



Chem 132A

Shane Flynn

What We Know

The First Law

Enthalpy

The Second Law

Helmholtz Free
Energy

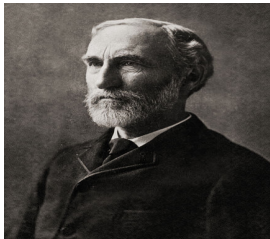
Reversible Work

Gibbs Free Energy

Conclusion

Physical Chemistry (Chem 132A)

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Navigating The Equations

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■ The First Law of Thermodynamics

$$\Delta U = q + w \quad (1)$$

$$w_{PV} = - \int_{V_i}^{V_f} P_{\text{ext}} dV \quad (2)$$

Assume an Equation of State to solve for work! ... $q=?$, $U(T,V)$

■ State Functions and Total Differentials

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad (3)$$

■ Giving Names to Partial Derivatives

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V \Rightarrow q = C_V \Delta T \quad (4)$$



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■ Different Thermodynamic Potentials

$$H \equiv U + PV \quad (5)$$

■ Consider a Different Total Differential $H(T,P)$

$$C_P \equiv \left(\frac{\partial H}{\partial T} \right)_P \quad (6)$$

And using a new set of assumptions we were able to express the heat in a different form.

$$q = C_P \Delta T \quad (7)$$



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- Heat and Energy . . . Chemists Want Direction
- Enter The Second Law of Thermodynamics

$$dS \equiv \frac{\delta q_r}{T}, \quad \Rightarrow \quad \Delta S = \int_i^f \frac{\delta q_r}{T} \quad (8)$$

- And we claimed without any justification that Entropy was a state function (Integrating Factor).
- We think of entropy as the 'disorder', and people discuss things like 'number of micro-states'.
- Take Statistical Mechanics if you would like a more rigorous definition!

$$dS \geq \frac{\delta q}{T} \quad (9)$$



Accounting For Entropy

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- Perpetual Motion, Maxwell's Demon . . . No Free Lunch.
- Entropy as the Universal Tax, we MUST account for it.

Defining a new Thermodynamic Potential:

- Closed system; constant Volume, constant Temperature.

$$dU = \delta q$$

$$dS \geq \left(\frac{dU}{T} \right)_V$$

$$TdS \geq dU$$

$$0 \geq dU - TdS$$

$$0 \geq d(U - TS)$$

(10)



The Helmholtz Free Energy

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- What does this mean and why should we care?

$$A \equiv U - TS \quad (11)$$

- A is called the **Helmholtz Free Energy**
- All of these variables are in terms of the **SYSTEM**.
- The derivation assumes constant T and V $\Rightarrow A(T,V)$.
- A system with a negative Helmholtz implies a spontaneous process.

$$\Delta A = \Delta U - T\Delta S \quad (12)$$

- If S is negative, U would have to be negative to be spontaneous; heat enters the environment.



Helmholtz as the Work Function

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$$\Delta A = \Delta U - T\Delta S \quad (13)$$

- Clearly we need either negative Internal Energy or positive Entropy, to generate a spontaneous Helmholtz Free Energy.
- Consider a reversible process with constant Temperature.

$$\begin{aligned}\Delta A_r &= \Delta U_r - T\Delta S_r \\ &= \Delta U_r - T\frac{q_r}{T} \\ &= \Delta U_r - q_r \\ &= q_r + w_r - q_r \\ \Delta A_r &= w_r\end{aligned} \quad (14)$$



Accounting For Entropy ... Again

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Defining Another Thermodynamic Potential:

- Experimentalists would really like a thermodynamic potential with characteristic variables T and P.
- A(T,V). Let's try our strategy again!

Consider a constant pressure process, and only PV work.

$$\delta q = dH \quad (15)$$

Assuming a constant temperature we can use the Second Law

$$\begin{aligned} dS &\geq \frac{\delta q}{T} \Rightarrow dS - \frac{\delta q}{T} \geq 0 \\ TdS - dH &\geq 0 \Rightarrow \\ d(H - TS) &\leq 0 \end{aligned} \quad (16)$$



The Gibbs Free Energy

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$$G \equiv H - TS \quad (17)$$

- G is called the **Gibbs Free Energy**
- Again we see that a spontaneous process must have a negative Gibbs Free Energy. $\Rightarrow G(T,P)$.

$$\Delta G = \Delta H - T\Delta S \quad (18)$$

- If $\Delta G = 0$, a chemical reaction has no drive to move towards products or reactants. This is equilibrium!

Gibbs: Maximum Non-Expansion Work

If you assume constant Temperature, constant Pressure, and a reversible process you find (Page 135).

$$dG = \delta w_{\text{non-PV}} \quad (19)$$



Summary

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- We are developing various equations for different sets of physical conditions.
- The method for developing each set of equations is VERY similar, and depends on what variables you wish to hold constant.
- Entropy defines spontaneity. There is no way to avoid The Second Law.
- The Free Energies (Helmholtz and Gibbs) account for the entropy by construction.
- The Free Energies are in terms of the **SYSTEM**.
- These potentials are naturally functions of:
 $A(T,V)$ $G(T,P)$