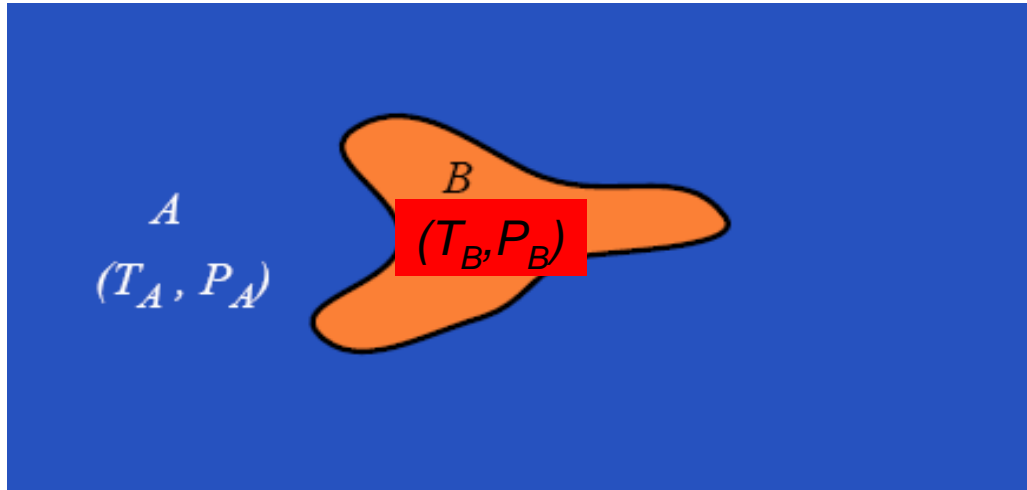
$$\delta S^{\text{total}} = \left( \frac{1}{T_A} - \frac{1}{T_B} \right) \delta U_A + \left( \frac{P_A}{T_A} - \frac{P_B}{T_B} \right) \delta V_A$$

$$\left( \frac{1}{T_A} - \frac{1}{T_B} \right) = 0 \implies T_A = T_B$$

$$\left( \frac{P_A}{T_A} - \frac{P_B}{T_B} \right) = 0 \implies P_A = P_B$$

# *Isolated system: $dU=0, dV=0$*

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$$T_A = T_B$$

$$P_A = P_B$$

No variation in pressure can exist if the volume can move from region to region ( $\delta V$ ) and no spatial variation in temperature can exist if energy can flow from region to region ( $\delta U$ ).

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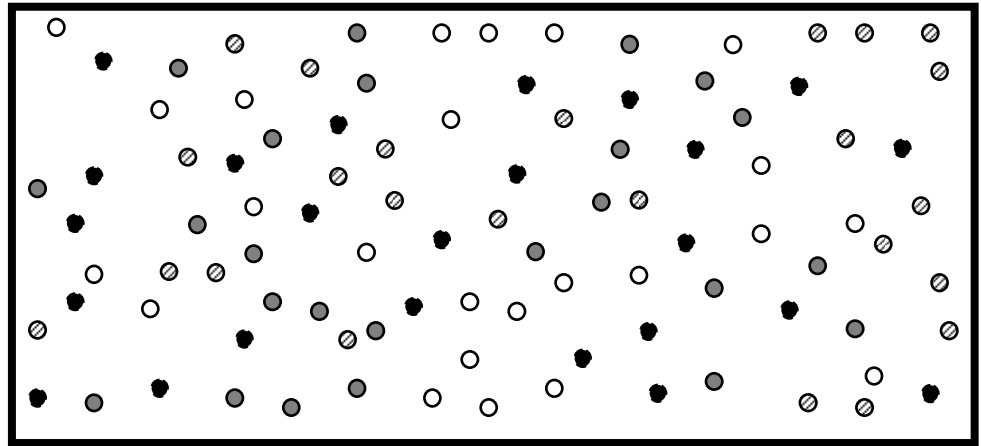
*Introduction to mixture  
properties...the molal  
basis*

# Generalized mixture properties

Assume a single phase, multi-component mixture.

The mixture comprises several gases.

Each extensive property,  $X$ , is given as:

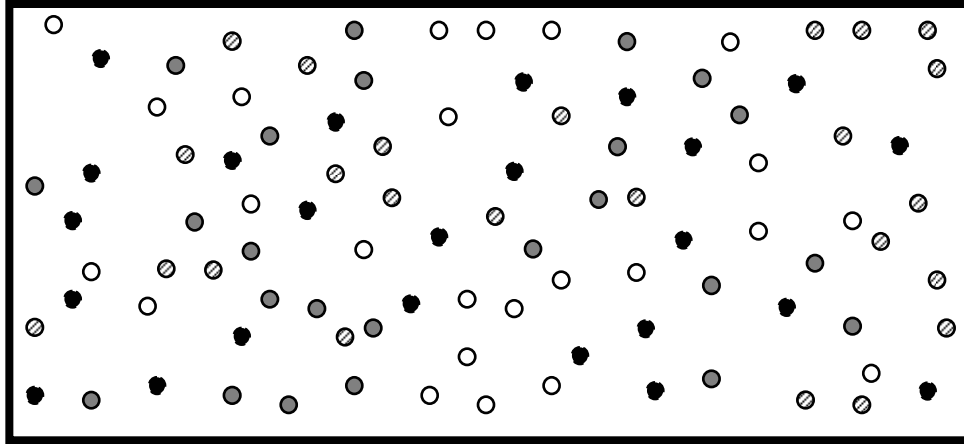


Gas Mixture:  $n_1 + n_2 + n_3 + \dots + n_N = n_{\text{Total}}$

$$X = X(p, T, n_1, n_2, \dots, n_N)$$

# *Generalized mixing rules*

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**Gas Mixture:**  $n_1+n_2+n_3+\dots+n_N = n_{\text{Total}}$

Increase each component,  $n_i$ , by the same amount, say  $\alpha$ . Then:

$$\alpha X = X(p, T, \alpha n_1, \alpha n_2, \dots, \alpha n_N)$$

# Partial molal quantities

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$$\alpha X = X(p, T, \alpha n_1, \alpha n_2, \dots, \alpha n_N)$$

Differentiate with respect to  $\alpha$ :

$$\left( \frac{\partial \alpha X}{\partial \alpha} \right)_{P, T, n_i} = \sum_{i=1}^N \left( \frac{\partial X}{\partial (\alpha n)} \right)_{i, P, T, n_k} \left( \frac{d(\alpha n_i)}{d\alpha} \right)_{n_k}$$

# Partial molal quantities

---

Set  $\alpha = 1$

$$X = \sum_{i=1}^N n_i \left( \frac{\partial X}{\partial n_i} \right)_{p, T, n_k}$$

Define the partial molal property:

$$\left( \frac{\partial X}{\partial n_i} \right)_{p, T, n_k} = \tilde{X}_i$$

# Properties of multi-component mixtures

Thus, in terms of partial molal properties:

$$X = \sum_{i=1}^N n_i \tilde{X}_i$$

The property  $X$  can be chosen as any extensive property, such as,  $U$ ,  $H$ ,  $V$ , and  $S$ .

# Properties of multi-component mixtures

$$X = \sum_{i=1}^N n_i \tilde{X}_i \left\{ \begin{array}{l} S = \sum_{i=1}^N n_i \tilde{S}_i \\ H = \sum_{i=1}^N n_i \tilde{H}_i \\ U = \sum_{i=1}^N n_i \tilde{U}_i \end{array} \right.$$