Week 4 Recitation

Chapter 3 and Chapter 4

Ch 4 reading: 101-117, 135-138, 143-146 (equations)

Questions?

HW2 Mistakes: Sign Errors

Some fixed by paying careful attention to the language used:

- Absorbed, stored, (+)dT = +
- Evolved, gives off, (-)dT = -

Others by thinking a bit about the number:

- Does reporting a negative mass make sense?
- What is the sign of dH_{vap} for vaporization? Condensation?

Finally, check your answer after executing your code.

HW2 Mistakes: 3.24b

Process: **Isobaric** expansion of 1 mol water vapor from 20 to 25 L

dS = n*Cp$_m$*ln(V2/V1)

dS = 8.14 J/K

$$dS = \frac{dq_{rev}}{T} = \frac{Cp_m dT}{T}$$

$$\int dS = Cp_m \int_{T_1}^{T_2} \frac{1}{T} dT$$

$$\Delta S = Cp_m \ln \frac{T_2}{T_1} = Cp_m \ln \frac{V_2}{V_1}$$

Some treated as **isothermal** expansion…

dS = n*R*ln(V2/V1)

dS = 1.86 J/K

$$dS = \frac{dq_{rev}}{T} = \frac{dU - dw_{rev}}{T}, dU = 0$$

$$dS = \frac{-dw_{rev}}{T} = \frac{pdV}{T}, \text{sub. } \frac{p}{T} = \frac{nR}{V}$$

$$\int dS = nR \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$\Delta S = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2}$$

Example 3.7: Method 1

$\Delta_r G(T) \cong \Delta_r H(25) - T\Delta_r S(25)$, where T is not significantly different from 25 deg C

$$\Delta_r G(T) - \Delta_r G(25^\circ C) =$$
$$\Delta_r H(25^\circ C) - \Delta_r H(25^\circ C) - T\Delta_r S(25^\circ C) + (298)\Delta_r S(25^\circ C)$$

$$\Delta_r G(T) - \Delta_r G(25^\circ C) = -(T - 298)\Delta_r S(25^\circ C)$$

Same equation used to solve Ex. 3.7, but what did Mark mean about pV work?

ΔG and pV work

$dG = dH – TdS – SdT$	Substitute/assume:
$= dU + pdV + Vdp – TdS – SdT$	$dH = dU + d(pV)$
$= dq_{rev} + dw_{rev} + pdV + Vdp – TdS – SdT$	First Law, rev
$= TdS + dwr_{rev} + pdV + Vdp – TdS – SdT$	$dS = dq_{rev}/T$
$dG = Vdp – SdT + dw_{other}$	$dw_{rev} = -pdV + dw_{other}$

If we disregard non-expansion work:

$dG = Vdp – SdT$	All state variables!

ΔG and pV work

Take the equation previously derived and assume constant p:

dG_p = -SdT

Consider two temperatures, integrate over T1 to T2:

$\int_{\Delta_r G(T_1)}^{\Delta_r G(T_2)} dG = -\Delta_r S \int_{T_1}^{T_2} dT$, render in terms of a reaction:

$$\Delta_r G(T_2) - \Delta_r G(T_1) = -(T_2 - T_1)\Delta_r S$$

Example 3.7: Method 2, Gibbs-Helmholtz

$\int_{\Delta_r G(T_1)}^{\Delta_r G(T_2)} dG = -\int_{T_1}^{T_2} \Delta_r S dT$

dS = q_{rev}/T = dH/T, div. by 1/T

$$\frac{\Delta_r G(T_2)}{T_2} - \frac{\Delta_r G(T_1)}{T_1} = -\Delta_r H \int_{T_1}^{T_2} \frac{1}{T_2} dT = -\Delta_r H \left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

In summary, we can derive an expression for dG at constant p that is a function of state variables. This can be further refined into functions of dS/dH, the calculations for which are simplified at small dT (i.e. assume dS/dH are constant).

4.2a: ATP hydrolysis

Calculate the free energy change of ATP hydrolysis in muscle at 25C.

[ATP] = 1.25e-3 M, [ADP] = 0.50e-3 M, [Pi] = 2.5e-3 M

Calculating K: ATP hydrolysis

$$\Delta_r G = -RT\ln(K)$$

$$K = e^{-\frac{\Delta_r G}{RT}}$$

Assume standard state:

$\Delta_r G$ = -31.0 kJ/mol

```
# You will need to be able to find equilibrium constants.
# Let's use the standard state free energy of ATP hydrolysis.
import math as m
units_bad = dGss*1000 # We don't want units in the exponential.
K_ATPlys = m.exp(-units_bad/(scc.R*T))
print("K of ATP hydrolysis is %2.2g at 25 deg C." % K_ATPlys)
# This is a tad cold for physiological context, let's up the temp.
units_bad = -35.0*1000 # J/mol, decreases at higher temp.
T = 37 + 273.15
K_ATPlys = m.exp(-units_bad/(scc.R*T))
print("K of ATP hydrolysis is %2.2g at 37 deg C." % K_ATPlys)
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K of ATP hydrolysis is 1.7e+05 at 25 deg C.
K of ATP hydrolysis is 7.8e+05 at 37 deg C.
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Activities

Not going to cover in-depth here, has yet to be introduced in lecture.

Read pages 108-109, 115-119 for specifics

Read equilibrium sections to better understand the effect of activity on chemical equilibria

Relevant equations: Debye-Huckel, see page 145

Questions?

Feel free to leave if you’re good!