Lecture 15 Conformational Equilibrium

$$aA + bB \rightleftharpoons cC + dD$$

(a, b, c, d: ν_i)

$$\Delta\bar{G}_{rxn} = \bar{G}_{products} - \bar{G}_{reactants}$$

$$\Delta\bar{G}_{rxn} = \sum_i \nu_i \mu_i \quad (\text{@ const } P, T)$$

$$\mu_i = \mu_i^\circ + RT\ln[i]$$

$$\Delta\bar{G}_{rxn} = \Delta\bar{G}^\circ_{rxn} + RT\ln Q$$

$$Q = \prod_i [i]^{\nu_i}$$

$$Q = \prod_i [i]^{\nu_i} = [A]^{\nu_A}[B]^{\nu_B}[C]^{\nu_C} \ldots$$

$$\ln(\prod) = \sum \ln$$

@ Eq $\Delta \bar{G}_{rxn} = 0$

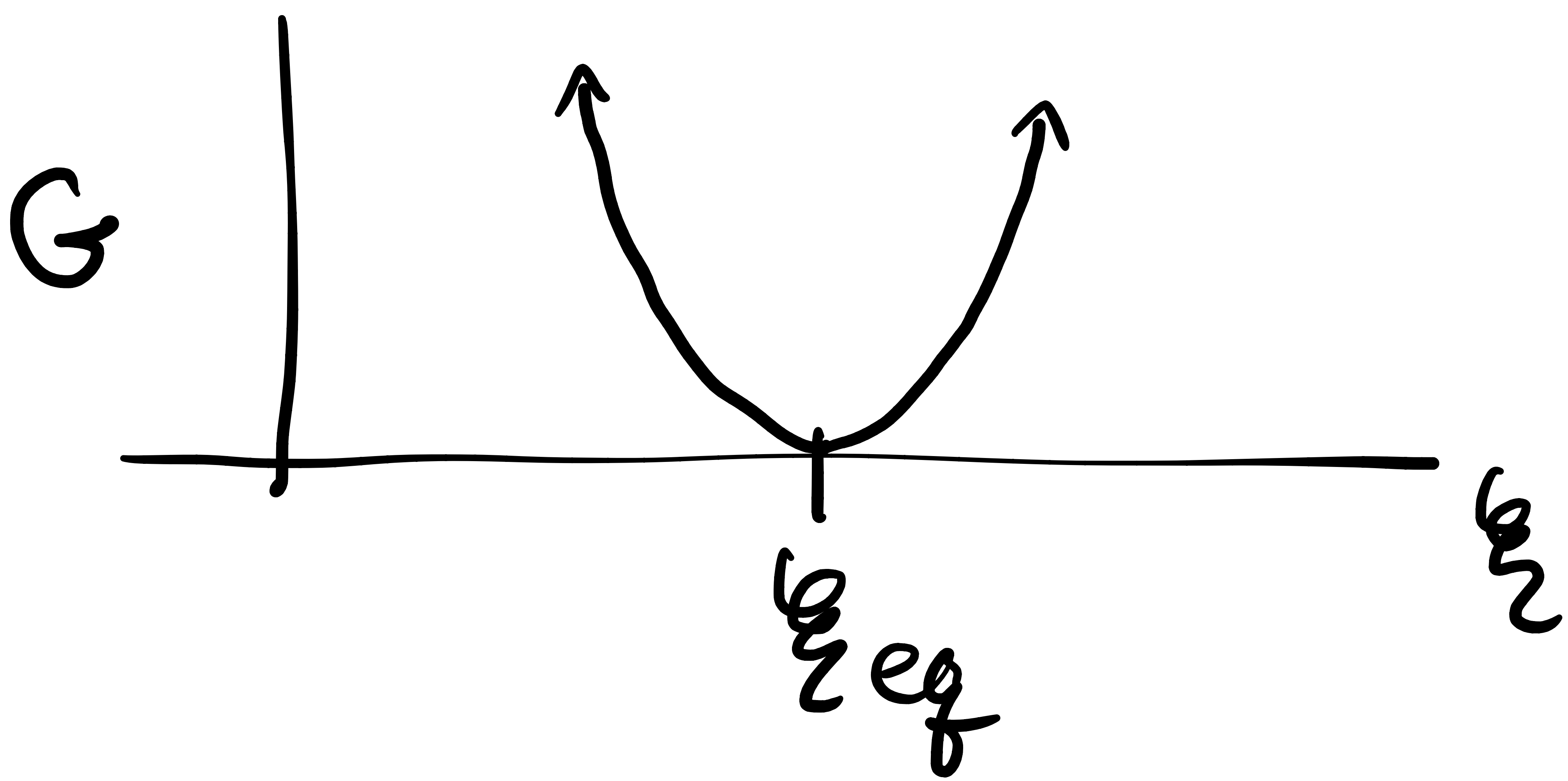
$$\Delta \bar{G}^\circ = -RT\ln(K_{eq})$$

$$\Delta \bar{G}_{rxn} = \Delta \bar{G}^\circ + RT\ln Q$$

$$= -RT\ln K + RT\ln Q = RT\ln(Q/K_{eq})$$

$$aA + bB \rightleftharpoons cC + dD$$

$$a\xi = b\xi = -c\xi = -d\xi$$



$$A \rightleftharpoons 2B$$

1M	0M	know K_{eq}
$1M - x$	$0M + 2x$	

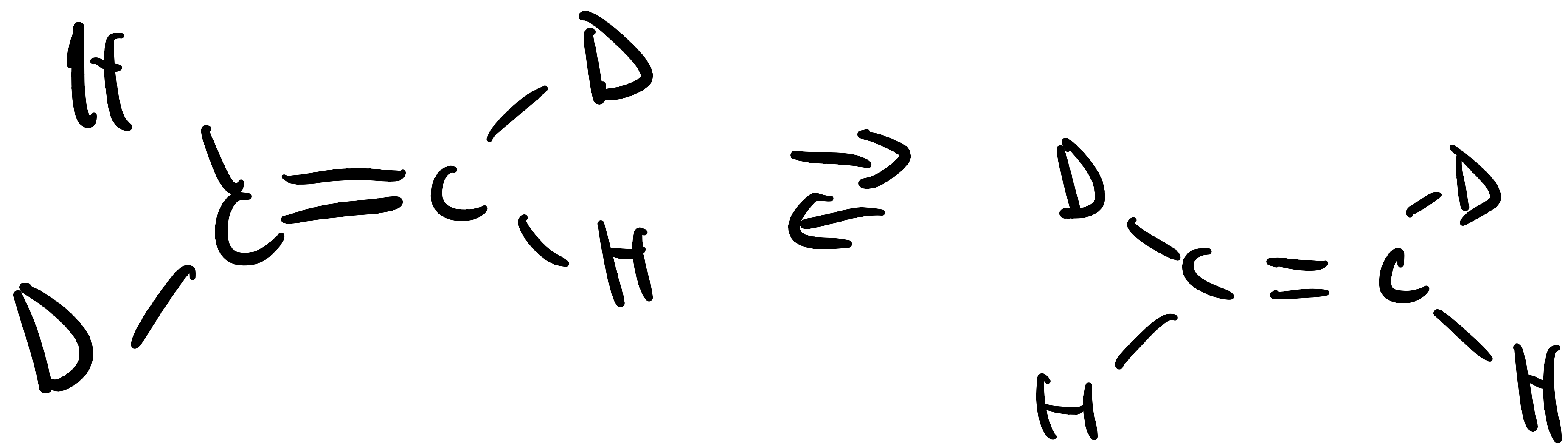
$$K_{eq} = \frac{(2x)^2}{1-x} \Rightarrow K - Kx = 4x^2$$

$$4x^2 + Kx - K = 0$$

$$x = \frac{-K \pm \sqrt{K^2 + 16K}}{8}$$

$$A \rightleftharpoons B \qquad K(T,P) = \frac{[B]}{[A]} = 1$$

If



if equally stable

$$\begin{array}{ccc} A & \rightleftharpoons & B \\ 1-x & & x \end{array}$$

$$\frac{x}{1-x} = 1$$

$$x = 1 - x$$

$$2x = 1 \Rightarrow x = 1/2$$

Dependence on temperature

$$-RT\ln(K_{eq}) = \Delta\bar{G}^{o} = \Delta\bar{H}^{o} - T\Delta\bar{S}^{o}$$

diff in entropy

diff btwn reactants & products

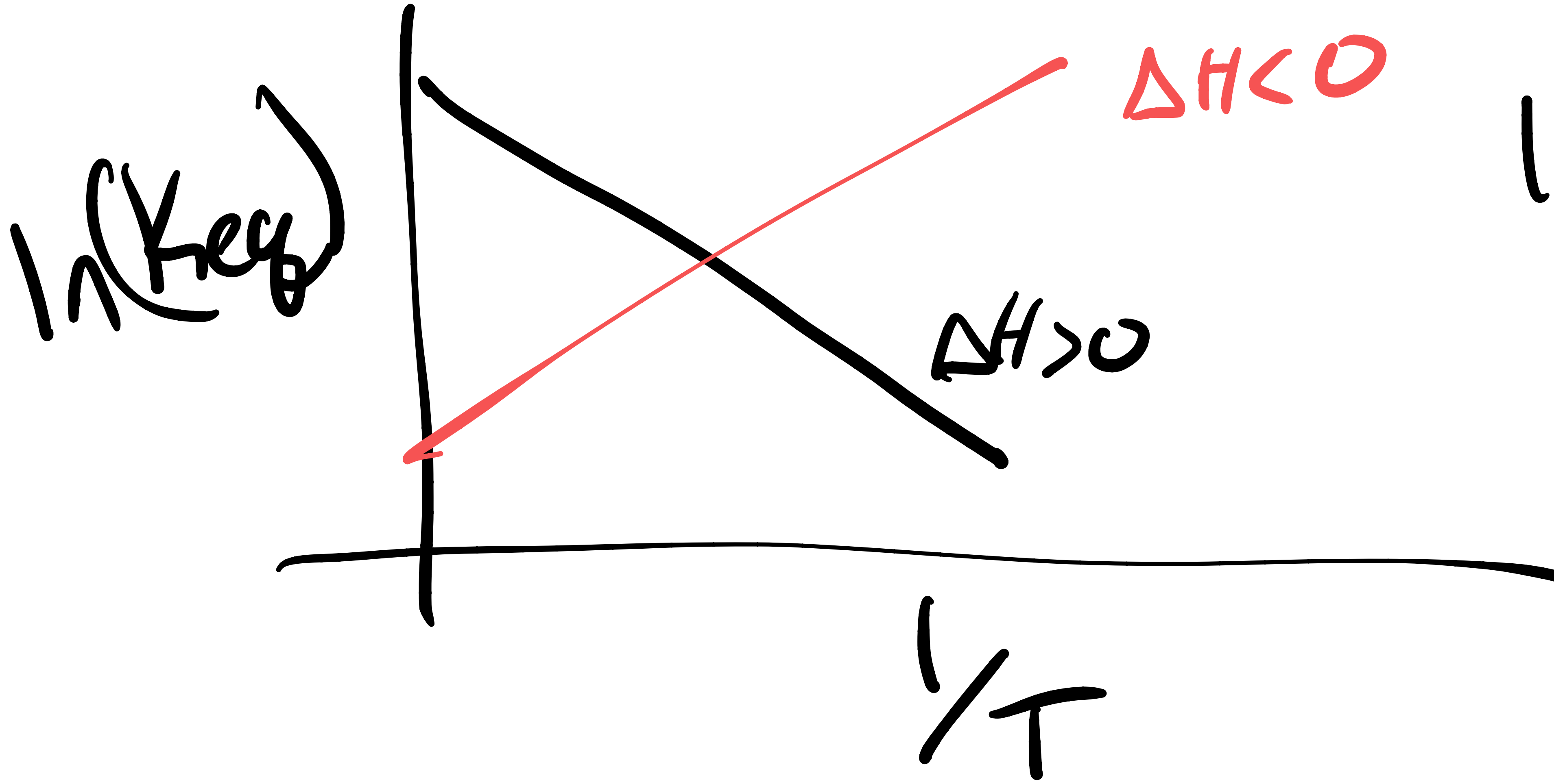
$\Delta\bar{H} < 0$

Exothermic reaction if heat is produced

Endothermic reaction, $\Delta\bar{H} > 0$

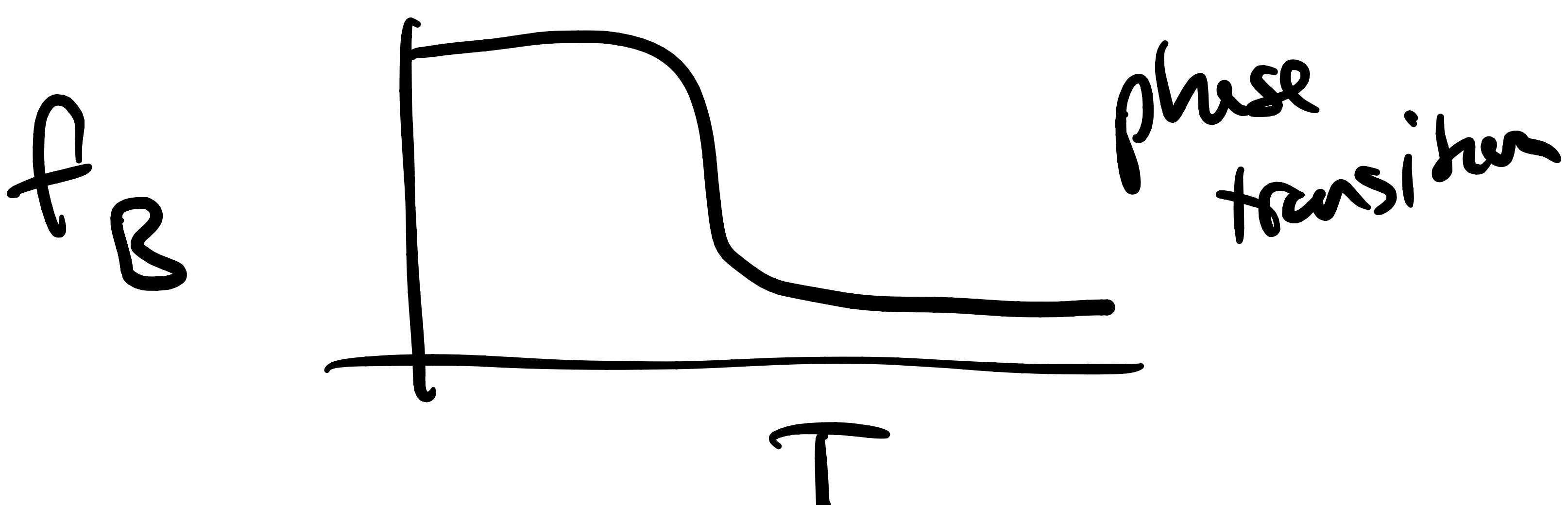
$$\ln(K_{eq}) = \frac{\Delta\bar{S}^{o}}{R} - \Delta\bar{H}^{o}/RT$$

Van't Hoff equation



$$\ln K = \frac{\Delta \bar{S}}{R} - \frac{\Delta \bar{H}}{R} \cdot \left(\frac{1}{T}\right)$$

(no phase transition)



$$A \rightleftarrows B$$

water   ice

Dependence on pressure

$$d(\Delta G_{rxn}) = -\Delta \bar{S}\, dT + \Delta \bar{V}\, dp$$

const T

$$\Delta \bar{V}^\circ = \left(\partial \Delta G^\circ / \partial p \right)_T \quad \text{(standard conditions)}$$

$$\Delta G^\circ(p) = \Delta G^\circ(p^{ref}) + (p - p^{ref}) \Delta \bar{V}^\circ$$

$$A(l) \rightleftarrows B(l) + C(gas)$$

$$\Delta \bar{V}^\circ >> 0$$

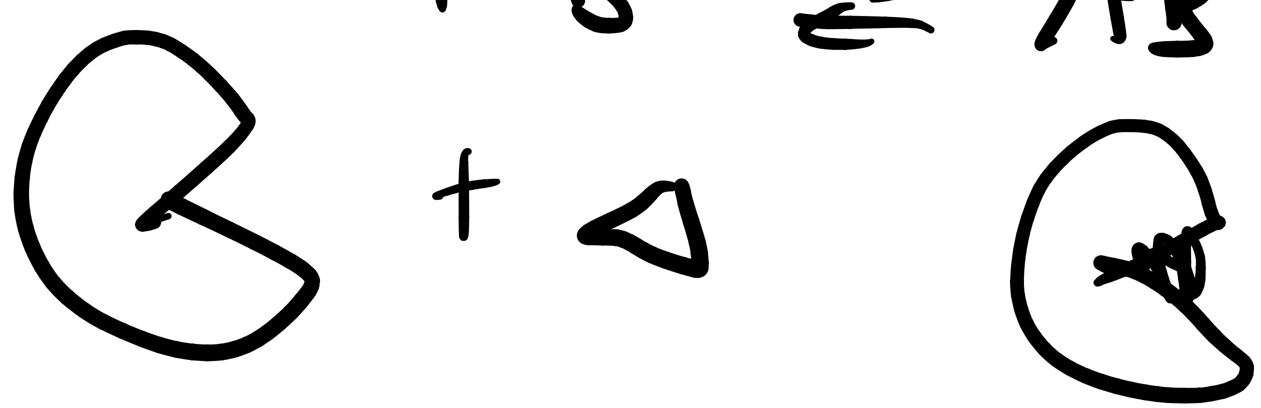
$$-RT \ln K_{eq}(p) = -RT \ln K_{eq}(p^{ref}) + (p - p^{ref}) \Delta \bar{V}^\circ$$

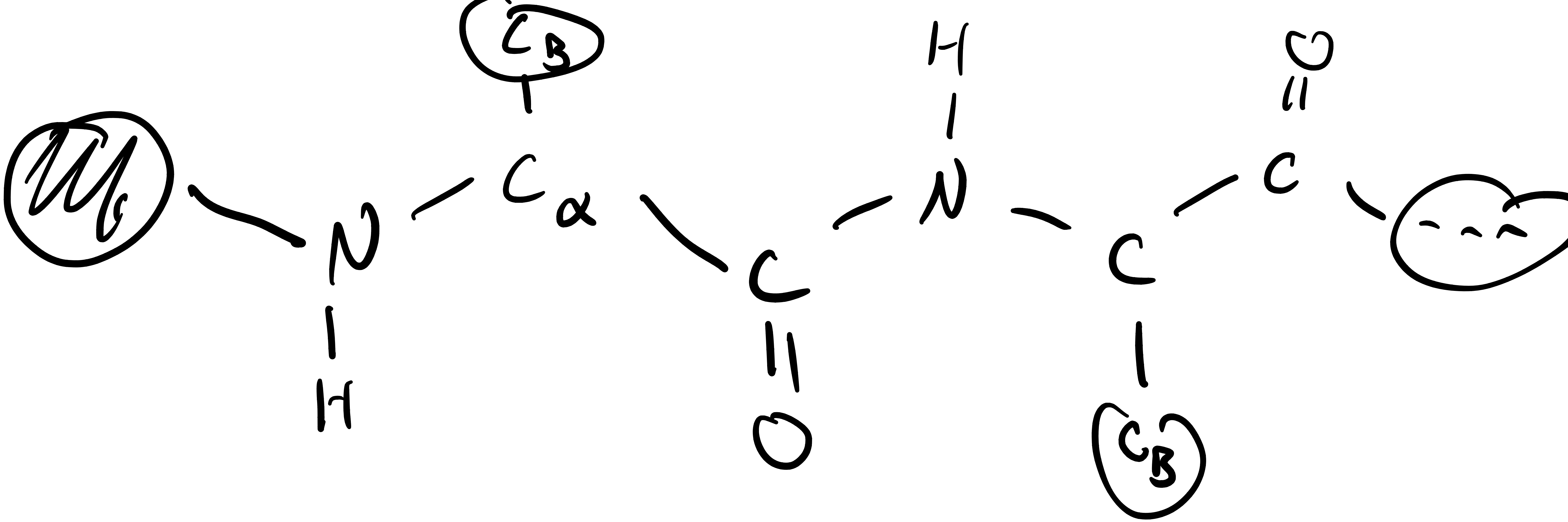
Conformational Equilibrium

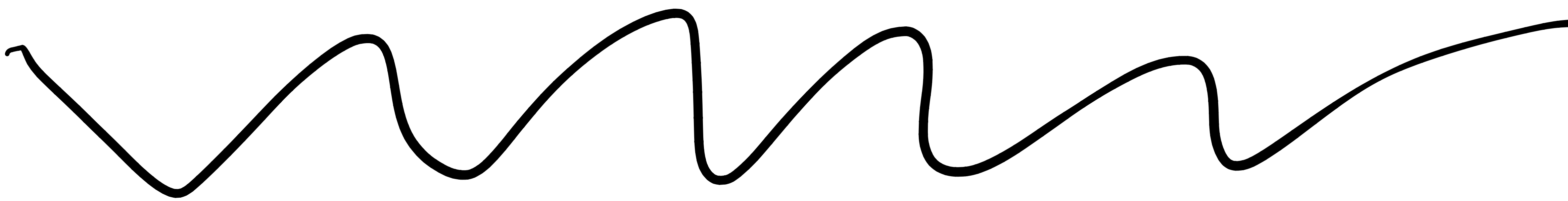
$$A \rightleftarrows B$$

Example: folded & unfolded state of a protein

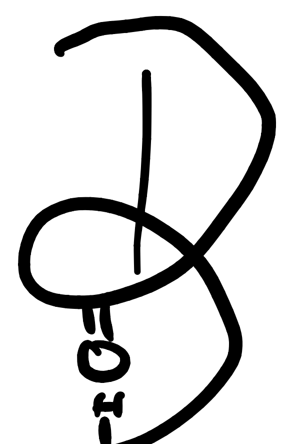
$$A + B \rightleftarrows AB$$







Unfolded
denatured



α Helix

$\Delta H < 0$

$\Delta S < 0$ usually

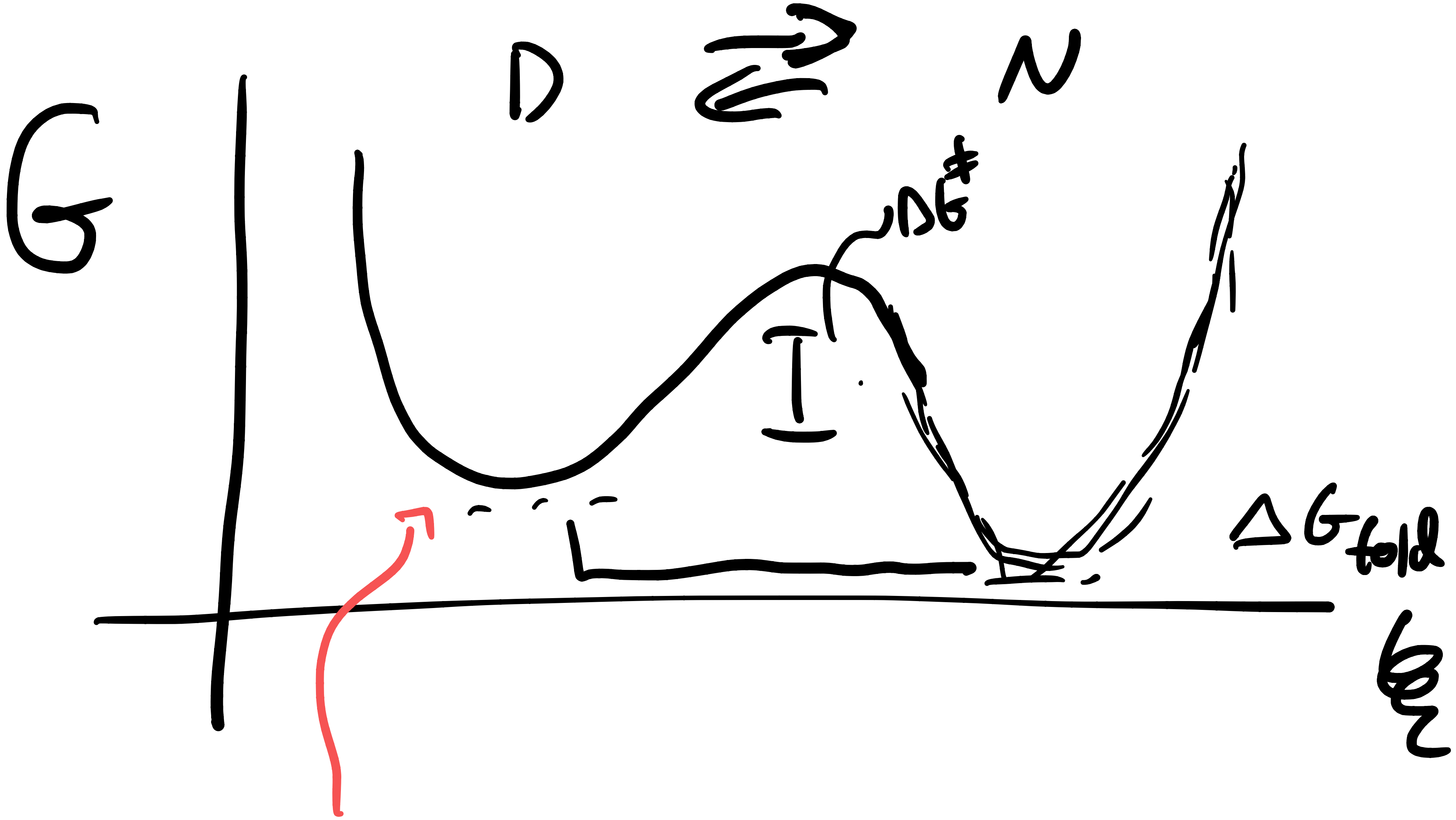
ΔG folding ~ -10 Kcal/mol

U $\rightleftharpoons$ Folded

Denatured $\rightleftharpoons$ Native

(@ Room temp)

How to measure ΔH_{fold}, ΔS folding



"metastable"

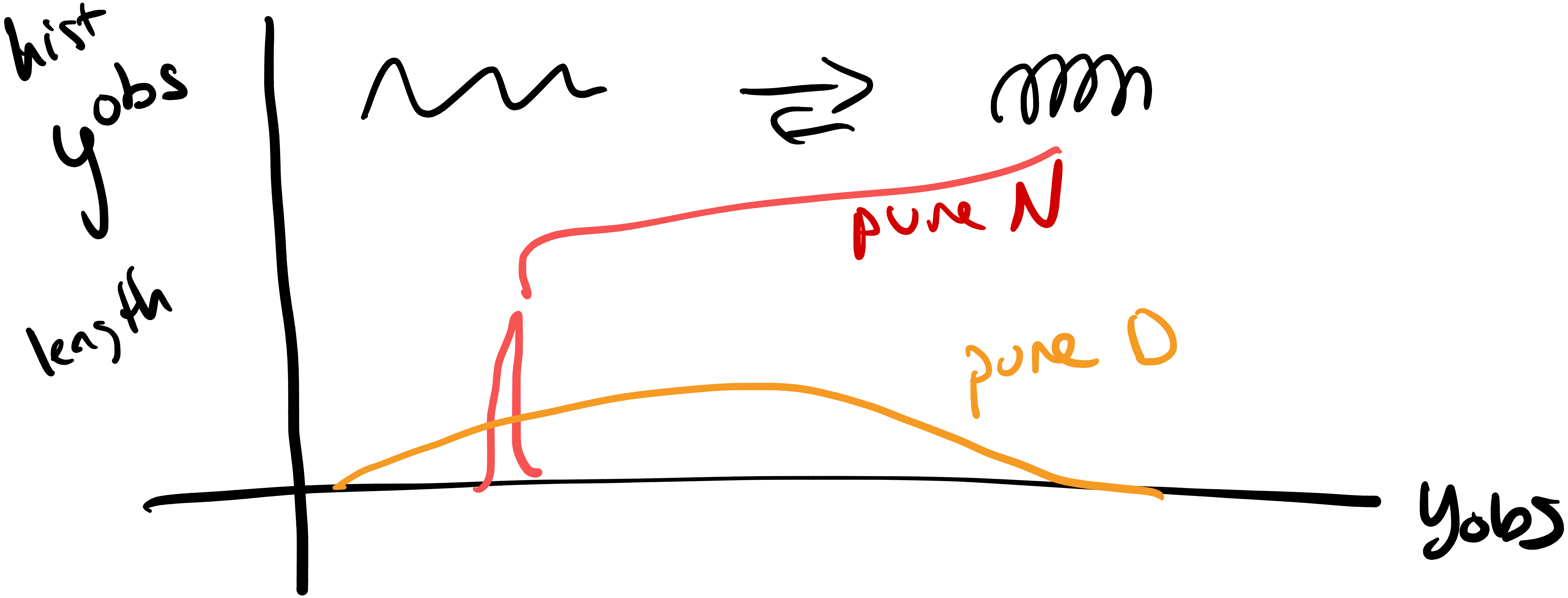
$D \rightleftharpoons N$

ξ

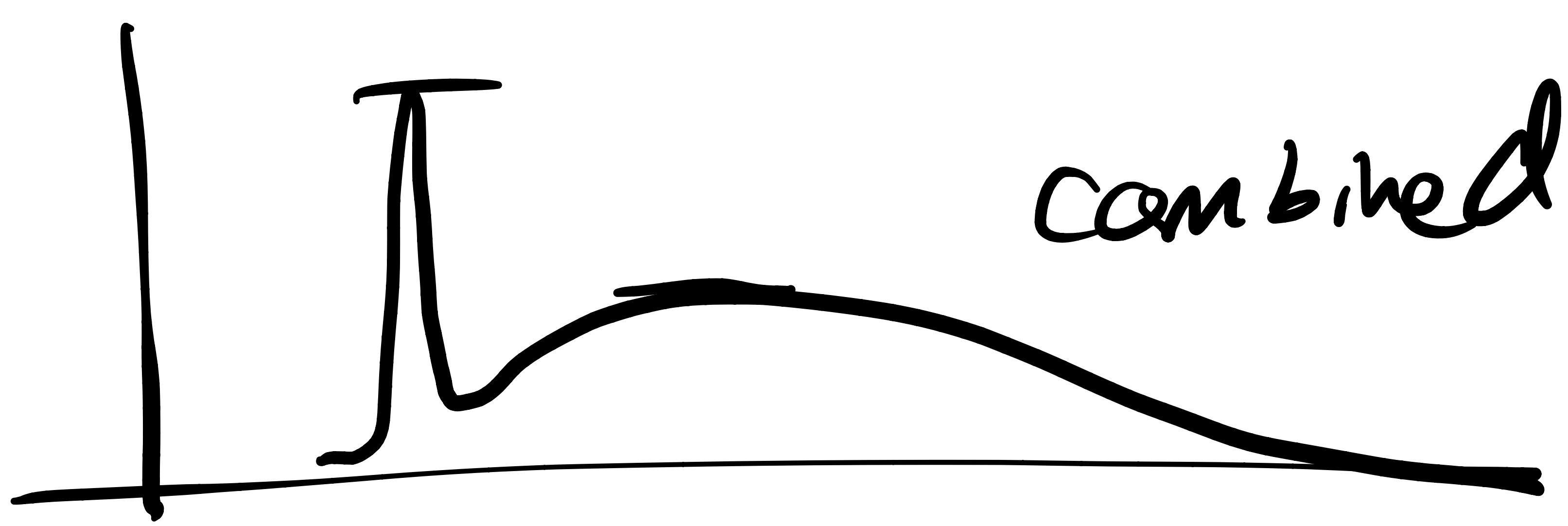
-10 kcal/mol

$$K_{eq} = e^{-\Delta G^\circ / RT}$$

↳ 0.6 kcal/mol

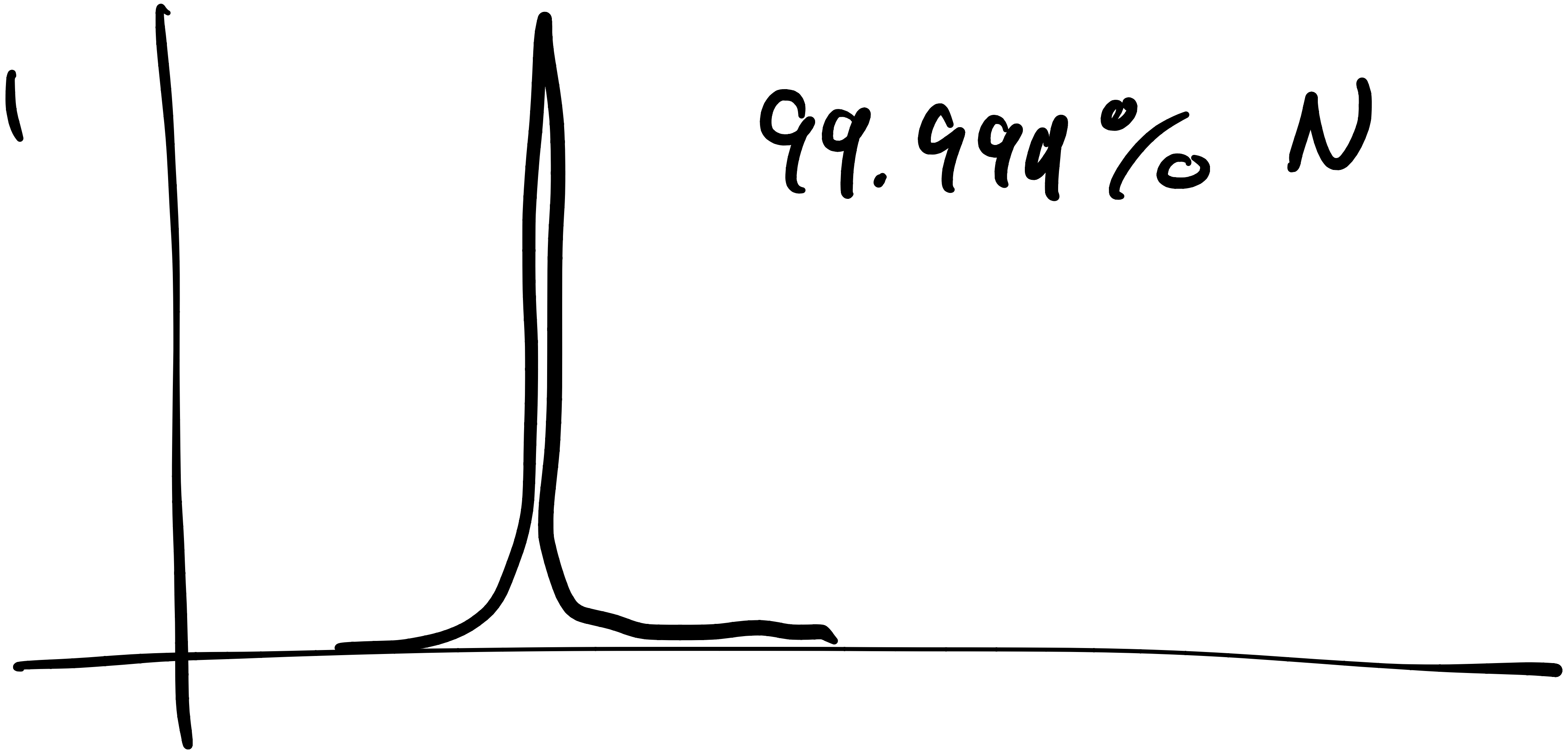


If 50/50 mixture



~> 50%
50% ~> K=1

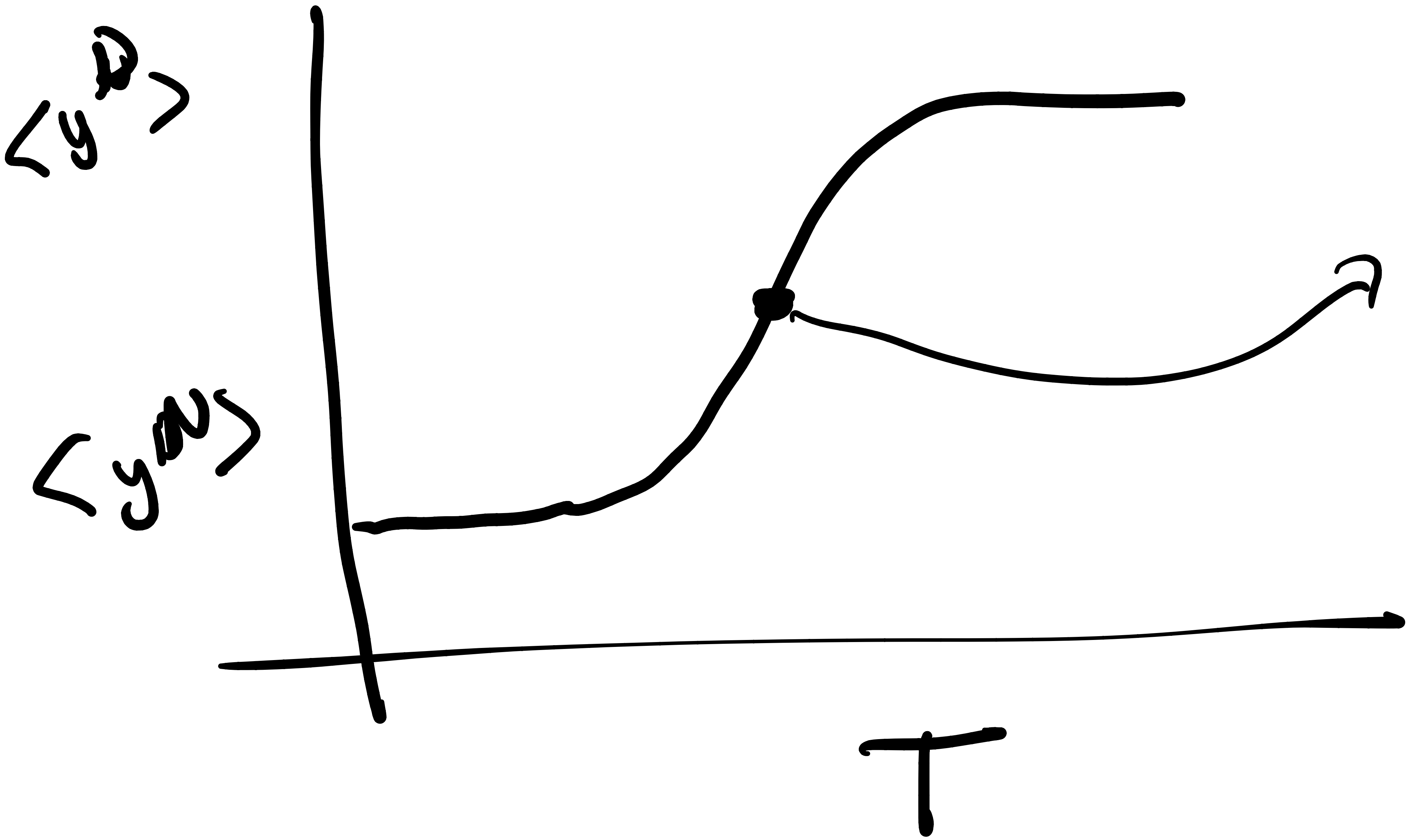
typical



99.999% N

how can we tell 98 from 99
from 99.9

Key is change conditions


$\langle y^D \rangle$
$\langle y^N \rangle$
T