1.4 Free classical particles: The ideal gas

"Free particles" implies that there exists no interaction between the particles, i.e. only the kinetic energy has to be taken into account. The system of classical particles with such properties is very famous: the ideal gas! The molar volume for an ideal gas is $V_m = RT/p$. For constant T and N we have $dG_m = V_m dp$ leading to

$$G_m(p_f) = G_m(p_i) + \int_{p_i}^{p_f} V_m dp = G_m(p_i) + RT \int_{p_i}^{p_f} \frac{1}{p} dp = G_m(p_i) + RT \ln \frac{p_f}{p_i} \quad , \tag{1.29}$$

respectively

$$\mu = \mu^0 + RT \ln \frac{p}{p^0} \quad , \tag{1.30}$$

where μ^0 is the standard chemical potential at 1 bar (p^0).
We now discuss mixing two ideal gases A and B, i.e. there is no interaction neither between A-A and B-B nor between A-B. At fixed temperature T ($dT = 0$) and pressure p ($dp = 0$) under the special condition that the ratio n_A/n_B respectively dn_A/dn_B stays constant the chemical potentials are fix, i.e. $\mu_A = const.$, $\mu_B = const.$. Taking into account that

$$\frac{\partial G}{\partial n_A} = \mu_A \quad , \quad \frac{\partial G}{\partial n_B} = \mu_B \quad , \tag{1.31}$$

we can integrate

$$dG = \mu_A dn_A + \mu_B dn_B \tag{1.32}$$

to get

$$G(n_A, n_B, T, p) = \int_0^{n_A} \mu_A dn_A + \int_0^{n_B} \mu_B dn_B = \mu_A \int_0^{n_A} dn_A + \mu_B \int_0^{n_B} dn_B = \mu_A n_A + \mu_B n_B \quad . \tag{1.33}$$

This result is the generalization of Eq. (1.28) and we found it for choosing a special "path" in coordinate space. Just knowing that $G(n_A, n_B, T, p)$ is a thermodynamic potential tells us that this result holds in general.
So before mixing the Gibbs energy of the total system is

$$G_i = n_A \mu_A + n_B \mu_B = n_A \left(\mu_A^0 + RT \ln \frac{p}{p^0} \right) + n_B \left(\mu_B^0 + RT \ln \frac{p}{p^0} \right) \quad . \tag{1.34}$$

After mixing we find

$$G_f = n_A \left(\mu_A^0 + RT \ln \frac{p_A}{p^0} \right) + n_B \left(\mu_B^0 + RT \ln \frac{p_B}{p^0} \right) \quad . \tag{1.35}$$

The difference $\Delta_{mix} G = G_f - G_i$, i.e. the Gibbs energy of mixing is

$$\Delta_{mix} G = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p} = RT \ln \left[\left(\frac{p_A}{p} \right)^{n_A} * \left(\frac{p_B}{p} \right)^{n_B} \right] \quad . \tag{1.36}$$

Defining molar fractions $x_A = n_A/n$, $x_B = n_B/n$ and taking into account that partial pressures add up according to their molar fractions, i.e. $p_A = x_A p$ resp. $p_B = x_B p$ we can rewrite Eq. (1.36)

$$\Delta_{mix} G = nRT \left(x_A \ln x_A + x_B \ln x_B \right) \quad . \tag{1.37}$$

Because molar fractions are always smaller than 1 the logarithms are always negative, i.e. $\Delta_{mix} G < 0$.
Since $(\partial G/\partial T)_{p,n} = -S$ we find for the entropy of mixing

$$\Delta_{mix} S = -nR \left(x_A \ln x_A + x_B \ln x_B \right) \quad , \tag{1.38}$$

i.e. mixing increases the entropy!!!
Since $\Delta G = \Delta H - T\Delta S$ we find for ideal mixtures

$$\Delta_{mix} H = 0 \quad . \tag{1.39}$$

In ideal mixtures particles do not interact; thus there is no (inner) "energy" contribution in addition to the entropy gain. Since pressure work has to be taken into account (p is the coordinate) it is the enthalpy H which summarizes all relevant energy contributions.
One further consequence even for ideal mixing we see when taking $x_A \to 0$. According to Eq. (1.30) $\mu_A \to -\infty$ stabilizing the extremely diluted state in a mixture. This explains why it is so difficult to extract very small concentrations out of a mixture; the gain in mixing entropy does not allow for this.