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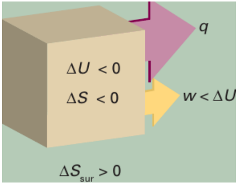

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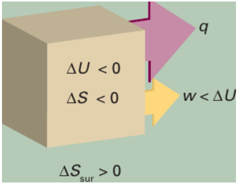

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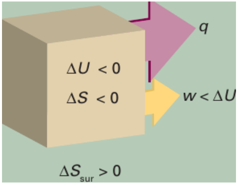

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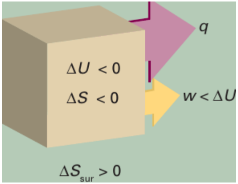

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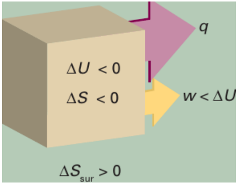

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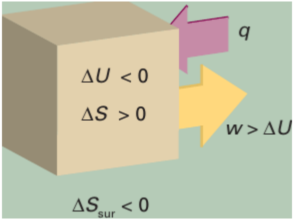

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$\Delta_r U^{\ominus} = -2808$ kJ mol^{-1} and $\Delta_r S^{\ominus} = 259.1$ J K^{-1}mol^{-1}

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max work $=2885$ kJ mol$^{-1} > |\Delta_r U^\ominus| \quad \because \Delta_r S^\ominus > 0$

system can draw in energy from the surroundings (reducing their entropy) and make it available for work

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$$\Delta_r G^\ominus = \sum_{\text{products}} \nu \Delta_f G^\ominus - \sum_{\text{reactants}} \nu \Delta_f G^\ominus$$

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$\therefore \Delta_f G^\ominus$ (Cl^-,aq)$= -131.23$kJ mol^{-1}

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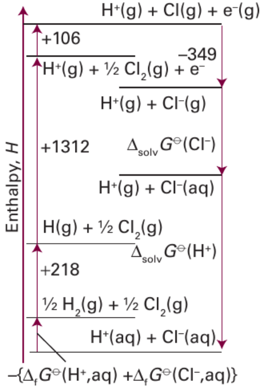
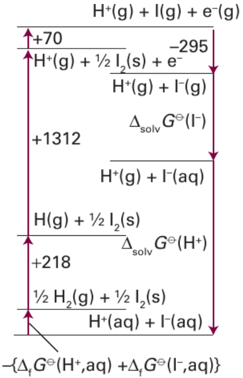
thermodynamic cycle:
solvation of (a) chloride and (b) iodide ions:



$\Delta_f G^\ominus$ of an ion X is not determined by properties of X alone but includes contributions from dissociation, ionization, and hydration of hydrogen



Gibbs energy of solvation of individual ions

$$\Delta_f G^\ominus(\mathrm{Cl}^-,\ \mathrm{aq}) = 1287\mathrm{kJ\ mol}^{-1} + \Delta_{\mathrm{solv}} G^\ominus(\mathrm{H}^+) + \Delta_{\mathrm{solv}} G^\ominus(\mathrm{Cl}^-)$$

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$$= -\frac{z_i^2 e^2}{8\pi\varepsilon_0 r_i}\left(1 - \frac{1}{\varepsilon_r}\right)$$

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Ex. : $\Delta_{\text{solv}} G^{\ominus}\ (\text{Cl}^{-1}) - \Delta_{\text{solv}} G^{\ominus}\ (\text{I}^{-1})$

$$= -\left(\frac{1}{181} - \frac{1}{220}\right) \times \left(6.86 \times 10^4 \text{kJmol}^{-1}\right) = -67 \text{kJmol}^{-1}$$

Chemical potential : $\mu = \left(\frac{\partial G}{\partial n_i}\right)_{p,\, T\ n_j,\, j \neq i}$

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For irreversible processes, $dS > \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN$

analysis of one-component, two-phase isolated system :
definition of an isolated system : the following must be constant

1. internal energy, U
2. total volume, V
3. total no. of moles, N

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and

$$dS = dS^{(1)} + dS^{(2)} = \frac{1}{T^{(1)}}dU^{(1)} + \frac{1}{T^{(2)}}dU^{(2)} + \frac{p^{(1)}}{T^{(1)}}dV^{(1)} + \frac{p^{(2)}}{T^{(2)}}dV^{(2)} - \frac{\mu^{(1)}}{T^{(1)}}dN^{(1)} - \frac{\mu^{(2)}}{T^{(2)}}dN^{(2)}$$

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2. thermal equilibrium, flexible, impermeable, diathermal wall
$$\Longrightarrow \ T^{(1)} = T^{(2)} \text{ and } dN^{(1)} = dN^{(2)} = 0$$

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2. thermal equilibrium, flexible, impermeable, diathermal wall
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3. thermal and mechanical equilibrium, flexible, permeable, diathermal wall
$$\Longrightarrow \; T^{(1)} = T^{(2)} \text{ and } p^{(1)} = p^{(2)}$$

impermeable, rigid, diathermal wall $\Longrightarrow$ $\begin{array}{l} dV^{(1)} = dV^{(2)} = 0 \\ dN^{(1)} = dN^{(2)} = 0 \end{array}$

impermeable, rigid, diathermal wall $\implies$ $\begin{array}{l} dV^{(1)} = dV^{(2)} = 0 \\ dN^{(1)} = dN^{(2)} = 0 \end{array}$

$\because dU^{(1)} + dU^{(2)} = 0 \quad \implies dU^{(1)} = -dU^{(2)} = dU$ (say) impermeable, rigid, diathermal wall $\Longrightarrow$ $\begin{array}{l} dV^{(1)} = dV^{(2)} = 0 \\ dN^{(1)} = dN^{(2)} = 0 \end{array}$

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$\therefore dS = \frac{1}{T^{(1)}} dU - \frac{1}{T^{(2)}} dU = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) dU > 0$

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if $dU > 0$ (flow of energy from phase 2 to phase 1),

then $T^{(1)} < T^{(2)}$, i.e. energy must flow from higher to lower temperature for thermal equilibrium to be reached

At $T^{(1)} = T^{(2)}$ (thermal equilibrium), $dS = 0$

Since there is no work involved, the energy here is heat

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if $dV > 0$ (wall moves away from phase 1 to phase 2),

then $p^{(1)} > p^{(2)}$, i.e. mechanical equilibrium requires movement of the wall from higher pressure to lower pressure region

When $p^{(1)} = p^{(2)}$ (mechanical equilibrium), $dS = 0$

thermal and mechanical equilibrium, flexible, permeable, diathermal wall

$$\Longrightarrow \quad \begin{array}{c} T^{(1)} = T^{(2)} \\ p^{(1)} = p^{(2)} \end{array}$$

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if $dN > 0$ (mass moves from phase 2 to phase 1)

then $\mu^{(2)} > \mu^{(1)}$, i.e., mass moves spontaneously
from higher to lower chemical potentials

When $\mu^{(1)} = \mu^{(2)}$ (chemical equilibrium), $dS = 0$