

## 14.6: The Change Criteria in A System Composed of Subsystems

Let us now consider a closed, constant temperature, constant pressure system that is composed of open subsystems. Chemical substances can pass from one subsystem to another, but they cannot enter or leave the system. We assume that our model for  $dG$  applies in every subsystem. Each subsystem is at the same temperature and pressure. For the  $r$ -th subsystem,

$$G_r = G_r(P, T, \theta_{r,1}, \theta_{r,2}, \dots, \theta_{r,\lambda}, n_{r,1}, n_{r,2}, \dots, n_{r,\omega})$$

For a physical system in which all of these assumptions correspond closely to physical reality, we have, for the  $r$ -th subsystem,

$$dG_r = -S_r dT + V_r dP + (dw_{NPV})_r + \sum_{j=1}^{\omega} \mu_j dn_{r,j}$$

For the closed system, we have

$$\sum_r dG_r = -dT \sum_r S_r + dP \sum_r V_r + \sum_r (dw_{NPV})_r + \sum_r \sum_{j=1}^{\omega} \mu_j dn_{r,j}$$

Since Gibbs free energy, entropy, volume, and work are extensive variables, we have, for the closed system,  $dG = \sum_r dG_r$ ,  $dS = \sum_r S_r$ ,  $V = \sum_r V_r$ , and  $dw_{NPV} = \sum_r (dw_{NPV})_r$ . Therefore,

$$dG = -SdT + VdP + dw_{NPV} + \sum_r \sum_{j=1}^{\omega} \mu_j dn_{r,j}$$

For any process that occurs in this closed system at constant pressure and temperature, we have  $(dG)_{PT} \leq dw_{NPV}$ , and

$$\sum_r \sum_{j=1}^{\omega} \mu_j dn_{r,j} \leq 0$$

expresses the criteria for change in the closed system as a sum of conditions on the open subsystems.

Now let us consider the possibility that, for the  $\rho$ -th open subsystem, we have

$$\sum_{j=1}^{\omega} \mu_j dn_{\rho,j} > 0$$

If this were true, the sum over all of the subsystems could still be less than or equal to zero. In this case, the energy increase occurring in the  $\rho$ -th subsystem would have to be offset by energy decreases occurring in the other subsystems. This is at odds with the way that physical systems are observed to behave. To see this, let us suppose that the process is a chemical reaction. Then the composition changes are related to the extent of reaction as  $dn_{\rho,j} = \nu_j d\xi_{\rho}$ . For the open subsystem, we have

$$\sum_{j=1}^{\omega} \mu_j \nu_j d\xi_{\rho} > 0$$

Now, we can alter the boundary of this subsystem to make it impermeable to matter, while keeping its state functions unchanged. This change converts the open subsystem to a closed system, for which we know that

$$\sum_{j=1}^{\omega} \mu_j \nu_j d\xi_{\rho} < 0$$

If the criterion for spontaneous change switches from  $\sum_{j=1}^{\omega} \mu_j \nu_j d\xi_{\rho} > 0$  to  $\sum_{j=1}^{\omega} \mu_j \nu_j d\xi_{\rho} < 0$  the sign of  $d\xi_{\rho}$  must change. The supposition that  $\sum_{j=1}^{\omega} \mu_j \nu_j d\xi_{\rho} > 0$  is possible in an open subsystem implies that the direction of a spontaneous change in a closed system can be opposite the direction of a spontaneous change in an otherwise identical open system. No such thing is ever observed. We conclude that the criterion for spontaneous change,

$$\sum_{j=1}^{\omega} \mu_j dn_j < 0$$

must be satisfied in every part of any system in which the various potentials are the same throughout. Since

$$d_i S = -\frac{1}{T} \sum_{j=1}^{\omega} \mu_j dn_j$$

it follows that  $d_i S > 0$  must also be satisfied in every part of the system.

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