# Focus 3: The Second and Third Laws

- Entropy
- Entropy changes in processes
- Entropy measurement
- Free energy
- Combining 1<sup>st</sup> and 2<sup>nd</sup> laws

 $dS \ge dq/T$ 

Clausius inequality and criteria for spontaneity





entropy change for a reversible process

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Helmholtz energy, A,

A = U - TS

Gibbs energy, G:

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at constant T

dA = dU - TdS

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at constant T dG = dH - TdS

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$$dA = dW_{rev}$$

at constant T and V:

 $dA = dW_{add, max}$ 

If the volume is constant (dV=0), then the work is nonexpansion work only. (e.g., electrical, surface tension, chemical work)

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At constant T and V, the  $\Delta A$  gives the maximum work the system can perform in a reversible process.

This is why Helmholtz free energy is particularly useful for systems where volume does not change (e.g., electrochemical cells, surface reactions, and magnetic systems), where nonexpansion work is the primary focus.

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at constant T and P:

$$dw_{add,max} = dG$$

Maximum non-expansion work [constant *T*, *p*]

$$\Delta_{\rm r}G^{\rm e} = \Delta_{\rm r}H^{\rm e} - T\Delta_{\rm r}S^{\rm e}$$

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How much energy is available for sustaining muscular and nervous activity from the oxidation of 1.00 mol of glucose molecules under standard conditions at  $37 \,^{\circ}$ C (blood temperature)? The standard entropy of reaction is +182.4 J K<sup>-1</sup> mol<sup>-1</sup>.

## At 25 <sup>O</sup>C $\Delta_r H^{\ominus} := -2808 \text{ kJ mol}^{-1}$

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The reaction can be used to do up to 2865 kJ of non-expansion work

## Gibbs energy of formation

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	$\Delta_{\rm f} G^{\Theta} / ({\rm kJ  mol^{-1}})$
Diamond, C(s)	+2.9
Benzene, $C_6H_6(l)$	+124.3
Methane, $CH_4(g)$	-50.7
Carbon dioxide, $CO_2(g)$	-394.4
Water, $H_2O(l)$	-237.1
Ammonia, $NH_3(g)$	-16.5
Sodium chloride, NaCl(s)	-384.1

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Standard reaction Gibbs energy of formation of a compound from its elements in their reference state

	$\Delta_{\rm f} G^{\Theta}/({\rm kJmol^{-1}})$	$\Lambda G^{\ominus} = \sum v \Lambda G^{\ominus} - \sum v \Lambda G^{\ominus}$
Diamond, C(s)	+2.9	$\Delta_{\rm r} {\bf O} = \sum_{\rm Products} V \Delta_{\rm f} {\bf O} \qquad \sum_{\rm Reactants} V \Delta_{\rm f} {\bf O}$
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## Example

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$$\Delta_{\mathbf{r}}G^{\ominus} = \Delta_{\mathbf{f}}G^{\ominus}(\mathbf{CO}_{2},\mathbf{g}) - \{\Delta_{\mathbf{f}}G^{\ominus}(\mathbf{CO},\mathbf{g}) + \frac{1}{2}\Delta_{\mathbf{f}}G^{\ominus}(\mathbf{O}_{2},\mathbf{g})\}$$

$$= -394.4 \text{ kJ mol}^{-1} - \{(-137.2) + \frac{1}{2}(0)\} \text{ kJ mol}^{-1}$$

 $= -257.2 \,\mathrm{kJ}\,\mathrm{mol}^{-1}$ 

 $\Delta_{\rm f}G^{\ominus}({\rm H}^+,{\rm aq})=0$ 

 $\Delta_{\rm f}G^{\oplus}({\rm H}^+,{\rm aq})=0$ 

 $\frac{1}{2} \operatorname{H}_{2}(g) + \frac{1}{2} \operatorname{Cl}_{2}(g) \to \operatorname{H}^{+}(aq) + \operatorname{Cl}^{-}(aq)$ 

If the Gibbs free energy of the reaction is -120 kJ mol<sup>-1</sup>, what is the Gibbs free energy of the formation of Cl<sup>-</sup>(aq)?

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The standard Gibbs free energy of formation  $(\Delta G_f)$  of an element in its reference state is defined as zero by convention.

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$$\begin{split} \Delta_{\mathbf{r}} G^{\oplus} &= -120 \text{ kJ mol}^{-1} \\ &= \Delta_{\mathbf{f}} G^{\oplus} (\mathbf{H}^{+}, \mathbf{aq}) + \Delta_{\mathbf{f}} G^{\oplus} (\mathbf{Cl}^{-}, \mathbf{aq}) \\ \Delta_{\mathbf{r}} G^{\oplus} &= \Delta_{\mathbf{f}} G^{\oplus} (\mathbf{Cl}^{-}, \mathbf{aq}) \end{split}$$



$$\Delta_{\rm solv}G^{\ominus} = -\frac{z_{\rm i}^2 e^2 N_{\rm A}}{8\pi\varepsilon_0 r_{\rm i}} \left(1 - \frac{1}{\varepsilon_{\rm r}}\right)$$









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 $\mathcal{E}_{0:}$  8.854 x 10<sup>-12</sup> F/m (farad per meter)



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$$\Delta_{\rm solv} G^{\oplus}({\rm Cl}^{-}) - \Delta_{\rm solv} G^{\oplus}({\rm I}^{-}) = -\left(\frac{1}{181} - \frac{1}{220}\right) \times 6.86 \times 10^4 \, \rm kJ \, mol^{-1}$$
$$= -67 \, \rm kJ \, mol^{-1}$$

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