Lecture 10

Tuesday, October 8, 2024 10:07

Topic 3D Concentrating on the System

Recall the Clausius Inequality:

$$dS \geq \frac{dq}{T}$$

Constant Volume

$$dq_V = dU, \text{ so } dS - \frac{dU}{T} = 0$$

$$\boxed{TdS \geq dU}$$

Constant Pressure

$$dq_P = dH, \text{ so } dS - \frac{dH}{T} = 0$$

$$\boxed{TdS \geq dH}$$

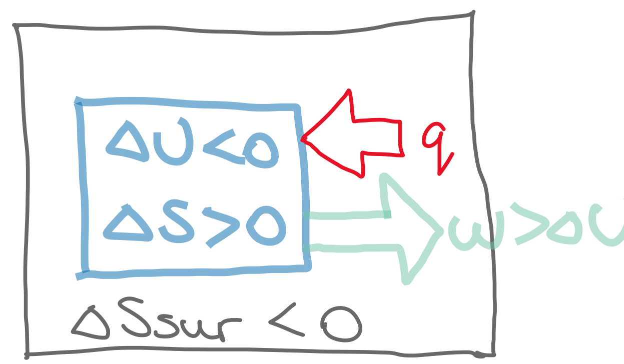
Define two new thermodynamic quantities:

"arbeit", German for "work"

Helmholtz energy: $A = U - TS$

Gibbs energy : $G = H - TS$

In a spontaneous process, $A < 0$, or $G < 0$. (At equilibrium, $A = 0$, or $G = 0$.)



less work than ΔU is obtained

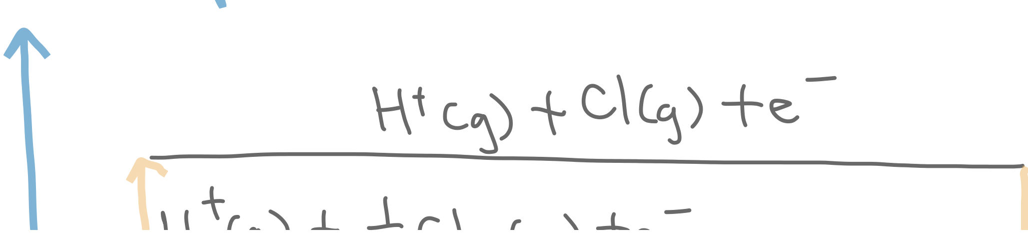
the work done can exceed ΔU

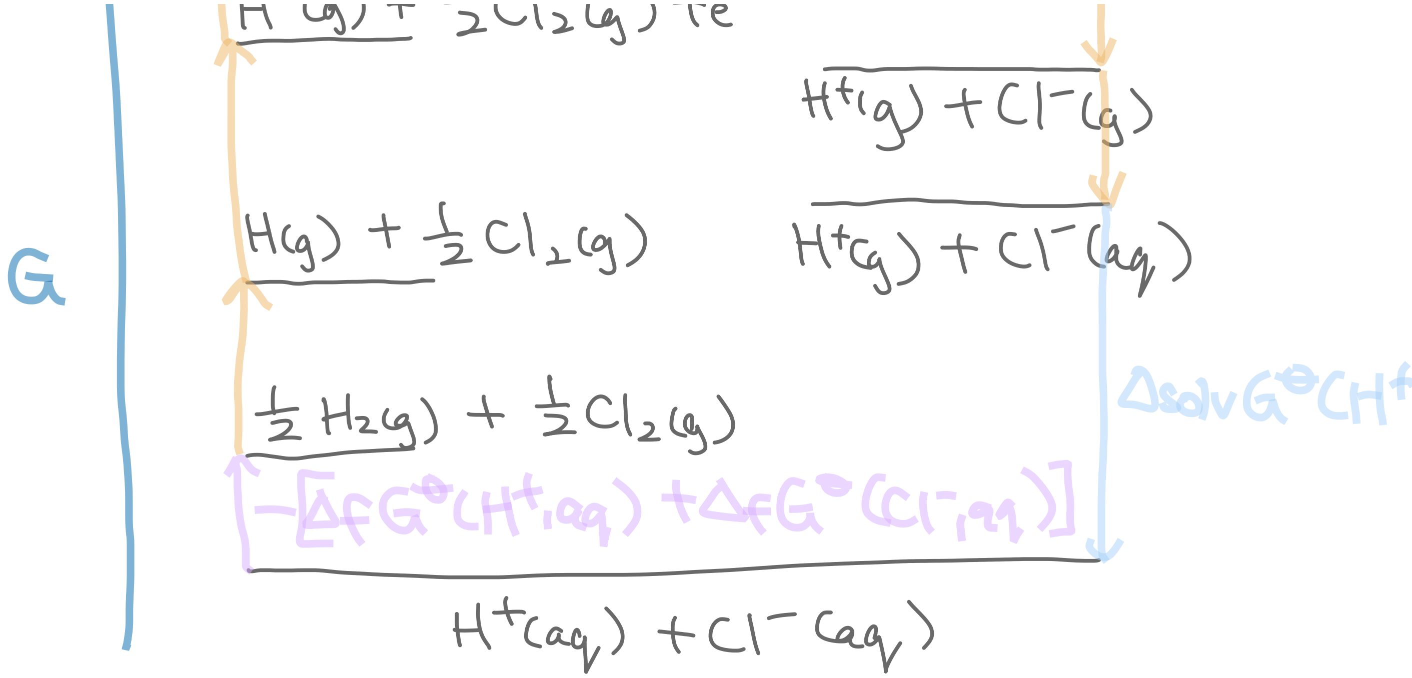
Standard Molar Gibbs Energies

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus$$

Gibbs Energy of Formation (Reaction

$$\Delta_r G^\ominus = \sum_{\text{products}} \nu \Delta_f G^\ominus - \sum_{\text{reactants}} \nu \Delta_f G^\ominus$$





$\Delta_f G^\ominus(H^+, aq) = 0$ by definition

Topic 3E: Combining the First and Second Laws

$$dU = dq + dw$$

$dq_{rev} = TdS$ $\qquad$ $dw_{rev} = -pdV$

$$\boxed{dU = \boxed{T}dS \boxed{-p}dV}$$

The Fundamental Equation

$U(S,V)$

$$dU = \boxed{\left(\frac{\partial U}{\partial S}\right)_V} dS + \boxed{\left(\frac{\partial U}{\partial V}\right)_S} dV$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V , \quad -P = \left(\frac{\partial U}{\partial V}\right)_S$$

Exact Differentials :

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y$$

$$f(x,y) = 3x^4y^3$$

$$\left(\frac{\partial f}{\partial x}\right)_y = 12x^3y^3$$

$$\left(\frac{\partial f}{\partial y}\right)_x = 9x^4y^2$$

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = 36x^3y^2$$

$$\left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = 36x^3y^2$$

$$df = g(x,y)dx + h(x,y)dy$$

$$dF = g(x,y)dx + h(x,y)dy$$

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V}$$

A Maxwell Relation

$$A = U - TS$$

$$dA = dU - d(TS)$$

$$dA = \cancel{TdS} - pdV - \cancel{TdS} - SdT$$

$$\boxed{dA = -pdV - SdT} \quad A(V,T)$$

$$H = U + pV$$

$$dH = dU + d(pV)$$

$$dH = TdS - \cancel{pdV} + \cancel{pdV} + Vdp$$

$$\boxed{dH = TdS + Vdp} \quad H(S,p)$$

$$G = H - TS$$

$$dG = dH - d(TS)$$

$$dG = \cancel{TdS} + Vdp - \cancel{TdS} - SdT$$

$$\boxed{dG = Vdp - SdT} \qquad G(p, T)$$

Exact Differentials	Maxwell Relations
$dU = TdS - pdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
$dH = TdS + Vdp$	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
$dA = -pdV - SdT$	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
$dG = Vdp - SdT$	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

Practice Problem

Show that the entropy of a perfect gas is linearly dependent on $\ln V$, i.e. $S = a + b \ln V$.

Solution:

need this

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$ ← need this Maxwell relation

$$pV = nRT$$

$$p = \frac{nRT}{V}$$

$$\left(\frac{\partial(nRT/V)}{\partial T}\right)_V = \frac{nR}{V} = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V}$$

$$\int dS = nR \int \frac{1}{V} dV$$

$$\boxed{S = nR \ln V + C}$$

The Variation of the Gibbs Energy with Temperature

$$K = {}^{-\Delta_r G^\circ/RT}$$

We are interested in $\left(\frac{\partial(G/T)}{\partial T}\right)_p$.

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad , \quad \boxed{\left(\frac{\partial G}{\partial T}\right)_p = \frac{G-H}{T}}$$

$$G = H - TS$$

$$TS = H - G$$

$$S = \frac{H-G}{T}$$

$$\left(\frac{\partial (G/T)}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p + G\left(-\frac{1}{T^2}\right)$$

$$= \frac{1}{T}\left[\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T}\right]$$

$$= \frac{1}{T}\left(\frac{G-H}{T} - \frac{G}{T}\right)$$

$$\boxed{\left(\frac{\partial (G/T)}{\partial T}\right)_p = -\frac{H}{T^2}}$$

Gibbs-Helmholtz Equation

$$\left(\frac{\partial (\Delta G/T)}{\partial T}\right)_p = -\frac{\Delta H}{T^2}$$