

## Summary

$$\Delta G = \Delta H - T\Delta S$$

- For a closed system at constant  $T$  and  $P$ , change of  $H$  inside system equals opposite of change in  $TS$  outside system. Therefore,  $\Delta G$  inside system accounts for changes in  $S$  both inside and outside system
- A spontaneous chemical change will occur in a **closed system** at **fixed  $P$  and  $T$**  if and only if the total chemical potential energy (Gibbs energy) decreases
- The  $\Delta G$  associated with a change in system conditions can be dominated by the change in either  $H$  or  $S$ . Thus, a spontaneous change can occur via a decrease in  $H$ , even if  $S$  decreases (e.g., precipitation of a solid), or by an increase in  $S$  even if  $H$  increases (e.g., evaporation of water)

## Defining 'Potential'

- Potential energy can be viewed as the result of interaction between a property of the environment (the **potential**) and a property of the object of interest, e.g., gravitational potential and mass, electrical potential and charge, etc.
- Formally, the **potential** at a location is the increment in total potential energy of the system per unit amount of the property on which the potential acts when a differential amount of the property is added at that location, e.g.:

$$\overline{\text{PE}}_{\text{grav}} = \frac{\partial \overline{\text{PE}}_{\text{grav,tot}}}{\partial m_i} = k_{\text{grav}}^{\circ} + gh$$

- Gravitational potential acts on mass. It characterizes the gravitational environment and has units of potential energy per unit mass
- Electrical potential acts on charge. It characterizes the electrical environment and has units of potential energy per unit charge
- **Mechanical potential** acts on volume. It characterizes the mechanical environment and has units of potential energy per volume

$$\overline{\text{PE}}_{\text{mech}} = \frac{\partial \overline{\text{PE}}_{\text{mech,tot}}}{\partial V_i} = k_{\text{mech}}^{\circ} + P$$

- **Chemical potential** acts on chemical species. It characterizes the chemical environment and has units of potential energy per mole of species

$$\overline{\text{PE}}_{\text{chem}} = \frac{\partial \overline{\text{PE}}_{\text{chem,tot}}}{\partial n_i} = k_{\text{chem}}^{\circ} + ??$$

$$\overline{\text{PE}}_{\text{chem}} = \frac{\partial \overline{\text{PE}}_{\text{chem,tot}}}{\partial n_i} = k_{\text{chem}}^{\circ} + ??$$

$$\overline{G}_i = \left. \frac{\partial G_{\text{tot}}}{\partial n_i} \right|_{P,T,n_{j \neq i}} = \overline{G}_i^{\circ} + ??$$

## Quantifying Chemical Energy and Potential

- The contributions of individual species to  $G$ ,  $H$ , and  $S$  are additive and can be normalized to the number of moles of that species ( $n_i$ ).

$$X_{tot} = \sum_{all\ i} X_i = \sum_{all\ i} n_i \bar{X}_i \text{ where } X \text{ is } G, H, \text{ or } S$$

$$(\mu_i =) \bar{G}_i = \frac{G_i}{n_i} = \frac{\partial G_{sys}}{\partial n_i} \quad \bar{H}_i = \frac{H_i}{n_i} = \frac{\partial H_{sys}}{\partial n_i} \quad \bar{S}_i = \frac{S_i}{n_i} = \frac{\partial S_{sys}}{\partial n_i}$$

$\mu_i$  is the **total** potential of  $i$ , which in principle includes terms for other forms of potential (electrical, gravitational, etc.); if non-chemical contributions are constant,  $\Delta\mu_i = \Delta\bar{G}_i$ .

We want to relate changes in the molar thermodynamic properties to changes in more accessible, conventional parameters. The key relationship is (§2.5.3 in text):

*Note that this is the increase in the potential energy per mole; when  $a_i$  is increased, both the number of moles of  $i$  and the potential energy per mole increase.*

$$d\bar{G}_i = RT \, d \ln a_i$$

$$\bar{G}_i = \bar{G}_i^{\circ} + RT \ln a_i$$

The **standard molar Gibbs energy** of  $i$  is the molar Gibbs energy of  $i$  when  $a_i=1.0$ . At 25°C,  $2.303RT=5.71$  kJ/mol, so:

$$\bar{G}_i = \bar{G}_i^{\circ} + \left( 5.71 \frac{\text{kJ}}{\text{mol}} \right) \log a_i$$

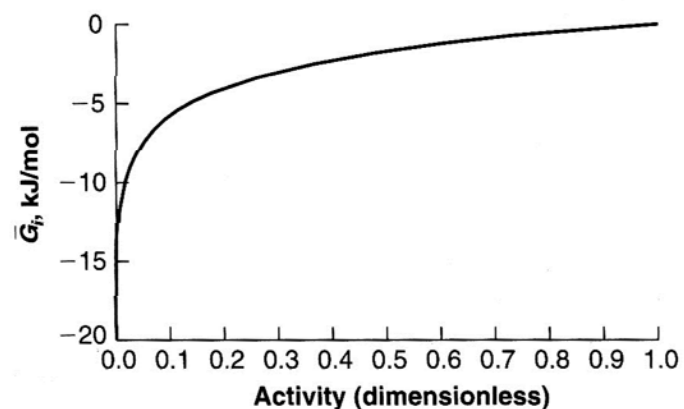
- To establish absolute scales for molar Gibbs energy, enthalpy, and entropy, we define a baseline for each element:

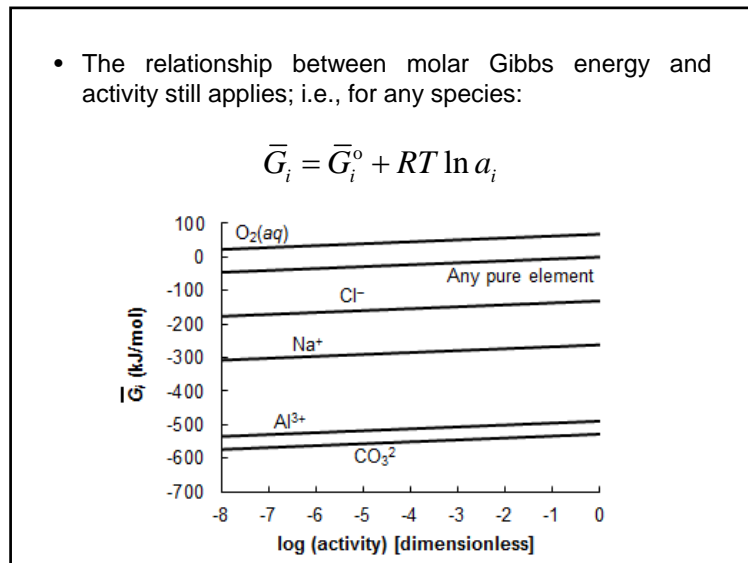
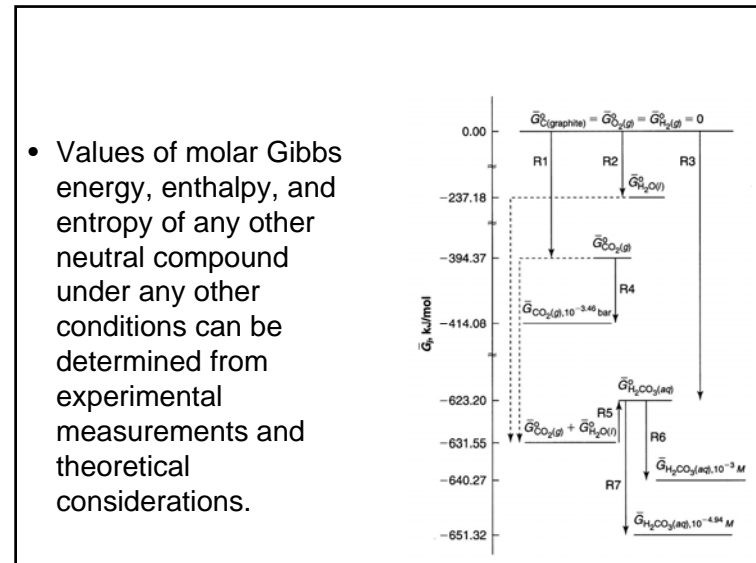
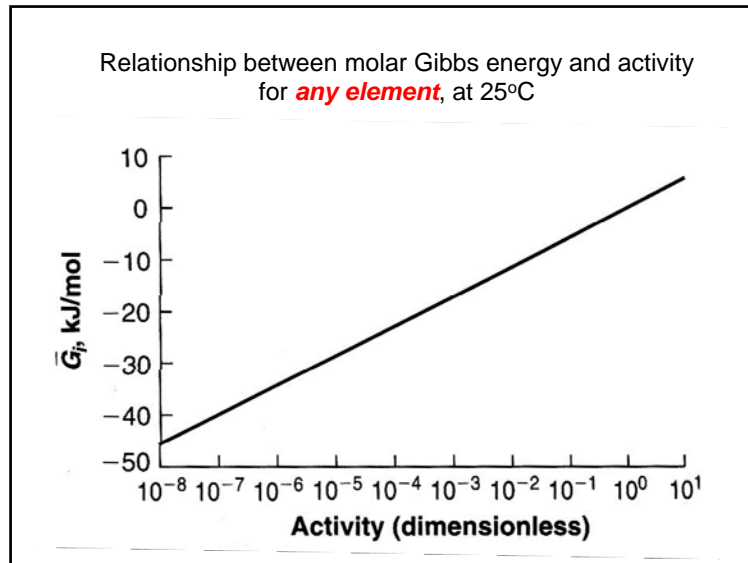
- For pure **elements** in their standard state:

$$\bar{G}_i^{\circ} = \bar{H}_i^{\circ} = 0$$

For theoretical reasons, molar entropy is defined to be zero for crystalline solids at 0 K, so it is positive for elements at STP

Relationship between molar Gibbs energy and activity for **any element**, at 25°C





### Quantifying Chemical Energy and Potential

- Since it is not possible to form a single ion without forming an oppositely charged ion, an additional baseline is needed for ions. This is that, for  $H^+$  in its standard state

$$\bar{G}_{H^+}^{\circ} = \bar{H}_{H^+}^{\circ} = 0$$

- Note: The concentration of dissolved electrons ( $e^-$ ) is unmeasurably small in most solutions. It is nevertheless useful to define a finite activity for these species. To do this, the standard state of  $e^-$  is defined as the conditions in equilibrium with  $H_2(g)$  and  $H^+$  in their standard states. For reasons explained later in the term, this leads to:

$$\bar{G}_{e^-}^{\circ} = \bar{H}_{e^-}^{\circ} = 0$$