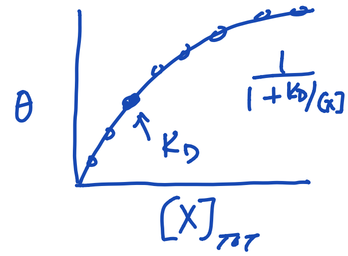
BINDING (11/6/19) BINDING METHODS?

$MX \rightleftharpoons M + X$

- SPECTROSCOPIC
- PULL DOWN
- ...

MEASURE $\theta = \frac{[MX]}{[M]_{TOT}}$



KNOW: $[M]_{TOT}$ $[X]_{TOT}$, NOT $[MX]$, (X), OR $[M]$

$$K_D = \frac{[M][X]}{[MX]} = \frac{(M_{TOT} - MX)(X_{TOT} - MX)}{MX}$$

IF $M \ll K_D$, $X \doteq X_{TOT}$. (MX NEVER DEPLETES X UNDER BINDING CONDITIONS).

$$K_D = \frac{(M_{TOT} - MX)X_{TOT}}{MX}$$

$$K_D MX = M_{TOT}X_{TOT} - MX \cdot X_{TOT}$$

$$K_D M_X + X_{TOT}M_X = M_{TOT}X_{TOT}$$

$$MX(K_D + X_{TOT}) = M_{TOT}X_{TOT}$$

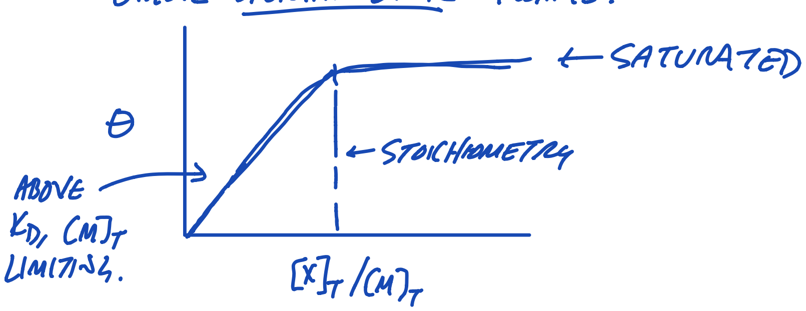
$$MX = \frac{M_{TOT}X_{TOT}}{K_D + X_{TOT}}$$

$$\theta = \frac{MX}{M_{TOT}} = \frac{\cancel{M_{TOT}}X_{TOT}}{\cancel{M_{TOT}}(K_D + X_{TOT})}$$

$$\theta = \frac{X_{TOT}}{K_D + X_{TOT}} = \frac{1}{K_D/X_{TOT} + 1}$$ ⇐ FIT THIS MODEL TO DATA.

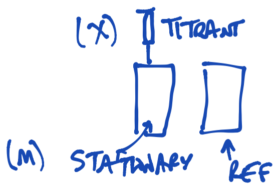
WHAT IF $M_{TOT} > K_D$?

- GET MORE COMPLEX FORM (SEE NOTES).
- ENTER STOICHIOMETRIC REGIME.

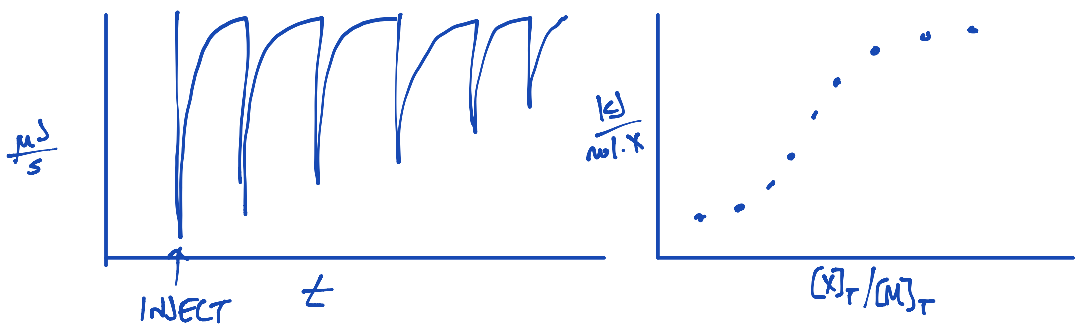


CAN WE LEARN ABOUT MORE THAN JUST ΔG?

PROBE BY ISOTHERMAL TITRATION CALORIMETRY.



1. INJECT SMALL AMOUNT OF TITRANT
2. APPLY POWER TO STATIONARY OR REF CELL TO MAINTAIN SAME TEMP IN BOTH CELLS.
3. MEASURE POWER



$$M + X \rightleftharpoons MX \qquad M_T = \text{TOTAL } [M]$$
$$\downarrow \quad \uparrow \qquad \uparrow \qquad X_T = \text{TOTAL } [X]$$

IF ENTHALPY CHANGE, THIS WILL EVOLVE / TAKE UP HEAT.

EXOTHERMIC ENDOTHERMIC

$dH = \delta Q$ (NO PdV WORK)

IF WE DUMP A TON OF TITRANT IN, GO TO ALL MX. $\oint \delta Q \rightarrow \underline{\Delta H}$.

WANT MORE INFORMATION.

ADD A LITTLE TITRANT:

$$\frac{MX_i}{M_T} \longrightarrow \frac{MX_{i+1}}{M_T} \quad (0 \rightarrow)$$

$$q_{i+1} \propto \Delta H \left(\frac{MX_{i+1}}{M_T} - \frac{MX_i}{M_T} \right)$$

ENTHALPY FOR RXN

STEP ON RXN COORD

SO WHAT DETERMINES MX_i? $[M]_T$, $[X]_T$, K_1

$$K_D = \frac{[M][X]}{[MX]}$$

$$K_D = \frac{(M_T - MX)(X_T - MX)}{MX}$$

$$K_D M_T = M_T X_T - M_T MX - X_T MX + MX^2$$

$$\emptyset = M_T X_T - K_D MX - M_T MX - X_T MX + MX^2$$

$$\emptyset = M_T X_T - (K_D + M_T + X_T) MX + MX^2$$

$$MX = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$MX = \frac{(K_D + M_T + X_T) - \sqrt{(K_D + M_T + X_T)^2 - 4[M]_T[X]_T}}{2}$$

IF WE KNOW K_D, WE CAN CALCULATE [MT]. IF WE KNOW ΔH AND MT, WE CAN CALCULATE q (WHAT WE OBSERVE). GUESS AND CHECK

FIT A MODEL WITH SINGLE K_D AND ΔH TO ALL OBSERVED HEATS VS. $[X]_T$.

IF YOU KNOW ΔH AND ΔG $(-RT\ln(K_D))$, YOU CAN FIND ΔS.

HOW CAN WE USE TO LEARN MECHANISM?

$\Delta H(T) = \Delta H_{REF} + \Delta C_p (T - T_{REF})$ DO ITC @ MULTIPLE TEMP. IF $\Delta C_p > \emptyset$, LARGE HYDROPHOBIC CONTRIBUTION!