

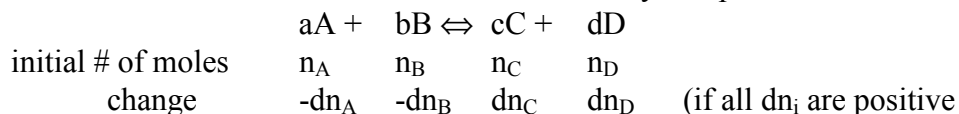
## Relationship between $\Delta_r G^\circ$ , $\Delta_r G$ , Q, and K

Fill in the blanks and boxes!!

At constant P and T and  $w_e=0$ ,  $dG$  is a criterion of spontaneity and  $dG = \sum_{i=1}^N \mu_i dn_i$

and for calculating  $\Delta G$  or  $dG$ , we take  $G = \sum_{i=1}^N \mu_i n_i$ .

Consider the balanced chemical reaction at some arbitrary composition



$$d\xi = \frac{dn_A}{a} = \frac{dn_B}{b} = \frac{dn_C}{c} = \boxed{\phantom{0}}$$

$$\text{Initial } G = G_i = \boxed{\phantom{0}}$$

$$\text{Final } G = G_f = \mu_A(n_A - ad\xi) + \mu_B(n_B - bd\xi) + \mu_C(n_C + cd\xi) + \mu_D(n_D + dd\xi)$$

$$dG = G_f - G_i = \boxed{\phantom{0}}$$

$$= d\xi (-a\mu_A - b\mu_B + c\mu_C + d\mu_D)$$

$$* \quad \Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{T,P} = (-a\mu_A - b\mu_B + c\mu_C + d\mu_D) = (c\mu_C + d\mu_D - a\mu_A - b\mu_B)$$

but  $\mu_i$  of a species in solution is related to activity via  $\mu_i = \mu_i^\circ + \boxed{\phantom{0}}$

$$\Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{T,P} = (c\mu_C^\circ + d\mu_D^\circ - a\mu_A^\circ - b\mu_B^\circ) + RT [c \ln(a_C) + d \ln(a_D) - a \ln(a_A) - b \ln(a_B)]$$

$$** \quad \Delta_r G = \Delta_r G^\circ + RT \ln \left[ \phantom{0} \right] = \Delta_r G^\circ + RT \ln( \phantom{0} )$$

recall that this equation  
applies to any arbitrary concentration!

## Study Questions

- 1) For a particular reaction at a particular temperature, how many values can  $\Delta_r G^\circ$  have?  
How many values can K have for the same reaction?
- 2) Is the value of  $\Delta_r G^\circ$  a function of the concentrations (activities) or pressures (fugacities) of reactants or products?  
Is the value of K a function of these quantities?
- 3) How does Q differ from K?
- 4) The value of Q can range from \_\_\_\_\_ (all reactants) to \_\_\_\_\_ (all products).
- 5) The units of Q are \_\_\_\_\_. The units of K are \_\_\_\_\_.
- 6) Given a value of K and Q, we can determine which way a reaction needs to shift to reach equilibrium (Circle one):  
 $Q < K$  reaction needs to shift to ( reactants / products ) to reach equilibrium.  
 $Q > K$  reaction needs to shift to ( reactants / products ) to reach equilibrium.
- 7) What is the meaning of  $\xi$  in the first definition of  $\Delta_r G$  on the previous page?
- 8) The value of  $\xi$  can range from \_\_\_\_\_ (all reactants) to \_\_\_\_\_ (all products).  
The units of  $\xi$  are \_\_\_\_\_.
- 9) What is the relationship between  $(\partial G / \partial \xi)$  and the slope of a plot of Gibbs Free Energy versus  $\xi$ ? \_\_\_\_\_  
What is the relationship between  $\Delta_r G$  and the slope? \_\_\_\_\_
- 10) If one plots Gibbs Free Energy versus  $\xi$  for a reaction (at constant T and P), what is the sign of  $(\partial G / \partial \xi)$  when:  
 $Q > K$ ? \_\_\_\_\_  
 $Q < K$ ? \_\_\_\_\_  
 the reaction is consuming “reactants” and producing “products”? \_\_\_\_\_  
 the reaction is consuming “products” and producing “reactants”? \_\_\_\_\_
- 11) What is the relationship between  $\Delta_r G^\circ$  and the endpoints of a plot of Gibbs Free Energy versus  $\xi$ ? \_\_\_\_\_