

Course 565/665 Lecturer Prof. Cavagnero
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Dealing with q and w in biology.

try to relate q and w to state fns.

$$du = \delta q + \delta w$$

for Adiabatic system: $\delta q = 0$. so $du = \delta w$.

under no work conditions. $\delta w = 0$, $du = \delta q$

$$\begin{aligned} du &= Tds - pdv \quad (\text{for closed system}) \\ &= \delta q + \delta w \end{aligned}$$

* under quasistatic conditions,

* only pV work. $\delta w = -pdv$

$$\delta q = Tds \quad \text{or} \quad ds = \frac{\delta q}{T}$$

reversible processes.

$$A \rightleftharpoons B$$

* go back & forth

* under quasi-static condition, maximum of w is produced.

$$\text{need } \Delta S_{\text{tot}} = 0$$

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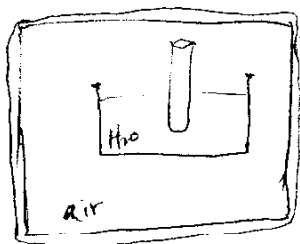
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Chapter 8: F. H. G

$U - S$: hard to measure.

— need new relations that apply to specific system.

Helmholtz Free energy F :



$$dS_{\text{combined}} = dS_{\text{sys}} + dS_{\text{bath}} \geq 0 \quad \dots \textcircled{1}$$

$$dU_{\text{tot}} = dU_{\text{sys}} + dU_{\text{bath}} = 0$$

if only one kind of molecule in surrounding

& if $T = \text{const.}$; $V_{\text{sys}} = \text{const.}$ $V_{\text{sur}} = \text{const.}$
 $N_{\text{sys}}, N_{\text{sur}} = \text{const.}$

$$dS_{\text{bath}} = \frac{1}{T} dU_{\text{bath}} + \frac{P}{T} dV_{\text{bath}} - \frac{\mu}{T} dN_{\text{bath}}$$

$$\therefore dU_{\text{bath}} = T dS_{\text{bath}}$$

$$= -dU_{\text{sys}}$$

$$\therefore dS_{\text{bath}} = -\frac{dU_{\text{sys}}}{T}$$

back to $\textcircled{1}$:

$$dS_{\text{sys}} - \frac{dU_{\text{sys}}}{T} \geq 0$$

$$\Rightarrow dU_{\text{sys}} - T dS_{\text{sys}} \leq 0$$

$$d(U_{\text{sys}} - T S_{\text{sys}}) \leq 0$$

define $F_{\text{sys}} = U_{\text{sys}} - T S_{\text{sys}}$

$$dF_{\text{sys}} \leq 0 \quad \text{const } T, V, N$$

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