4.2 Gibbs phase rule including chemical reactions and other restraints

To explicitly take into account chemical restrictions we now slightly modify the phase rule

$$F = C - P + 2 \quad \Rightarrow \quad F = S - R - m - P + 2 \tag{4.1}$$

S = number of chemical species
R = restraints, number of independent chemical and charge equilibrium conditions
m = further restraints, e.g. compounds with fixed compositions
As an example we will discuss phases composed of S = H_2, Cl_2, Br_2, HCl, HBr, and BrCl. First we have to define the set of independent chemical equilibrium conditions. The meaning of "independent" here is that at least one new chemical species per equilibrium condition is found. We find

1. H_2 + Cl_2 $\rightarrow$ 2 HCl
2. H_2 + Br_2 $\rightarrow$ 2 HBr
3. Br_2 + Cl_2 $\rightarrow$ 2 BrCl

All other "hypothetical" equilibrium conditions can be composed from these three conditions, thus those are not independent, e.g.

- H_2 + BrCl $\rightarrow$ HCl + HBr (1. + 2. - 3.) / 2

Thus to find a homogeneous gas phase we have $F = 6 - 3 - 0 - 1 + 2 = 4$, e.g. temperature, pressure and two mole fractions may be varied.