University of Washington
Department of Chemistry
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Lecture 11 07/18/14

A. The Helmholtz Free Energy and Reversible Work

The entropy change ΔS provides an absolutely general criterion for assessing the spontaneous direction for physical processes. However, the Second Law specifies that $\Delta S_{universe} \geq 0$ so a entropy calculation must include ΔS_{system} and ΔS_{surr}.

- Suppose a system is isolated, meaning it cannot exchange energy or matter with its surroundings. If this system is not at equilibrium, it must undergo transport processes, which are irreversible process that establish equilibrium. Transport occurs until equilibrium is established and an indication that an isolated system is at equilibrium is that it's entropy is maximum. This isolated system cannot decreases its entropy because to do so would be to violate the Second Law.
- Suppose a system is closed, meaning it cannot matter with its surroundings, but it can exchange energy in the forms of heat and work. If the system and the surroundings are not at equilibrium, again irreversible transport processes must establish equilibrium. Transport occurs until equilibrium is established and an indication that the entropy of the surroundings and the system is maximum. The universe cannot decrease its entropy because to do so would be to violate the Second Law.
- Suppose a closed system is not at equilibrium. It exchanges heat and work with the surroundings. Now the surroundings are massive compared to the system and thus any exchange of energy with the system will not perturb the surroundings much from equilibrium. Therefore the surrounding exchange heat reversibly or $dS_{surr} = \frac{dq}{T}$.
- But the system is not at equilibrium and does not exchange heat reversibly. This means that $dS_{sys} \neq \frac{dq}{T}$, because $dq = dq_{irrev}$. The best we can say is $dS_{sys} > \frac{dq_{irrev}}{T}$ because $q_{rev} > q_{irrev}$
- Once the system reaches equilibrium any slight perturbation from equilibrium results in an entropy change $dS_{sys} = \frac{dq_{rev}}{T}$. What is always true is $dS \geq \frac{dq}{T}$.
- From the First Law $dU_{sys} = dq + dw$. From the Second Law $dS \geq \frac{dq}{T}$. Combining the two… $dU \leq TdS + dw$. For a reversible exchange of heat and P-V work $dU = dq_{rev} + dw_{rev} = TdS - PdV$
- Now consider the state function U-TS. The differential change in this state function is

$$d\left(U - TS\right) = dU - TdS - SdT = \delta q - PdV - TdS - SdT \qquad (11.1)$$

- If the process is reversible then dq=TdS. If the process is irreversible dq<TdS. Therefore is it always safe to say that

$$d\left(U-TS\right)\le -SdT-PdV \tag{11.2}$$

- . And at constant V and T (i.e. dT=dV=0) equatyion 11.2 reduces to

$$d\left(U-TS\right)\le 0 \tag{11.3}$$

- This means that the state function A=U-TS decreases via irreversible processes until it reaches a minimum when equilibrium is reached. Note that although A, the Helmholtz energy, has units of Joules, A is not a conserved quantity.
- The Helmholtz energy is also called the work function or the reversible work because for a reversible change at constant temperature (dT=0) $dA=-SdT+\delta w_{rev}=dw_{rev}$

B. Gibbs Energy: non-PV Work and Applications at Constant P and T

- For calculating the spontaneous direction of processes occurring at constant P and T, the Gibbs' Free energy G is used : G=H-TS=U+PV-TS
- Analogous behavior to A:

$$\begin{aligned} dG&=d(U+PV)-d(TS)=dU+PdV+VdP-TdS-SdT\\ &=\delta q-PdV+PdV+VdP-TdS-SdT\\ &=\delta q+VdP-TdS-SdT \end{aligned} \tag{11.4}$$

If the process is reversible then $\delta q_{rev}=TdS$ and so

$$dG=TdS+VdP-TdS-SdT=-SdT+VdP \tag{11.5}$$

- At constant P and T for reversible changes with only PV work: dG=0
- If the change is irreversible $\delta q_{irrev}<\delta q_{rev}=TdS$ and then

$$dG<-SdT+VdP \tag{11.6}$$

- Similarly at constant P and T dG<0. It is therefore certain that for both irreversible and reversible changes at constant P and T:

$$dG\le 0 \tag{11.7}$$

- Equation 11.7 is basically the criteria for a system being at equilibrium or undergoing an irreversible change.
- The Gibbs energy or Gibbs function is also used to quantify reversible work at constant P and T. Assume in addition to PV there are other work terms including electrical work (to move charge in a potential gradient), osmotic work (to move mass in a concentration gradient), etc.

$$\begin{aligned} dG&=dH-d\left(TS\right)=d\left(U+PV\right)-d\left(TS\right)\\ &=\delta q_{rev}+\delta w_{rev}+PdV+VdP-SdT-TdS\\ &=TdS+\delta w_{other}-PdV+PdV+VdP-SdT-TdS\\ &=\delta w_{other}+VdP-SdT \end{aligned} \tag{11.8}$$

- Note at constant P and T (i.e. dP=dT=0)

$$dG=dw_{other} \tag{11.9}$$

    - $\Delta G = w_{other}$ means the Gibbs' free energy change ΔG measures the amount of non-P-V work that a physical process can produce if it is conducted reversibly. Because the reversible work is the maximum work that can be produced, ΔG measures the upper limit of work that can be obtained from a spontaneous process at constant P and T.
    - Example…for a electrochemical cell…$\Delta G = w_{elec} = -n\Im\Delta \mathrm{E}$, where w_{elec} is the reversible electrical work, n is the number of moles of electrons transported by the electrochemical cell, $\Im$ is Faraday's constant, and $\Delta \mathrm{E}$ is the potential difference between the half cell.
- If no work other than P-V work is performed then $dG = VdP - SdT$
    - At constant T (i.e. dT=0) $dG=VdP$.
        - Example: Calculate the free energy change when 1 mole of an ideal gas changes its pressure from 1 atm to 10 atm.

$$dG = VdP \Rightarrow \int_1^2 dG = G_2 - G_1 = \Delta G = \int_{P_1}^{P_2} VdP$$

$$= \int_{P_1=1atm}^{P_2=10atm} \frac{nRT}{P} dP = nRT \int_{P_1=1atm}^{P_2=10atm} \frac{dP}{P} = nRT \ln\left(\frac{P_2}{P_1}\right)$$

$$= (1mole)(8.31J/mole\cdot K)(300K)\ln 10 = 5.74kJ$$

        - The absolute standard free energy of a gas with a pressure of one atmosphere is designated G^0.

$$G = G^0 + nRT\ln\left(\frac{P}{1atm}\right) = G^0 + nRT\ln(P)$$

- Standard Free Energy Changes
    - Definition: The standard molar free energy of formation ΔG_f^0 is the free energy change required to form one mole of a pure compound in its standard state from its constituent elements, all in their standard states.
    - $\Delta G_f^0 = \Delta H_f^0 - T\Delta S_f^0$
    - Example: $C(s,gr) + O_2(g) \rightarrow CO_2(g)$

$$\Delta H^0 = (1mole)\Delta H_f^0(CO_2) = -393.51kJ$$

$$\Delta S^0 = S_f^0(CO_2(g)) - S_f^0(O_2(g)) - S_f^0(O_2(s,gr))$$

$$= (1mole)(213.63 - 205.03 - 5.74)J/mole\cdot K = 2.86J/K$$

$$\Delta G_f^0 = \Delta H^0 - T\Delta S^0 = -393.51kJ - (298K)(2.86J/K) = -394.36kJ$$

- The Gibbs Equations

All thermodynamic relationships can be derived from six basic equations…

$$dU = TdS - PdV\ ,\ H = U + PV,\ A = U - TS,$$
$$G = H - TS,\ C_{V,m} = \left(\frac{\partial U}{\partial T}\right)_V,\ C_{P,m} = \left(\frac{\partial H}{\partial T}\right)_P \qquad (11.10)$$

applicable to closed system, reversible, PV work only.

- The Gibbs equations are expressions for dH, dA, and dG that are analogous to $dU = TdS - PdV$ for closed, systems undergoing reversible changes, and PV work only. They are:

$$\begin{aligned} dU &= TdS - PdV; \quad dH = TdS + VdP \\ dA &= -SdT - PdV; \quad dG = -SdT + VdP \end{aligned} \qquad (11.11)$$

- It is the basic strategy of thermodynamics to provide any change in any state function U, H, G, A, or S resulting from a change in any state variable V, T, or P in terms of a few easily measured properties. As it turns out, all state functions changes as a result of changes in state variables (e.g. $\left(\frac{\partial S}{\partial P}\right)_T, \left(\frac{\partial U}{\partial V}\right)_T, etc.$) can be expressed in terms of P, V, T and only three properties:

$$C_{P,m} = \left(\frac{\partial H}{\partial T}\right)_P,\ \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P,\ \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad (11.12)$$

- The first property $C_{P,m}$ is just the heat capacity at constant pressure.
- The second property β is called the thermal expansivity, which measures the degree to which the volume of a material changes with temperature.
- The third property κ is called the isothermal compressibility and measures the degree to which the volume of a material changes with pressure.
- The Gibbs equations are combined with the exact differential expressions for dU, dH, dA and dG to give the Maxwell relations. The exact differential expressions are

$$\begin{aligned} dU &= TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \\ \therefore \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V \end{aligned} \qquad (11.13)$$

and similarly using dH, dA, and dG we get the three other Maxwell relations…

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P,\ \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V,\ \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad (11.14)$$

.Only the last two relations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V,\ \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right) \qquad (11.15)$$

are of practical use.

Example: Determine the differential $\left(\frac{\partial U}{\partial V}\right)_T$ in terms of state variables P, V, and/or T and the three properties: $C_{P,m} = \left(\frac{\partial H}{\partial T}\right)_P$, $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$.

Solution:

$$dU = TdS - PdV \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\partial V}{\partial V}\right)_T$$

$$\therefore dU = T\left(\frac{\partial S}{\partial V}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Given We have already shown that

$$\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T = -1 \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\beta}{\kappa}$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{\beta T}{\kappa} - P$$

- Similarly, for example, $\left(\frac{\partial H}{\partial P}\right)_T = -TV\beta + V$