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Standard reaction entropy : $\Delta_r S^\ominus = \sum_{\text{products}} \nu S_m^\ominus - \sum_{\text{reactants}} \nu S_m^\ominus$

$\Delta_r S^\ominus$ is likely to be > 0 if there is a net formation of gas in a reaction, and < 0 if there is a net consumption of gas

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so we need better criteria for spontaneity that depend only on the system

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and ignoring extra non-mechanical work

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Legendre transform : changing the natural variables :

$$y(x) = mx + c; \quad c(m) = -xm + y; \quad m = \frac{dy}{dx}$$

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Try with $U \equiv U(S, V); \quad \left(\frac{\partial U}{\partial S}\right)_V T, \quad \therefore \text{Legendre transform,}$

$$f = -S \left(\frac{\partial U}{\partial S}\right)_V + U = U - TS$$

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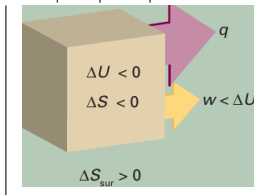
the **most negative value of dw** , and therefore the max. energy that can be obtained from system as work, is

$$dw_{\max} = dU - TdS; \quad \text{equality} \implies \text{reversible process}$$

$$\text{At const. } T, \quad dw_{\max} = dA; \quad \Delta A = \Delta U - T\Delta S$$

if $\Delta S < 0$, then RHS is not as negative as ΔU , $\therefore |w_{\max}| < |\Delta U|$

some energy must escape as heat
to generate enough entropy in surroundings
to overcome reduction in entropy in the system



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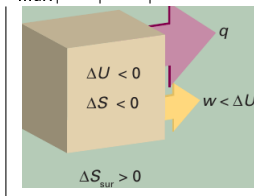
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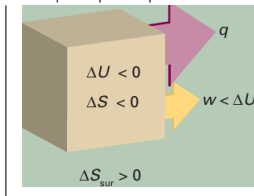
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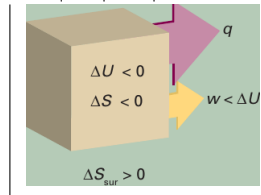
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$T \times S$ = energy stored as thermal motion, unavailable part of U for work

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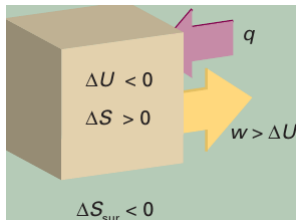
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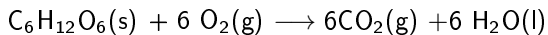
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Nature is providing a tax refund



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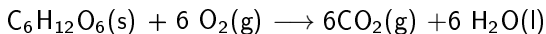


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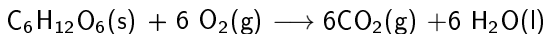


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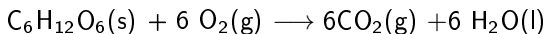
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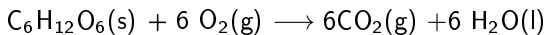
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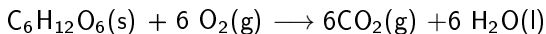
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system can draw in energy from the surroundings (reducing their entropy) and make it available for work

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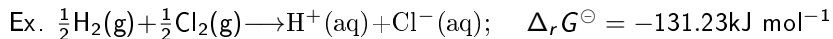
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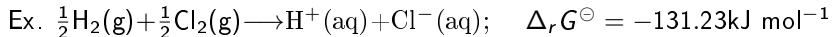
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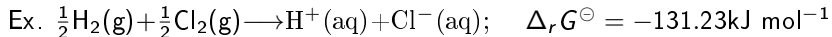
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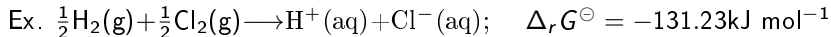


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With $\therefore \Delta_f G^\ominus(\text{Cl}^-, \text{aq})$ known, we can find $\Delta_f G^\ominus$ for other ions

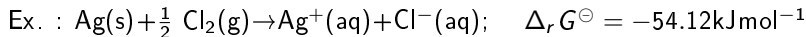
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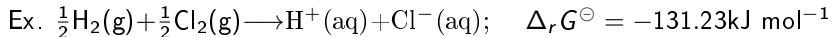
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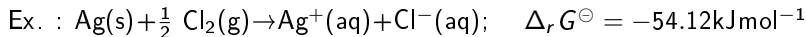
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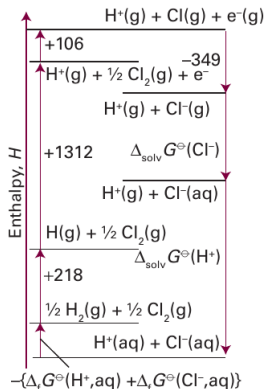
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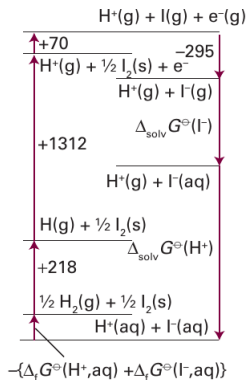
$$\Delta_f G^\ominus(\text{Ag}^+, \text{aq}) = -54.12 + 131.23 = 77.11 \text{ kJ mol}^{-1}$$

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

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

Born equation :

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$\Delta_{\text{sol}} G^{\ominus}$ = work of transferring an ion from a vacuum into solvent

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

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

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 mass of the one component, N (no. of moles)

1	2
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and

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

Let us consider three different cases for the wall between the phases :

1. impermeable, rigid, diathermal wall $\implies dV^{(1)} = dV^{(2)} = 0$ and $dN^{(1)} = dN^{(2)} = 0$
2. thermal equilibrium, flexible, impermeable, diathermal wall $\implies T^{(1)} = T^{(2)}$ and $dN^{(1)} = dN^{(2)} = 0$
3. thermal and mechanical equilibrium, flexible, permeable, diathermal wall $\implies T^{(1)} = T^{(2)}$ and $p^{(1)} = p^{(2)}$

impermeable, rigid, diathermal wall \Rightarrow

$$\begin{aligned} dV^{(1)} &= dV^{(2)} = 0 \\ dN^{(1)} &= dN^{(2)} = 0 \end{aligned}$$

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

$\therefore dU^{(1)} + dU^{(2)} = 0 \implies dU^{(1)} = -dU^{(2)} = dU$ (say)

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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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thermal equilibrium, flexible, impermeable, diathermal wall \Rightarrow $T^{(1)} = T^{(2)} = T$
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$$\therefore dS = \frac{p^{(1)}}{T} dV - \frac{p^{(2)}}{T} dV = \frac{1}{T} (p^{(1)} - p^{(2)}) dV > 0$$

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$$\therefore dS = \frac{p^{(1)}}{T} dV - \frac{p^{(2)}}{T} dV = \frac{1}{T} (p^{(1)} - p^{(2)}) dV > 0$$

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

$$\Rightarrow \begin{array}{l} T^{(1)} = T^{(2)} \\ p^{(1)} = p^{(2)} \end{array}$$

thermal and mechanical equilibrium, flexible, permeable, diathermal wall

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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), $dS = 0$

