

Previously, in Chapter 2, we saw that for simple heating or cooling (no phase change, or reaction).

At constant P

$$\Delta H = n\bar{C}_p(T_2 - T_1) = C_p(T_2 - T_1)$$

(what is difference between $\bar{C}_p$ and C_p ?)

But at constant V ,

$$\Delta E = C_v(T_2 - T_1)$$

What about ΔS for heating/cooling?

We know that at: ~~any~~

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{REV}}{T} \quad \text{but } dq = C dT$$

$$\text{So } \Delta S = \int_{T_1}^{T_2} \frac{C dT}{T}$$

At constant P, $C = C_p = \text{constant}$

IF C_p is independent of temperature then

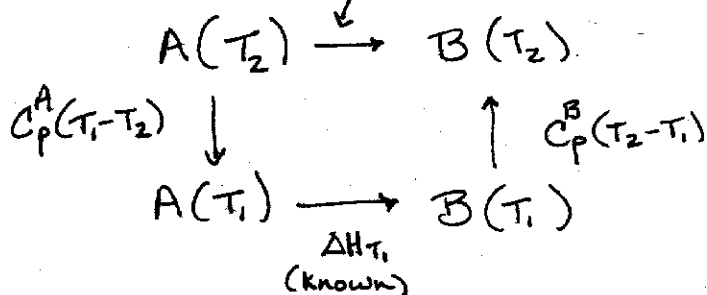
$$\Delta S = C_p \int_{T_1}^{T_2} \frac{dT}{T} = C_p \ln T_2/T_1$$

Similarly, at constant V , and C_v independent of T

$$\Delta S = C_v \int_{T_1}^{T_2} \frac{dT}{T} = C_v \ln T_2/T_1$$

(2)

Before, if we wanted ΔH ^{for a reaction} at some new temperature, we could use ^{unknown}

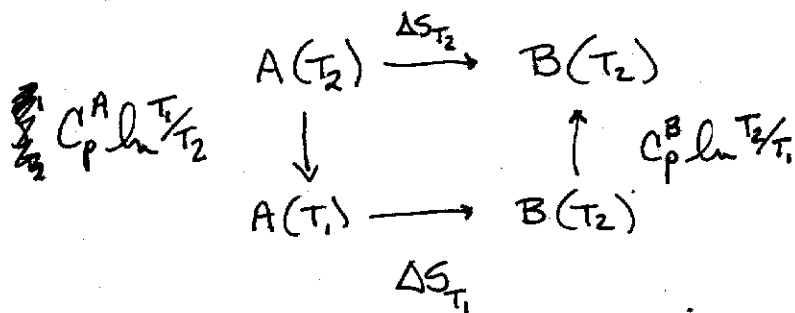


(p 47 Chapt 2)

For constant P

$$\Delta H_{T_2} = C_p^A(T_1-T_2) + \Delta H_{T_1} + C_p^B(T_2-T_1) = \Delta H_{T_1} + (C_p^B - C_p^A)(T_2-T_1)$$

Why T_1/T_2 ? Similarly for ΔS at some new temperature



Therefore,

$$\begin{aligned}
 \Delta S_{T_2} &= C_p^A \ln T_1/T_2 + \Delta S_{T_1} + C_p^B \ln T_2/T_1 \\
 &= (C_p^B - C_p^A) \ln T_2/T_1 + \Delta S_{T_1}
 \end{aligned}$$

The above is well and good for simple heating

WITH NO PHASE TRANSITIONS or other chemical changes...

ΔS for phase transitions

$$\Delta S = \frac{q_{REV}}{T}$$

If the ~~reaction~~ phase transition occurs at the temperature (T_m) at which the transition is reversible
(e.g. melting ice at 0°C or condensing steam at 100°C)

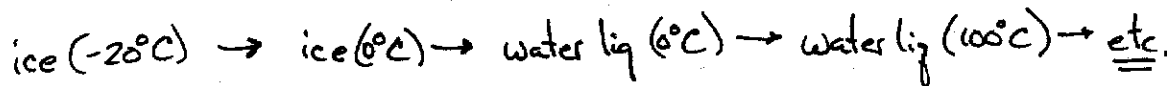
then the process is reversible, and therefore the measured heat (q_m) is q_{REV}

$$\text{and } \Delta S = \frac{q_m}{T_m}$$

We have seen in the homework how this is useful.

So we know how to figure ΔS for temp changes and for (isothermal) phase changes.

Often we need both



Pressure dependence $S_{P_2} - S_{P_1} = -nR \ln \frac{P_2}{P_1} \quad (\text{gases})$

Gibbs Free Energy

Most reactions that life scientists care about occur at constant T and P

$$(P = 1 \text{ atm}) \quad (T = \overset{(25^\circ\text{C})}{298\text{K}} \text{ or } \overset{(37^\circ\text{C})}{310\text{K}})$$

Gibbs Free Energy tells us this

$$G = H - TS$$

Extensive
State
Variable

$$\text{OR } \Delta G = \Delta H - T\Delta S \quad (\text{why not } \Delta(TS)?)$$

Molar Gibbs Free Energy: $\bar{G} = \bar{H} - T\bar{S}$ (per mole)

(to a 1st approx.)

In principle, the chemical potential is given by

$$\mu = \bar{G}$$

$\Delta\mu < 0 \Rightarrow$ Reaction or process CAN occur spontaneously

$\Delta\mu > 0 \Rightarrow$ Reaction cannot/will not occur spontaneously.

$\Delta\mu = 0 \rightarrow$ Reaction is at equilibrium.

(replace $\Delta\mu$ by ΔG - same thing)

Let's explore WHY.

Remember that ~~Eq 2.10~~ $\Delta S = \frac{q_{REV}}{T}$ for reversible process

and $\Delta S > \frac{q_{IRREV}}{T}$ for irreversible process
(p. 80) (spontaneous)

Constant T

$$\therefore \Delta S \geq \frac{q}{T} \quad (\text{both cases})$$

From $\Delta E = q + w$, we have $q = \Delta E - w$

$$\underline{\underline{\text{So}}} \quad \Delta S \geq \frac{\Delta E - w}{T}$$

if we allow only expansion/compression work (Const P, but not V)
then

$$w = -P \Delta V$$

$$\begin{aligned} \therefore \Delta S &\geq \frac{\Delta E + P \Delta V}{T} \quad (\text{Const T and P}) \\ &\geq \frac{E_2 - E_1 + PV_2 - PV_1}{T} = \frac{(E_2 + PV_2) - (E_1 + PV_1)}{T} \quad \leftarrow \text{Eq 2.12} \\ &\geq \frac{H_2 - H_1}{T} = \frac{\Delta H}{T} \quad (\text{Remember } H = E + PV) \end{aligned}$$

$$\underline{\underline{\text{So}}} \quad \Delta S \geq \frac{\Delta H}{T}$$

$$\underline{\underline{\text{OR}}} \quad T \Delta S \geq \Delta H$$

$$\Delta H - T \Delta S \leq 0$$

$$\Delta G \leq 0$$

$\Delta G < 0$ spontaneous

$\Delta G = 0$ equilibrium

$\Delta G > 0$ not spontaneous

(6)

G is derived from state variables and so therefore is a state variable itself.

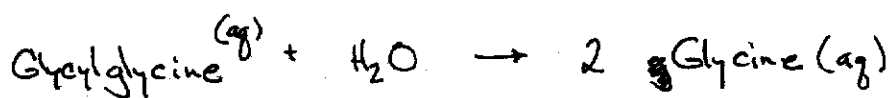
Consequently, all the familiar rules/games apply

$$\Delta G^\circ = \sum \bar{G}_f^\circ (\text{prods}) - \sum \bar{G}_f^\circ (\text{reactants})$$

Look things up in the tables.

(or look up $\bar{H}_f^\circ$ and $\bar{S}_f^\circ$ values and combine)

Are proteins stable?



P. 91

$$\Delta G_{25}^\circ = 2\bar{G}^\circ (\text{glycine, s}) - \bar{G}^\circ (\text{glycylglycine, s}) - \bar{G}^\circ (\text{H}_2\text{O})$$

[We use $\bar{G}^\circ(\text{s})$ because we don't have $\bar{G}^\circ(\text{aq})$
book says they're close]

Result

$$\Delta G_{25}^\circ = -27.6 \text{ kJ} \cdot \text{mol}^{-1}$$

Answer: No, the dipeptide (and proteins) are not stable
and CAN spontaneously hydrolyze.

The converse of this is that amino acids will not spontaneously (even with a catalyst) assemble into proteins (we must couple to other spontaneous rxns).

Fortunately, KINETICS saves us!

Another implication:

Proteases can speed up the spontaneous reaction and so need no ATP, etc

IF (and this is NOT true for rxns like protein folding)
 ΔH and ΔS are relatively independent of T ,
 then

$$\Delta G_{T_2} = \Delta H_{25^\circ\text{C}} - T_2 \Delta S_{25^\circ\text{C}}$$

Note that

$$\Delta G_{25^\circ} = \Delta H_{25^\circ} - (298\text{K}) \Delta S_{25^\circ}$$

Subtracting: $\Delta G_{T_2} - \Delta G_{25} = 0 + (298 - T_2) \Delta S_{25}$

If $\Delta S < 0$ then ΔG increases (less spont) w/ $T \uparrow$

If $\Delta S > 0$ then ΔG decreases (more spont) w/ $T \uparrow$

From $\frac{\Delta G_{25}}{298} = \frac{\Delta H_{25}}{298} - \Delta S_{25}$

and $\frac{\Delta G_{T_2}}{T_2} = \frac{\Delta H_{T_2}}{T_2} - \Delta S_{T_2}$

Again if $\Delta H_{25} \approx \Delta H_{T_2}$ and $\Delta S_{25} \approx \Delta S_{T_2}$ (temp indep)

then $\frac{\Delta G_{T_2}}{T_2} - \frac{\Delta G_{25}}{298} = \left(\frac{1}{T_2} - \frac{1}{298} \right) \Delta H$

If ΔH and ΔS ARE dependent on T , the calculations get more complicated.

One result:

$$\frac{\Delta G_{T_2}}{T_2} - \frac{\Delta G_{T_1}}{T_1} = - \int_{T_1}^{T_2} \frac{\Delta H(T)}{T^2} dT$$

↖ Function of T

Phase Changes

If a phase change takes place at its equilibrium temperature and pressure, then

$$\Delta G = 0 \quad (\text{equilibrium})$$

To characterize $\Delta G_{\text{phase change}}$ at other T 's use previous equations
