

Given a system containing the chemical reaction  $A \rightarrow B$ , let  $n_i$  denote the amount of species  $i$ ;  $\mu_i$ , the chemical potential of species  $i$ ;  $T$ , the system's temperature;  $S$ , its entropy;  $V$ , its volume;  $p$ , its pressure; and  $G$ , its Gibbs free energy. Then by definition of  $G$ :

$$dG = Vdp - SdT + \sum_i \mu_i dn_i = Vdp - SdT + \mu_A dn_A + \mu_B dn_B.$$

Let  $X$  be a reaction coordinate. Then:

$$n_A(X) + n_B(X) = n,$$

with  $n$  constant by conservation of matter. Thus, define the *extent of reaction*  $\xi$  as:

$$\xi(X) = n - n_A(X)$$

so that:

$$n_A = n - \xi$$

$$n_B = \xi.$$

The differential of the system's Gibbs free energy  $G$  is then:

$$dG = Vdp - SdT + \mu_A d(n - \xi) + \mu_B d(\xi) = Vdp - SdT + (\mu_B - \mu_A) d\xi,$$

as  $n$  is a constant. Thus, by the definition of total differential, we have:

$$\frac{\partial G}{\partial \xi} = \mu_B - \mu_A,$$

as asserted by the question.

However, notice that, since  $\xi = n_B$ , the answer “extent of reaction” is non-unique for the question as specified – at least “amount of product” is also obviously correct, but so is “amount of reactant” (since  $[n_A = n - \xi] \Rightarrow [dn_A = -d\xi]$ .) In fact, I would argue that “amount of product” is *more correct*, since our definition of extent of reaction is apparently not universal. I recall that we discovered another definition for extent of reaction as “the fraction of  $A$  that has reacted.” Let’s call this alternate definition  $\bar{\xi}$  such that:

$$\bar{\xi} = \frac{n - n_A}{n}.$$

Using this definition for extent of reaction, the amounts of  $A$  and  $B$  are:

$$n_A = (1 - \bar{\xi})n$$

$$n_B = \bar{\xi}n,$$

so that the differential of the system’s Gibbs energy is:

$$dG = Vdp - SdT + \mu_A d[(1 - \bar{\xi})n] + \mu_B d(\bar{\xi}n) = Vdp - SdT + (\mu_B - \mu_A)nd\bar{\xi}$$

and:

$$\frac{\partial G}{\partial \xi} = n(\mu_B - \mu_A)$$

which is otherwise than claimed in the question!

I wonder if there may exist a more refined definition of extent of reaction such that, if

$R$  is the set of reactants and  $P$  that of products:

$$\frac{\partial G}{\partial \xi} = \sum_{i \in P} \mu_i - \sum_{j \in R} \mu_j.$$

If such a definition does exist, it must collapse to  $\xi = n_B$  for  $A \rightarrow B$ .