

Chemical Thermodynamics

Mid 2 Review

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Outline

- 1 Concept Review
 - Thermodynamic Laws
 - Practical Formula
- 2 Classic Models
 - Free expansion
 - Calimeter
 - Heating curve
 - Trouton's rule
 - State function
 - Examples

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Thermodynamic Laws

1st Law

$$U = Q + W$$

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2nd Law

100 % (×)

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2nd Law

100 % (×)

3rd Law

$S \rightarrow c$ as $T \rightarrow 0$ K

$$S = k \ln W$$

Do not forget the zeroth law of thermodynamics

0th Law

If two thermodynamic systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

State functions

Enthalpy

$$H = U + pV$$

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Entropy

$$dS = \frac{\delta Q}{T}$$

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Entropy

$$dS = \frac{\delta Q}{T}$$

Gibb's free energy

$$G = H - TS$$

Properties

Heat capacity

$$C = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T}$$

	Atoms	Linear molecules	Nonlinear molecules
$C_{V,m}$	$\frac{3}{2}R$	$\frac{5}{2}R$	$3R$
$C_{P,m}$	$\frac{5}{2}R$	$\frac{7}{2}R$	$4R$

Figure: $C_{V,m}$ and $C_{P,m}$ of three types of molecules.

Practical Formula

$$Q_V = \Delta U \quad (1)$$

$$Q_p = \Delta H \quad (2)$$

$$C_V = \frac{\Delta U}{\Delta T} \quad (3)$$

$$C_p = \frac{\Delta H}{\Delta T} \quad (4)$$

$$\Delta S_{\text{surrounding}} = -\frac{\Delta H}{T} \quad (5)$$

$$S = k \ln W \quad (6)$$

Practical Formula

phase change

$$\Delta S = \frac{Q_R}{T} \quad (7)$$

physical change with constant pressure

$$\Delta S = nC_{V,m} \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{V_2}{V_1} \right) \quad (8)$$

physical change with constant volume

$$\Delta S = nC_{p,m} \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{p_1}{p_2} \right) \quad (9)$$

Practical Formula

Clausius–Clapeyron relation

$$\ln \left(\frac{p_2}{p_1} \right) = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (10)$$

constant temperature

$$\Delta G = \int V dp \quad \text{since} \quad dG = -s dT + V dp \quad (11)$$

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Free expansion

Differential form

$$\delta w = -pdV$$

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Free expansion

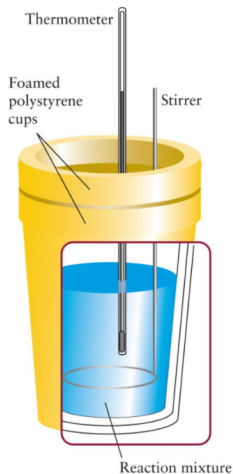
Differential form

$$\delta w = -p dV$$

Notice

- $\Delta U = 0$ and $\Delta H = 0$ for isothermal processes.
- $w = 0$ for free expansion.
- p is external pressure, *i.e.*, $p = p_{\text{ex}}$.

Calimeter



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- $Q = Q_V \Rightarrow \Delta U$

Calimeter

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- Combustion reaction.
- $Q = Q_V \Rightarrow \Delta U$
- Specific heat of water: $4.18 \text{ J}/(\text{g} \cdot ^\circ\text{C})$

Heating curve & Phase diagram

Notice

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- Phase changes of materials.

Heating curve & Phase diagram

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- Turning points.

Heating curve & Phase diagram

Notice

- Phase changes of materials.
- Turning points.
- Intervals, platforms, and slopes.

Trouton's rule

Liquid	Boiling Point (K)	ΔS° (J·K ⁻¹ ·mol ⁻¹)
Helium	4.22	20
Argon	87.3	74
Benzene	353.2	87.2
Ethanol	331.5	124
Mercury	629.7	94.2
Water	373.2	109

A pattern, now called **Trouton's rule**, emerges when comparing $\Delta S_{\text{vap}}^\circ$; many values are close to 85 J·K⁻¹·mol⁻¹.

- Semi-quantitative, not precise.

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- Pay attention to dependent variables.
- Design desired cycles.

How to design a cycle?

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- Constant conditions: isothermal, isochoric, isobaric, (adiabatic)
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Properties of state functions

- Only related to initial and final state, **nothing to do with paths.**
- From already known to unknowns, set proper path and intermediate state.

Lecture slides

Example 4B.1 Suppose that 1.00 mol of ideal gas molecules at 292 K at 3.00 atm expands from 8.00 L to 20.00 L and has a final pressure of 1.20 atm. Find the amount of work by two different paths.

(Hint: ideal gas isothermal expansion $\Delta U=0$)

(a) Path A is an isothermal, reversible expansion.

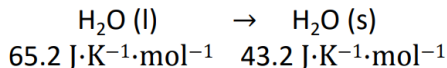
(b) Path B has two parts. In step 1, the gas is cooled at constant volume until its pressure has fallen to 1.20 atm. In step 2, it is heated and allowed to expand against a constant pressure of 1.20 atm until its volume is 20.00 L and $T = 292$ K. Determine for each path the work done, the heat transferred, and the change in internal energy (w , q , and ΔU).

Lecture slides

Example 4F.4 In an experiment, 1.00 mol $\text{O}_2(\text{g})$ was compressed suddenly (and irreversibly) from 5.00 L to 1.00 L by driving in a piston (like a big bicycle pump), and in the process, its temperature increased from 20.0°C to 25.2°C. What is the change in entropy of the gas? ($\text{O}_2 C_{V,m}$ is 20.79 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

Lecture slides

Freezing liquid water into a solid, is not a favorable process.



$$\Delta S_{\text{system}} = \sum n S_m^\circ (\text{products}) - \sum n S_m^\circ (\text{reactants})$$

$$\Delta S (\text{system}) = -22.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} (\text{unfavorable})$$

This is answered fully when we interpret ΔS (total) to include: $\Delta S (\text{surroundings}) = \frac{q_{\text{rev}}}{T}$

Lecture slides

Example 4I.1 Calculate the change in entropy of the *surroundings* when water freezes at $-10.^{\circ}\text{C}$; use $\Delta H_{\text{fus}}(\text{H}_2\text{O}) = 6.0 \text{ kJ}\cdot\text{mol}^{-1}$ at $-10.^{\circ}\text{C}$.

Bohn-Haber Cycle

Design desired cycle

The standard molar enthalpy of combustion of ethanol ($\text{C}_2\text{H}_5\text{OH}$) and acetic acid (CH_3COOH) is -136.50 and -67.50 kJ/mol.

The enthalpy of dissolution is 11.71 and 1.46 kJ/mol correspondingly. Calculate the enthalpy of oxidation of ethanol in water solution.

Liquid-Solution

Raoult's law and Dalton's law

Liquid A and B form an ideal solution. The solution containing 1 mol A and 2 mol B at 343.2 K has a vapor pressure of 50.663 kPa.

If 3 mol A is added, the vapor pressure of the solution increases to 70.928 kPa. Calculate (1) p_A^* and p_B^* at 343.2 K; (2) the gaseous composition of the first mixed solution.

Good Luck !