Entropy, the Helmholtz Energy and the Gibbs Energy

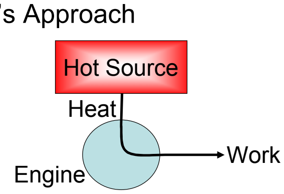
CHEM 323 Physical Chemistry I

Spontaneous Change

- Observations
  - Some changes require work, some don't
  - Some spontaneous changes have $\Delta U > 0$, some have $\Delta U < 0$
  - Same for ΔH
  - Spontaneous changes disperse energy
- First Law does not help
  - Predicts allowed changes
  - System and surroundings always balanced

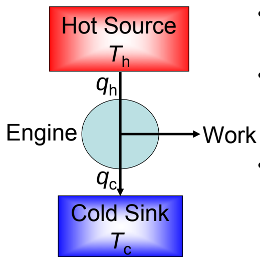
Disorder, Heat and Work

- Kelvin's Approach



  - No process is possible in which the sole result is absorption of heat from a reservoir and its complete conversion into work (Second Law)
  - Can not create order (work) from disorder (heat) with 100% efficiency

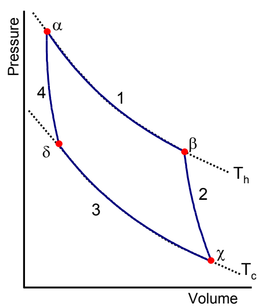
Disorder, Heat and Engines



- Engine is the System
  - Method of operation
- What do we know?
  - First Law: $q_h + q_c + w = 0$
  - Second Law: $q_c \neq 0$
- Define Efficiency, ε
  - Importance of heat
  - Perfect efficiency?

$$\varepsilon = \frac{|w|}{q_h} = 1 + \frac{q_c}{q_h}$$

Carnot Cycle



- Specially Constructed Cycle for an Ideal Gas
- Four Reversible Steps
  1. Isothermal expansion
  2. Adiabatic expansion
  3. Isothermal compression
  4. Adiabatic compression
- Allows us to connect q_h and q_c

Carnot Cycle

- For an Ideal Gas
  - Heat taken from hot source, q_h, along α to β
  - Heat given to cold source, q_c, along χ to δ
  - No heat β to χ or δ to α
- Leads to $\frac{q_h}{T_h} = -\frac{q_c}{T_c}$
- Consider Heat involved in entire Process
  - Must be a path integral: $\oint dq_{rev}/T$
  - And must be zero
  - Implies this is a state function

Entropy

- Extension to all Engines
  - Rewrite efficiency of Carnot engine $\varepsilon = 1 - \frac{T_c}{T_h}$
  - Implies that efficiency is independent of design
  - Any arbitrary thermodynamic cycle can be written as a sum of infinitesimally small Carnot cycles
- Define the State Function Entropy, *S*, as

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

Irreversible Processes and S

- Irreversible implies less Efficient Engine
  - Less work done
  - More heat sent to cold sink (surroundings)
- Less Efficient Engine implies total Entropy must be larger than reversible Change

$$dS_{system} + dS_{surroundings} \geq 0$$

  - Leads to Clausius inequality

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

Entropy and Changes

- For an isolated System only allowed spontaneous Changes have $\Delta S \geq 0$
  - Why?
  - Another version of Second Law
- All Expansions have $\Delta S \geq 0$
- Processes that disperse Energy have $\Delta S \geq 0$
  - Entropy is a signpost for spontaneous change

Entropy Changes

- General equation: $\Delta_{trs}S = \Delta_{trs}H / T_{trs}$
  - Trouton's rule ($\Delta_{vap}S \approx +85\ J\cdot K^{-1}\cdot mole^{-1}$)
- Variation of *S* with Temperature

$$S(T_f) = S(T_i) + \int_i^f \frac{dq_{rev}}{T}$$

- Measurement of *S*

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(s)}{T} dT + \frac{\Delta_{fus}H}{T} + \int_{T_f}^{T_b} \frac{C_p(l)}{T} dT + \frac{\Delta_{vap}H}{T} + \int_{T_b}^{T} \frac{C_p(g)}{T} dT$$

Third Law

- What is $S(0)$?
- Debye Extrapolation: $C_p = aT^3$
  - From data at low *T* (less than ~10 K)
- Nernst Heat Theorem
  - For any change $\Delta S \to 0$ as $T \to 0$ provided all substances involved are perfectly ordered
- Third Law
  - Entropy of all perfect crystalline substances is 0 at $T = 0$ K

Third Law Entropies

- Third Law defines Zero for Entropy Scale
  - Can calculate $S(T)$ at 1 bar of Pressure
  - Third Law, or standard entropies, S^0
- With Standard Entropies can calculate ΔS for any Chemical Process

$$\Delta_r S^0 = \sum_{products} \nu \cdot S_m^0 - \sum_{reactants} \nu \cdot S_m^0$$

- Note
  - $S_{gas} > S_{liquid} > S_{solid}$
  - *S* increases as molecular complexity increases
  - *S* increases as T increases

Entropy at Constant V or P

- Problem with Entropy's Definition
  - Remove surroundings from Clausius inequality by removing *q*
- Derive two new State Functions written only in terms of System
  - Helmholtz energy (*V* constant): $A = U - T \cdot S$
  - Gibbs energy (*p* constant): $G = H - T \cdot S$
- Criteria for a Spontaneous Process
  - Constant *V*: $dA_{T,V} \leq 0$
  - Constant *p*: $dG_{T,p} \leq 0$

More on G and A

- Both Signposts for Spontaneous Change
  - Account for "free" energy and energy used to arrange the system in a state
- Relationship to Work the System can do
  - *A* is maximum work
  - *G* is maximum non-expansion work
- For Chemistry define $\Delta_f G^0$ and define $\Delta_r G^0$ as $\Delta_r G^0 = \sum_{\text{products}} \nu \cdot \Delta_f G_m^0 - \sum_{\text{reactants}} \nu \cdot \Delta_f G_m^0$

The Fundamental Equation

- Combination of First and Second Laws
  - Substitute definitions of *w* and *S* into First Law

$$dU = T \cdot dS - p \cdot dV$$

  - Because *U* is a state function, we can write

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

  - Which implies

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

Maxwell Relations

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

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

- Four Relations between Differentials
  - Result of Euler condition for exact differentials
  - Used to change variables in thermodynamics
- Example Derivation
- Derivation of π_T

Fundamental Equation for the Gibbs Energy

$$dG = V \cdot dp - S \cdot dT$$

- Derivation
  - And from Euler condition for exact differentials

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

- Implications for Temperature and Pressure dependence of *G*
  - Phase diagrams, etc.

Variation of G with T and p

- Temperature Dependence
  - Gibbs-Helmholtz Equation

$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G-H}{T} \quad \text{or} \quad \left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_p = -\frac{H}{T^2}$$

- Pressure Dependence

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp$$

  - Solids and liquids
  - Gases

Fugacity

- For an Ideal Gas

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

- For a Real Gas replace *p* with Fugacity, *f*
  - Fugacity is an *effective* pressure, varies with *p*
  - Accounts for all non-ideality

$$G_m = G^0 + nRT\ln\left(\frac{f}{p^0}\right)$$

Fugacity

- Fugacity describes non-ideal Behavior, but how to measure it?
  - Relate it to the actual measured pressure
- Assume that $f = \phi p$
  - Fugacity coefficient, ϕ, is unitless
  - Why do this?
- Leads to the relation between ϕ, Z and p

$$\ln\phi = \int_0^p \frac{Z-1}{p}dp$$