20.110J / 2.772J / 5.601J
Thermodynamics of Biomolecular Systems
Instructors: Linda G. Griffith, Kimberly Hamad-Schifferli, Moungi G. Bawendi, Robert W. Field

20.110/5.60 Fall 2005   Lecture #8   page   1

Fundamental Equations, Equilibrium, Free Energy, Maxwell Relations

- **Fundamental Equations** relate functions of state to each other using 1st and 2nd Laws

    1st law with expansion work: $dU = đq - p_{ext}dV$

    need to express đq in terms of state variables because đq is path dependent

    Use 2nd law: $đq^{rev} = TdS$

    For a <u>reversible</u> process $p_{ext} = p$ and $đq = đq^{rev} = TdS$

    So……   ** $\boxed{dU = TdS - pdV}$ **

    This fundamental equation only contains <u>state</u> variables

    Even though this equation was derived for a reversible process, the equation is <u>always correct and valid</u> for a closed (no mass transfer) system, even in the presence of an irreversible process. This is because U, T, S, p, and V are all functions of state and independent of path.

    AND   The "best" or "natural" variables for U are <u>S and V</u>,

                        ** $\boxed{U(S,V)}$ **

20.110J / 2.772J / 5.601J
Thermodynamics of Biomolecular Systems
Instructors: Linda G. Griffith, Kimberly Hamad-Schifferli, Moungi G. Bawendi, Robert W. Field

20.110/5.60 Fall 2005   Lecture #8   page   2

$$** \boxed{U(S,V)} **$$

From dU = TdS – pdV $\Rightarrow$ ** $\boxed{\left(\frac{\partial U}{\partial S}\right)_V = T \quad ; \quad \left(\frac{\partial U}{\partial V}\right)_S = -p}$ **

We can write similar equations for <u>enthalpy</u>

H = U + pV $\Rightarrow$ dH = dU + d(pV) = dU + pdV + Vdp

inserting dU = TdS – pdV

$\Rightarrow$ ** $\boxed{\text{dH = TdS + Vdp}}$ **

The natural variables for H are then <u>S and p</u>

$$** \boxed{H(S,p)} **$$

From dH = TdS + Vdp $\Rightarrow$ ** $\boxed{\left(\frac{\partial H}{\partial S}\right)_p = T \quad ; \quad \left(\frac{\partial H}{\partial Vp}\right)_S = V}$ **

_____

We can use these equations to find how S depends on T.

From dU = TdS – pdV $\Rightarrow$ $\boxed{\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V = \frac{C_v}{T}}$

From dH = TdS + Vdp $\Rightarrow$ $\boxed{\left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p = \frac{C_p}{T}}$

20.110J / 2.772J / 5.601J
Thermodynamics of Biomolecular Systems
Instructors: Linda G. Griffith, Kimberly Hamad-Schifferli, Moungi G. Bawendi, Robert W. Field

20.110/5.60 Fall 2005   Lecture #8   page   3

Criteria for Spontaneous Change

The 2nd Law gave the Clausius inequality for spontaneous change

$$dS > đq/T_{surr.}$$

The 1st law gave us $dU = đq + đw$

Putting the two together, assuming only pV work, gives us the following <u>general</u> criterion for spontaneous change:

$$** \boxed{dU + p_{ext}dV - T_{surr}dS < 0} **$$

Equilibrium is when there is no possible change of state that would satisfy this inequality.

We can now use the general criterion above under <u>specific</u> conditions

- Consider first an <u>isolated system</u> (q=w=0, $\Delta V=0$, $\Delta U=0$)

    Since dU=0 and dV=0, from the general criterion above, then

$$\boxed{(dS)_{U,V} > 0}$$

    is the criterion for spontaneity for an <u>isolated</u> system

And equilibrium for an <u>isolated</u> system is then achieved when <u>entropy is maximized</u>. At maximum entropy, no spontaneous changes can occur.

- Consider now <u>S and V constant</u>

20.110J / 2.772J / 5.601J
Thermodynamics of Biomolecular Systems
Instructors: Linda G. Griffith, Kimberly Hamad-Schifferli, Moungi G. Bawendi, Robert W. Field

20.110/5.60 Fall 2005   Lecture #8   page   4

$$\Rightarrow \boxed{(dU)_{S,V} < 0}$$

is the criterion for spontaneity under <u>constant V and S</u>

At <u>constant S and V</u>, equilibrium is achieved when <u>energy is minimized</u>

- Consider now <u>S constant and $p=p_{ext}$ constant</u>

$$\Rightarrow \ dU + pdV < 0 \ \Rightarrow \ d(U + pV) < 0$$
$$=H$$

So $\Rightarrow \boxed{(dH)_{S,pext} < 0}$

is the criterion for spontaneity under <u>constant S and constant $p=p_{ext}$.</u>

- Consider now <u>H constant and $p=p_{ext}$ constant</u>

$$dU + pdV - T_{surr}dS < 0$$

but $dU + pdV = dH$, which is 0 (H is constant)

So $\boxed{(dS)_{H,p=pext} > 0}$

is the criterion for spontaneity under <u>constant H and constant $p=p_{ext}$.</u>

Now let's begin considering cases that are <u>experimentally</u> more controllable.

- Consider now <u>constant $T=T_{surr}$ and constant V</u>

20.110J / 2.772J / 5.601J
Thermodynamics of Biomolecular Systems
Instructors: Linda G. Griffith, Kimberly Hamad-Schifferli, Moungi G. Bawendi, Robert W. Field

20.110/5.60 Fall 2005   Lecture #8   page 5

$$\Rightarrow \ dU - TdS < 0 \ \Rightarrow \ d(U - TS) < 0$$

Define $\boxed{A = U - TS}$, the $\boxed{\text{Helmholtz Free Energy}}$

Then $\boxed{(dA)_{V,T=Tsurr} < 0}$

is the criterion for spontaneity under constant $T=T_{surr}$ and constant V.

For constant V and constant $T=T_{surr}$, equilibrium is achieved when the Helmholtz free energy is minimized.

We now come to the most important and applicable constraint:
- Consider now constant $T=T_{surr}$ and constant $p=p_{ext}$.

$$(dU + pdV - TdS) < 0 \ \Rightarrow \ d(U + pV - TS) < 0$$

Define $\boxed{G = U + pV - TS}$, the $\boxed{\text{Gibbs Free Energy}}$

(can also be written as $G = A + pV$ and $G = H - TS$)

Then $\boxed{(dG)_{p=pext,T=Tsurr} < 0}$

is the criterion for spontaneity under constant $T=T_{surr}$ and constant $p=p_{ext}$.

At constant $p=p_{ext}$ and constant $T=T_{surr}$, equilibrium is achieved when the Gibbs free energy is minimized.

Consider the process:

$$A(p,T) = B(p,T) \qquad \text{(keeping p and T constant)}$$

20.110J / 2.772J / 5.601J
Thermodynamics of Biomolecular Systems
Instructors: Linda G. Griffith, Kimberly Hamad-Schifferli, Moungi G. Bawendi, Robert W. Field

20.110/5.60 Fall 2005   Lecture #8   page   6

Under constant $p=p_{ext}$ and $T=T_{surr}$,

$$\Delta G < 0 \qquad A \rightarrow B \text{ is spontaneous}$$
$$\Delta G = 0 \qquad A \text{ and } B \text{ are in equilibrium}$$
$$\Delta G > 0 \qquad \text{then } B \rightarrow A \text{ is spontaneous}$$

Maxwell Relations

- With the free energies

    Helmholtz free energy $A = U - TS$
    Gibbs free energy $G = H - TS$

we've introduced all our state functions. For closed systems,

$$U(S,V) \quad \Rightarrow \quad dU = TdS - pdV$$
$$H(S,p) \quad \Rightarrow \quad dH = TdS + Vdp$$
$$A(T,V) \quad \Rightarrow \quad dA = -SdT - pdV$$
$$G(T,p) \quad \Rightarrow \quad dG = -SdT + Vdp$$

Fundamental equations

From $\qquad dA = \left(\dfrac{\partial A}{\partial T}\right)_V dT + \left(\dfrac{\partial A}{\partial V}\right)_T dV$

and $\qquad dG = \left(\dfrac{\partial G}{\partial T}\right)_p dT + \left(\dfrac{\partial G}{\partial p}\right)_T dp$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \left(\frac{\partial A}{\partial V}\right)_T = -p$$
$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$

20.110J / 2.772J / 5.601J
Thermodynamics of Biomolecular Systems
Instructors: Linda G. Griffith, Kimberly Hamad-Schifferli, Moungi G. Bawendi, Robert W. Field

20.110/5.60 Fall 2005   Lecture #8   page 7

The <u>Maxwell relations</u>: $\dfrac{\partial^2 A}{\partial V \partial T} = \dfrac{\partial^2 A}{\partial T \partial V}$ and $\dfrac{\partial^2 G}{\partial p \partial T} = \dfrac{\partial^2 G}{\partial T \partial p}$

now allow us to find how S depends on V and p.

$$\Rightarrow \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$
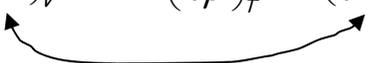
These can be obtained from an equation of state.

We can now also relate U and H to p-V-T data.

$$\left.\begin{array}{l} \left(\dfrac{\partial U}{\partial V}\right)_T = T\left(\dfrac{\partial S}{\partial V}\right)_T - p = T\left(\dfrac{\partial p}{\partial T}\right)_V - p \\[3mm] \left(\dfrac{\partial H}{\partial p}\right)_T = T\left(\dfrac{\partial S}{\partial p}\right)_T + V = V - T\left(\dfrac{\partial V}{\partial T}\right)_p \end{array}\right\} \rightarrow U \text{ and } H \text{ from equations of state!}$$

•   For an ideal gas $pV = nRT$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V} = \frac{p}{T} \quad \Rightarrow \quad \left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p} = \frac{V}{T} \quad \Rightarrow \quad \left(\frac{\partial H}{\partial p}\right)_T = 0$$

This <u>proves</u> that for an ideal gas $U(T)$ and $H(T)$, functions of T only. We had <u>assumed</u> this was true from Joule and Joule-Thomson expansion experiments. Now we know it is rigorously true.