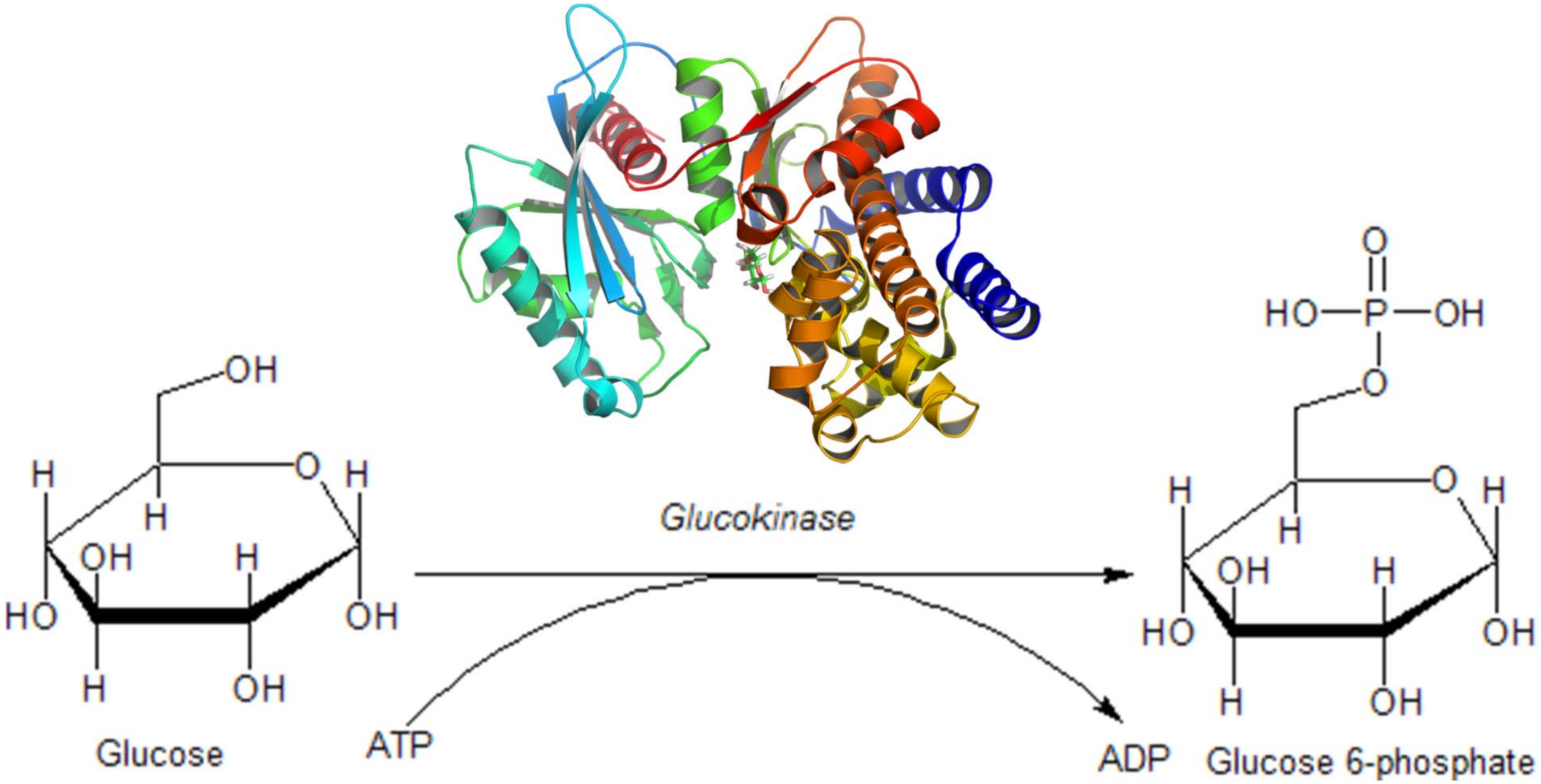
Metabolism: Glucokinase



- Physiological ΔG is -27 kJ mol^{-1}

Wikipedia, Glucokinase http://en.wikipedia.org/wiki/Glucokinase

How Does Equilibrium Change?

- Under physiological conditions, reaction is favorable – what about other conditions?
- We already know how to calculate changes in temperature, pressure:

$$dG = VdP - SdT$$

- What if we change the concentration of ATP?

Functions in Real Life

- **Think:** How do we use functions to characterize real-life experience?

- If we had a "Gibbs function," we could calculate G at one set of concentrations, and then at another: $\Delta G = G(N_{ATP,2}) - G(N_{ATP,1})$

First Step: Le Chatelier's Principle

- Le Chatelier's Principle (c. 1900):
  - Start at equilibrium
  - Change conditions (add ATP, change T, etc.)
  - Equilibrium will shift to counteract the change

- What does this mean?
  - Add ATP will favor the reaction which hydrolyzes ATP
  - Increase temperature will favor endothermic reaction (heat is a reaction product)
  - Increase pressure will favor product with smaller V

First Step: Le Chatelier’s Principle

- Le Chatelier’s Principle (c. 1900):
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  - Change conditions (add ATP, change T, etc.)
  - Ec

Can we make this mathematically rigorous?

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The “Gibbs” Function

- Consider a function that gives us the Gibbs energy:

$$G(P, T, N_{ATP}, N_G, N_{G6P})$$

- Consider the differential:

$$dG = VdP - SdT + \left(\frac{\partial G}{\partial N_{ATP}}\right)_{P,T,N_G,N_{G6P}} dN_{ATP} + \left(\frac{\partial G}{\partial N_G}\right)_{P,T,N_{ATP},N_{G6P}} dN_G + \left(\frac{\partial G}{\partial N_{G6P}}\right)_{P,T,N_{ATP},N_G} dN_{G6P}$$

- Or more simply:

$$dG = VdP - SdT + \left(\frac{\partial G}{\partial N_{ATP}}\right) dN_{ATP} + \left(\frac{\partial G}{\partial N_G}\right) dN_G + \left(\frac{\partial G}{\partial N_{G6P}}\right) dN_{G6P}$$

Chemical Potential

- Define the chemical potential μ_x:

$$\mu_x = \left(\frac{\partial G}{\partial N_x}\right)_{others\ const.}$$

- Then our differential becomes:

$$dG = VdP - SdT + \mu_{ATP}\, dN_{ATP} + \mu_G\, dN_G + \mu_{G6P} dN_{G6P}$$

- The red terms must tell us something about the non-PV work (dw^*)

Chemical Potential: Properties

- **It's a derivative:** at a minimum, $\frac{\partial G}{\partial N} = 0$
- **They are inter-related:** At equilibrium (dG = 0), a small increase in ATP (dN_{ATP}) must affect other dN's
- **It's path-independent:** because it's derived from variables of state
- **It's intensive:** Change in free energy *per mole of X*

Chemical Potential: Properties

- **Pure Substance:** At constant T, P, the μ for a pure substance is simple:

$$dG = \mu_a dn_a$$

$$\frac{dG}{dn_a} = \mu_a$$

  - Therefore: μ is simply the partial molar Gibbs energy ($\Delta\bar{G}$) for a pure substance

At Equilibrium: Open System

$$aA + bB \rightarrow cC$$

- What is the Gibbs Energy exact differential?

“Open System” Implications

- **Implication #1:** Gibbs energy (at constant T, P) is simply the sum of chemical potentials of components

$$G = \mu_a n_a + \mu_b n_b + \mu_c n_c + \cdots$$

- This is simply conservation of E (the first law) showing up again: **it applies to closed systems, too!**

“Open System” Implications

- **Implication #2:** If we’re interested in ΔG (we are), adding a constant to μ doesn’t matter:

$$\begin{array}{r} G_2 = (\mu_{a,2})n_a \\ -\,G_1 = (\mu_{a,1})n_a \\ \hline \Delta G = (\Delta\mu_a)n_a \end{array} \qquad \begin{array}{r} G_2 = (\mu_{a,2}-\mu_a^0)n_a \\ -\,G_1 = (\mu_{a,1}-\mu_a^0)n_a \\ \hline \Delta G = \qquad (\Delta\mu_a)n_a \end{array}$$

- We can define a “standard state” chemical potential

Far From Equilibrium: Closed System

*a*A + *b*B → *c*C

- What is the Gibbs Energy exact differential?

$$dG = -SdT + VdP + \mu_a dn_a + \mu_b dn_b + \mu_c dn_c$$

- At constant T, P:

$$dG = \mu_a dn_a + \mu_b dn_b + \mu_c dn_c$$

- Up to this point, this is has simply been applied math. What does the chemistry say?

What is this $d\alpha$?

$$\frac{dn_a}{a} = \frac{dn_b}{b} = -\frac{dn_c}{c} = -d\alpha$$

- A change per mole of reaction? What?!

- You've seen this before:

$$3O_2 + 2\ \mathrm{Gly} \rightarrow 4CO_2 + 2H_2O + 2NH_3$$

$$\Delta H = -1160\ \mathrm{kJ\ mol^{-1}}$$

  - Enthalpy *per mole of reaction*

Approaching Equilibrium: Closed System

$a\text{A} + b\text{B} \rightarrow c\text{C}$

- Express dG in terms of $d\alpha$ (const. T, P):

$$dG = (c\mu_c - a\mu_a - b\mu_b)d\alpha$$

- Generalizing, we have another situation with “products minus reactants” (times moles)

- Closed system does *not* mean *n* cannot change! It *does* mean that *n* must change in a predictable way.

At Equilibrium: Closed System

*a*A + *b*B → *c*C

- At equilibrium, $dG = d\alpha = 0$, so therefore:
$$(c\mu_c - a\mu_a - b\mu_b) = 0$$

- Additionally, the change in G per mole of reaction must be
$$\Delta\bar{G} = \frac{dG}{d\alpha} = (c\mu_c - a\mu_a - b\mu_b)$$

- Generalizing: products minus reactants (times moles)

What Does All This Mean?

- Used mathematical implications to define a new quantity, called the “chemical potential”
- For a pure substance chemical potential is simply molar Gibbs energy
- If we new chemical potentials of reactants and products, we could predict the change in Gibbs Energy (the “available” or “free” energy)