# Термодинамические функции растворов газов (газовых смесей)

## Внутренняя энергия и энтальпия

$$\overline{U}_i = U_i^\circ \qquad \overline{H}_i = H_i^\circ$$

$$U = \Sigma\, n_i \overline{U}_i = \Sigma\, n_i U_i^\circ$$

$$H = \Sigma\, n_i \overline{H}_i = \Sigma\, n_i H_i^\circ$$

## Энтропия

$$\overline{S}_i = S_{i,\text{o}} + \int_0^T \frac{c_{V,i}}{T}\, dT + R \ln V_i \qquad (V_i = V/n_i)$$

$$\bar{S}_i = S_i(T) + R\ln V_i$$

$$S = \Sigma n_i \bar{S}_i = \Sigma n_i S_i(T) + R\Sigma n_i \ln(V/n_i)$$

$$\boxed{S = \Sigma n_i S_i(T) - R\Sigma n_i \ln c_i}$$

$$V = \frac{\Sigma n_i RT}{p}; \qquad c_i = \frac{n_i}{V} = \frac{n_i}{\Sigma n_i} \cdot \frac{p}{RT} = \frac{x_i p}{RT} = \frac{p_i}{RT}$$

$$S = \Sigma n_i S_i(T) - R\Sigma n_i \ln x_i - R\Sigma n_i \ln(p/RT)$$

$$\boxed{S = \Sigma n_i S_i'(T,p) - R\Sigma n_i \ln x_i}$$

$$\boxed{S = \Sigma n_i S_i''(T) - R\Sigma n_i \ln p_i}$$

# Энергия Гельмгольца

$$F = U - TS$$

$$U = \Sigma\, n_i U_i^{\circ} \qquad S = \Sigma n_i\, S_i\,(T) - R\Sigma n_i \ln c_i$$

$$F = \Sigma n_i\, U_i^{\circ} - T\,\Sigma n_i S_i\,(T) + RT\,\Sigma n_i \ln c_i$$

$$\boxed{F = \Sigma n_i\, F_i\,(T) + RT\,\Sigma n_i \ln c_i}$$

$$\boxed{F = \Sigma n_i\, F_i'\,(T, p) + RT\,\Sigma n_i \ln x_i}$$

$$\boxed{F = \Sigma n_i\, F_i''\,(T) + RT\,\Sigma n_i \ln p_i}$$

## Зависимость химического потенциала компонента от концентрации

$$F = U - TS = \Sigma n_i U_i^{\circ} - T\,\Sigma n_i S_i(T) + RT\,\Sigma n_i \ln c_i$$

$$\mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{V,T,n_j} = U_i^{\circ} - TS_i(T) + RT\,\frac{\partial}{\partial n_i}\left(\Sigma n_i \ln\frac{n_i}{V}\right)$$

$$\frac{\partial}{\partial n_i}\left(n_i \ln n_i - n_i \ln V\right) = \ln n_i + \frac{n_i}{n_i} - \ln V =$$

$$= \ln\frac{n_i}{V} + 1 = \ln c_i + 1$$

$$\mu_i = U_i^{\circ} - TS_i(T) + RT\ln c_i + RT$$

$$\mu_i = U_i^{\circ} - TS_i(T) + RT\ln p_i - RT\ln RT + RT$$

$$\mu_i = U_i^{\circ} - TS_i(T) + RT\ln x_i - RT\ln p/RT + RT$$

$$\boxed{\mu_i = g(T) + RT\ln c_i}$$

$$\boxed{\mu_i = g'(T) + RT\ln p_i}$$

$$\boxed{\mu_i = g''(T, p) + RT\ln x_i}$$

$$\mu_i = \mu_i(T) + RT \ln f_i$$

$$\Delta\mu_i = \mu_i'' - \mu_i' = RT \ln(f_i''/f_i') = \int_{p'}^{p''} \overline{V}_i dp$$

$$\mu_i = \overline{G}_i; \qquad \Sigma n_i d\overline{G}_i = 0; \qquad \Sigma n_i d\mu_i = RT \Sigma n_i d\ln f_i = 0$$

$$\boxed{\Sigma n_i d\ln f_i = 0} \qquad \boxed{\Sigma x_i d\ln f_i = 0}$$

***уравнения Дюгема – Маргулеса***

# Идеальные, предельно разбавленные и неидеальные растворы

$$\Delta U_{\text{см}} = 0; \ \ \bar{U}_i = U_i^\circ$$

$$\Delta H_{\text{см}} = 0; \ \ \bar{H}_i = H_i^\circ; \ \bar{L}_i = 0; \ \Delta c_p = 0$$

$$\Delta V_{\text{см}} = 0; \ \bar{V}_i = V_i^\circ$$

$$\Delta S_{\text{см}} = -R\Sigma x_i \ln x_i; \ \ \bar{S}_i = S_i^\circ - R\ln x_i$$

$$\Delta G_{\text{см}} = RT\Sigma x_i \ln x_i$$

$$\mu_i = g'(T) + RT \ln p_i$$

$$\mu_i = g''(T, p) + RT \ln x_i$$

# Равновесие жидкий раствор – насыщенный пар

$$\mu_i^{\text{газ}} = \mu_i^{\text{р-р}}$$

$$\mu_i^{\text{газ}} = g_i^{'}(T) + RT\ \ln p_i \qquad \mu_i^{\circ\text{газ}} = g_i^{'}(T) + RT\ \ln p_i^{\circ}$$

$$\mu_i^{\text{газ}} = \mu_i^{\circ} + RT \ln \frac{p_i}{p_i^{\circ}}$$

$$\mu_i^{\text{р-р}} = g_i^{''}(T, p) + RT\ \ln x_i \qquad \mu_i^{\circ\text{р-р}} = g_i^{''}(T, p)$$

$$\mu_i^{\text{р-р}} = \mu_i^{\circ} + RT\ \ln x_i$$

$$RT \ln \frac{p_i}{p_i^{\circ}} = RT \ln x_i$$

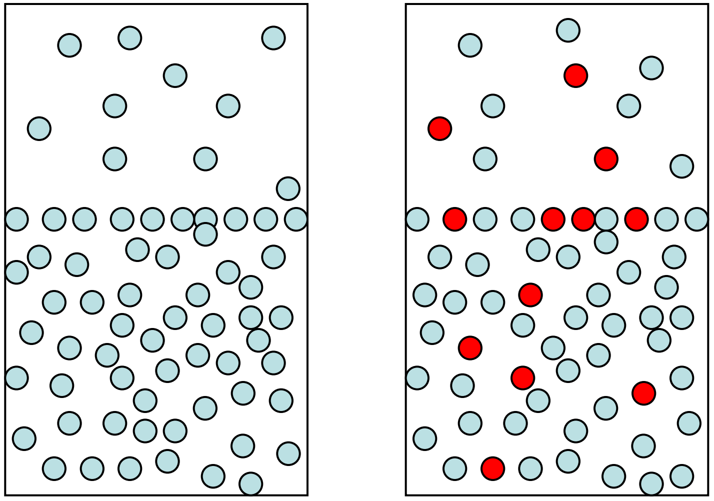
$$\boxed{p_i = p_i^{\circ} x_i}$$

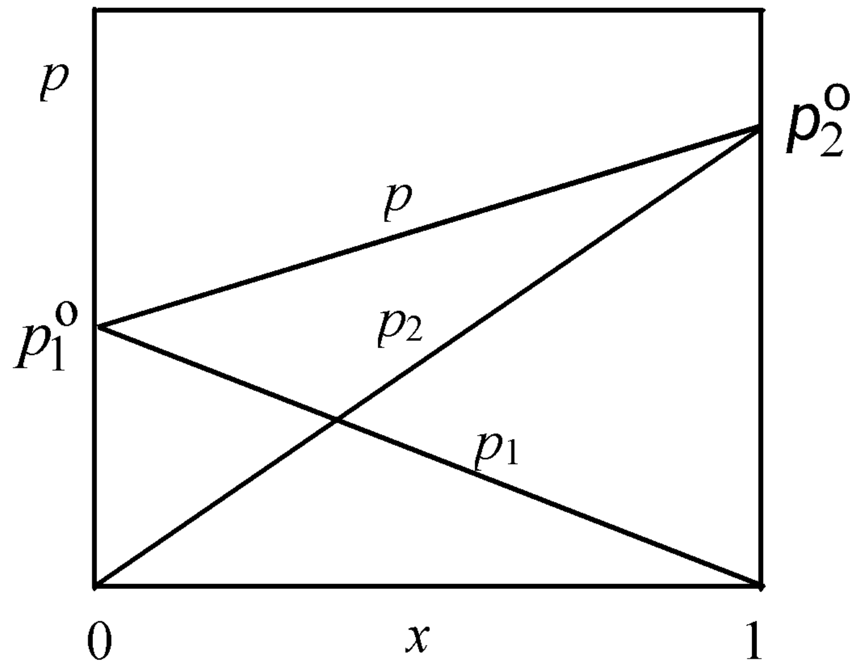
***закон Рауля***

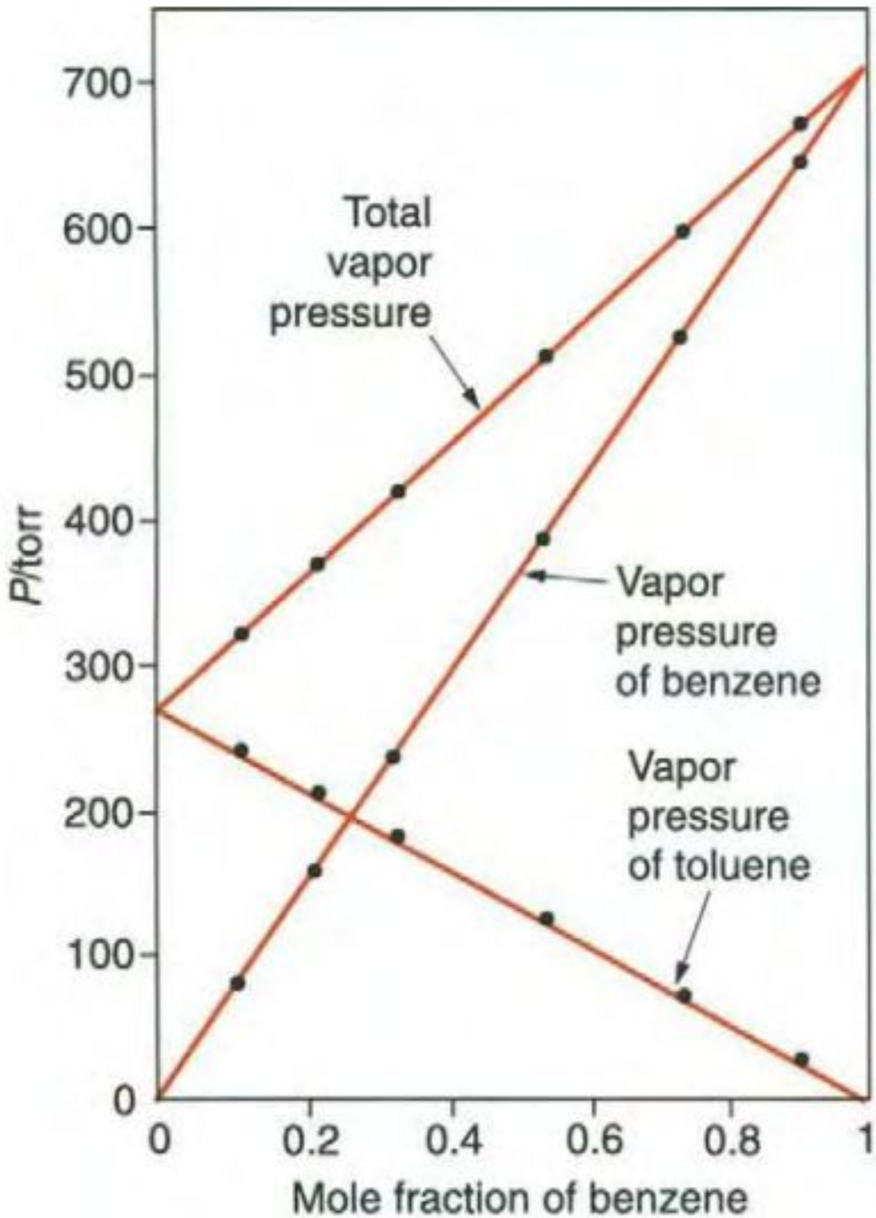
# Для бинарного раствора:

$$x_2 \equiv x \qquad p_1 = p_1^{o}(1-x) \qquad \frac{p_1^{o} - p_1}{p_1^{o}} = x$$

$$f_1 = f_1^{o} x_1 = f_1^{o}(1-x)$$








| | |
|---|---|
| *o*-xylene | *m*-xylene |
| *p*-xylene | toluene |
| ethylbenzene | 1-propanol |
| 2-propanol | naphthalane |
| anthracene | phenanthrene |
| 3-methylpentane | 2-methylpentane |
| 3-pentanone | 2-pentanone |
| propanol | propanone |

## Для неидеального раствора:

$$f_i = f_i^{\circ} x_i \qquad f_1 = f_1^{\circ} x_1 = f_1^{\circ}(1 - x)$$

$$\Sigma x_i \, d\ln f_i = 0; \qquad (1 - x)\, d\ln f_1 + x d\ln f_2 = 0$$

$$d\ln f_2 = -\frac{1 - x}{x}\, d\ln f_1$$

$$df_1 = f_1^{\circ} d(1 - x) = -f_1^{\circ} dx$$

$$d\ln f_2 = -\frac{1 - x}{x} \cdot \frac{df_1}{f_1} = \frac{1 - x}{x} \cdot \frac{f_1^{\circ} dx}{f_1^{\circ}(1 - x)} = \frac{dx}{x} = d\ln x$$

$$\ln f_2 = \ln x + \ln k \qquad \boxed{f_2 = kx}$$

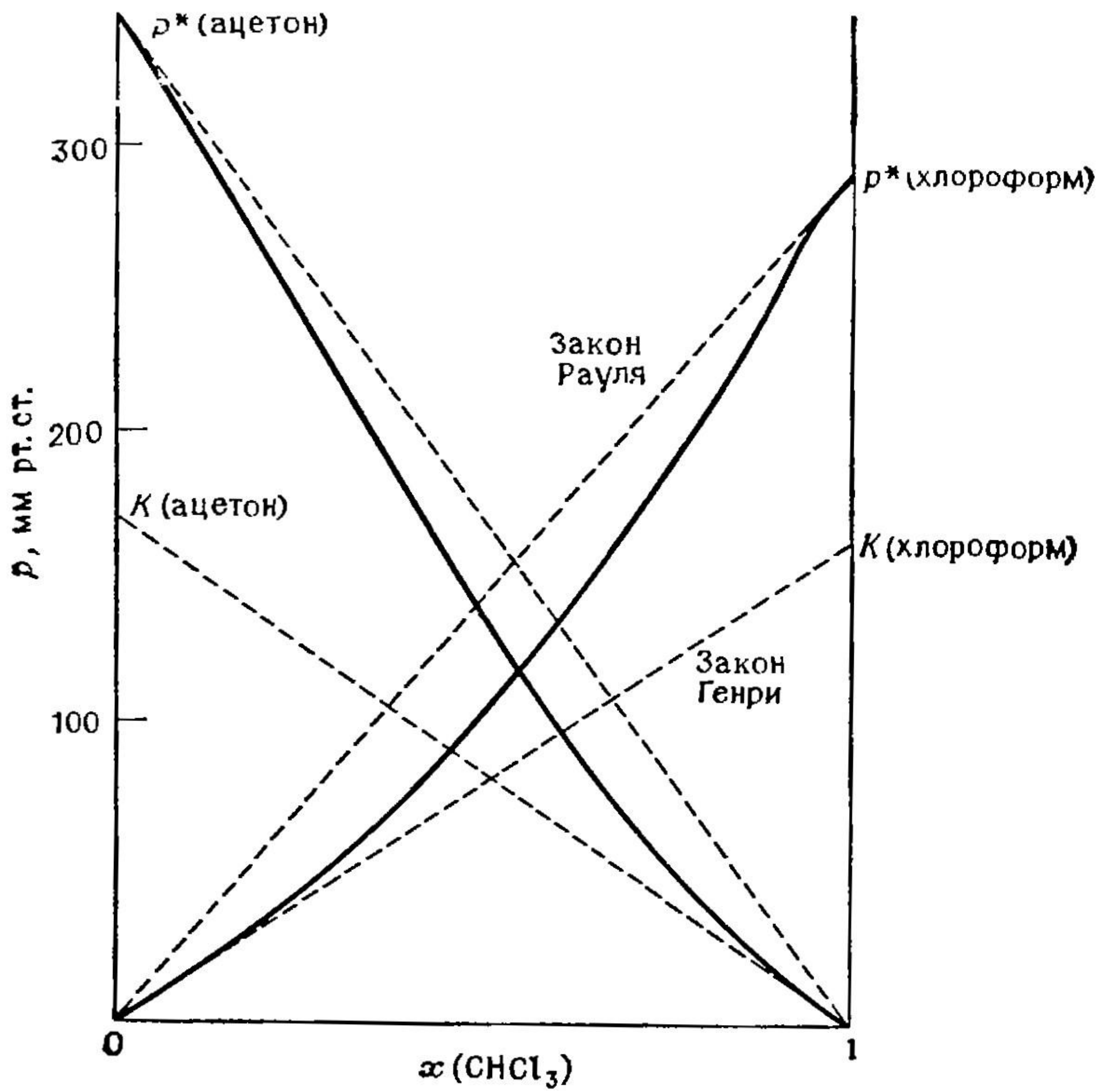
$$\boxed{p_2 = kx}$$ **закон Генри**

## III. *Experiments on the Quantity of Gases absorbed by Water, at different Temperatures, and under different Pressures. By Mr.* William Henry. *Communicated by the Right Hon. Sir* Joseph Banks, *K. B. P. R. S.*

Read December 23, 1802.

Though the solubility of an individual gas in water forms, generally, a part of its chemical history, yet this property has been overlooked, in the examination of several species of the class of aëriform substances. The carbonic acid, indeed, is the only gas whose relation to water has been an object of much attention; and, at a very early period of its history, Mr. Cavendish, in the course of inquiries, the results of which were the groundwork of the most important subsequent discoveries, ascertained, with peculiar care, the proportion of carbonic acid gas condensible in water, at the temperature of 55° of Fahrenheit. Dr. Priestley also, about the same period, directed his

***Phil. Trans. R. Soc.*** London, January 1, 1803, 93 P.29-42;




Парциальные давления компонентов
над жидким раствором ацетон - хлороформ