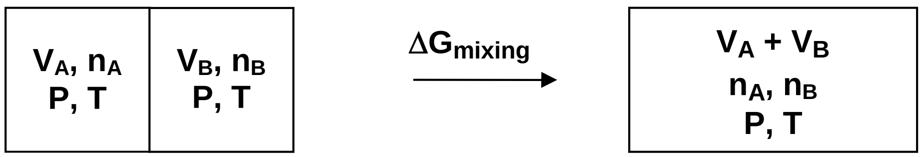
Handout of more complete proof of
$\mu_i = \mu_i^o + RT\,lnP_i$ for mixture of ideal gases

The object is a complete derivation of the relationship between chemical potential μ_i and partial pressure by $\mu_i = \mu_i^o + RT\ln P_i$. This relation and its counterparts for concentration of solutes is so important that it deserves a **HANDOUT**:
We calculate ΔG_{mixing} for the same arrangement used previously to calculate ΔS_{mixing}:



For ideal gas

$$\Delta H_{mixing} = 0; \quad \Delta S_{mixing} = -(n_A + n_B)R\left[X_A \ln X_A + X_B \ln X_B\right] = -R\left[n_A \ln X_A + n_B \ln X_B\right]$$
$$so \tag{1.1}$$
$$(\Delta G_{mixing})_{T,P} = -T\Delta S_{mixing} = RT\left[n_A \ln X_A + n_B \ln X_B\right]$$

also

$$\Delta G_{mix} = G_{A+B} - (G_A + G_B) \tag{1.2}$$

with

$$G_{A+B} = n_A\mu_A + n_B\mu_B$$
$$G_A = G_A^o + n_A RT \ln\left(\frac{P}{1\,atm}\right) \tag{1.3}$$
$$G_B = G_B^o + n_B RT \ln\left(\frac{P}{1\,atm}\right)$$
$$with \quad G_A^o = n_A \bar{G}_A^o \quad G_B^o = n_B \bar{G}_B^o$$

thus

$$\Delta G_{mix} = n_A\mu_A + n_B\mu_B - n_A\bar{G}_A^o - n_A RT\ln\left(\frac{P}{1\,atm}\right) - n_B\bar{G}_B^o - n_B RT\ln\left(\frac{P}{1\,atm}\right)$$
$$and \tag{1.4}$$
$$\Delta G_{mix} = RT\left[n_A \ln X_A + n_B \ln X_B\right]$$

equating and rearranging

$$n_A\left[\mu_A - \bar{G}_A^o - RT\ln\left(\frac{P}{1\,atm}\right) - RT\ln X_A\right] + n_B\left[\mu_B - \bar{G}_B^o - RT\ln\left(\frac{P}{1\,atm}\right) - RT\ln X_B\right] = 0 \tag{1.5}$$

next we differentiate both side by $\left(\frac{\partial}{\partial n_A}\right)_{n_B,T,P}$

$$\left[\mu_A - \bar{G}_A^o - RT\ln\left(\frac{P}{1\,atm}\right) - RT\ln X_A\right] + n_A\left(\frac{\partial \mu_A}{\partial n_A}\right)_{n_B,T,P} - n_A RT\frac{1}{X_A}\left(\frac{\partial X_A}{\partial n_A}\right)_{n_B,T,P}$$
$$+ n_B\left(\frac{\partial \mu_B}{\partial n_A}\right)_{n_B,T,P} - n_B RT\frac{1}{X_B}\left(\frac{\partial X_B}{\partial n_A}\right)_{n_B,T,P} = 0 \tag{1.6}$$

to get the derivatives of X_A and X_B with respect to n_A :

$$X_A = \frac{n_A}{n_A + n_B} \quad X_B = \frac{n_B}{n_A + n_B}$$

so

$$\left(\frac{\partial X_A}{\partial n_A}\right)_{n_B,T,P} = \frac{1}{n_A + n_B} - \frac{n_A}{(n_A + n_B)^2} = \frac{n_B}{(n_A + n_B)^2} = \frac{X_A X_B}{n_A} \tag{1.7}$$

and

$$\left(\frac{\partial X_B}{\partial n_A}\right)_{n_B,T,P} = -\frac{n_B}{(n_A + n_B)^2} = -\frac{X_B X_B}{n_B} = -\frac{X_B^{\,2}}{n_B}$$

substituting (1.7) into (1.6)

$$\left[\mu_A - \bar{G}_A^o - RT\ln\left(\frac{P}{1\,atm}\right) - RT\ln X_A\right] + n_A\left(\frac{\partial \mu_A}{\partial n_A}\right)_{n_B,T,P} - n_A RT\frac{1}{X_A}\frac{X_A X_B}{n_A}$$
$$+ n_B\left(\frac{\partial \mu_B}{\partial n_A}\right)_{n_B,T,P} - n_B RT\frac{1}{X_B}\left(\frac{-X_B^{\,2}}{n_B}\right) = 0 \tag{1.8}$$

note that the last four terms involve two cancellations:

$$-n_A RT\frac{1}{X_A}\frac{X_A X_B}{n_A} - n_B RT\frac{1}{X_B}\left(\frac{-X_B^{\,2}}{n_B}\right) = 0 \quad by\,algebra$$

and (1.9)

$$n_A\left(\frac{\partial \mu_A}{\partial n_A}\right)_{n_B,T,P} + n_B\left(\frac{\partial \mu_B}{\partial n_A}\right)_{n_B,T,P} = 0 \quad by\ the\ Gibbs-Duhem\ relationship\ proved\ elsewhere$$

FINALLY we are left with:

$$\left[\mu_A - \bar{G}_A^o - RT\ln\left(\frac{P}{1\,atm}\right) - RT\ln X_A\right] = 0$$
$$\left[\mu_A = \bar{G}_A^o + RT\ln\left(\frac{P}{1\,atm}\right) + RT\ln X_A\right] \tag{1.10}$$

ALMOST THERE

$$\mu_A = \bar{G}_A^o + RT\ln\left(\frac{X_A P}{1\,atm}\right)$$

$$with \quad PX_A P = \frac{n_A}{n_A + n_B}P = P_A \quad (partial\ pressure\ of\ gas\ A) \tag{1.11}$$

$$and \quad \mu_A^o(T) \equiv \mu_A(T, 1\,atm, pure\ A) = \bar{G}_A^o(T)$$

WE GET from (1.10)

$$\boxed{\mu_A(T) = \mu_A^o(T) + RT\ln\left(\frac{P_A}{1\,atm}\right)} \tag{1.12}$$

HOORAY !!