Physical Chemistry I for Biochemists
Chem340

Lecture 41 (4/27/11)

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Review for Ch2-4, Ch5.1-6

Announcement

• The Final Exam will be held at LC A1 on May 4 (Wed) at 1-3 pm (Note location change)

• Equation sheet (Single sheet in Letter size)
  - Handwritten
  - You can use both front and back of the sheet
• P9.29) Estimate the degree of dissociation of a 0.100 m solution of acetic acid ($K_a = 1.75 \times 10^{-5}$) that is also 0.500 m in the strong electrolyte given in parts (a)–(c). Use the data tables in Appendix B to obtain $\gamma_{\pm}$, because the electrolyte concentration is too high to use the Debye–Hückel limiting law.

\[
HA \rightarrow H^+ + A^-
\]

\[
K_a = \frac{a_+a_-(0.100 m - x)}{m^2} = \frac{m^2 \gamma_{\pm}^2}{(0.100 m - x)}
\]

(a) CaCl$_2$

Look up Table 9-3 in Appendix B-17. For CaCl$_2$, pick a value of $\gamma_{\pm}$ at 0.5 m (0.411) (assuming $m \ll 0.5$ m and $I$ is defined by CaCl$_2$).

• P9.18) (a) Calculate $I$, $\gamma_{\pm}$, and $a_{\pm}$ for a 0.0250 m solution of K$_2$SO$_4$ at 298 K. Assume complete dissociation.

(b) How confident are you that your calculated results will agree with experimental results?

• $\nu_+ = 2 \quad \nu_- = 1 \quad z_+ = 1 \quad z_- = -1$

• $I = (m\nu_+ z_+^2 + \nu_- z_-^2)/2$ (correction)

\[
\log \gamma_{\pm} = -0.50926|z_+z_-|(I)^{1/2}
\]

\[
a_{\pm} = [Q2]
\]

\[
m_{\pm} = [Q3]
\]

(b) See Figures 9.8 to find the deviation from DH limiting law using Davis equation (9.34)
Kinetic Energy of Gas

- \( v^2 = v_x^2 + v_y^2 + v_z^2 \)
- The probability of finding a molecule flying at \( v_x \) is
  \[ p(v_x) = \frac{\exp(-mv_x^2/2k_BT)}{Z} \]
  where \( Z = (2\pi k_BT/m)^{1/2} \) and \( a = m/2k_BT \).
- The expected kinetic energy due to \( v_x \)
  \[ \langle \frac{mv_x^2}{2} \rangle = \int_{-\infty}^{\infty} \frac{mv_x^2}{2} p(v_x) dv_x = \frac{m}{2} \int_{-\infty}^{\infty} v_x^2 p(v_x) dv_x \]
  \[ = \frac{m}{2Z} \int_{-\infty}^{\infty} v_x^2 \exp(-mv_x^2/2k_BT) dv_x = \frac{m}{4aZ} \sqrt{\frac{\pi}{a}} = k_BT / 2 \]
  \[ < mv_x^2 / 2 > = < mv_y^2 / 2 > = < mv_z^2 / 2 > = k_BT / 2 \]
  \[ < E_{\text{trans}} > = < mv^2 / 2 > = 3k_BT / 2 \]

Q. Is this energy for 1 mol?

Temperature Dependence of Distribution of \( |v_x| \)

- \( P(v_x) = \exp(-mv_x^2/(2kT))/Z \)
Distribution of speed $C$, $P(C)$ (Raff994)

$$P(C) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{mC^2}{2kT}\right] C^2$$

$$C = \{v_x^2 + v_y^2 + v_z^2\}^{1/2}$$

Distribution of Speed for O2 in Gas

How can $p(C)$ have a very different shape from $p(v_x)$?

$$P(v_x, v_y, v_z) dv_x dv_y dv_z = p(v_x)p(v_y)p(v_z) dv_x dv_y dv_z$$

$$= \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2kT}\right) / Z^3 dv_x dv_y dv_z$$

Change Cartesian velocity $(v_x, v_y, v_z)$ → Polar Velocity $(C, \theta, \phi)$

$$dv_x dv_y dv_z = C^2 \sin \theta dC d\theta d\phi$$

$$4\pi C^2 P(v_x, v_y, v_z) = P(C)$$

$$\left(\frac{P(C)}{4\pi C^2}\right) C^2 \sin \theta dC d\theta d\phi = \exp\left(-\frac{mC^2}{2kT}\right) / Z^3 C^2 \sin \theta dC d\theta d\phi$$

$$P(C) = 4\pi C^2 \exp\left(-\frac{mC^2}{2kT}\right) / Z^3$$
<C>, \langle C^{2}\rangle^{1/2}, Most probable C

(Raff 998-999)

- Average speed, \langle C\rangle:

\[
\langle C \rangle = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_{0}^{\infty} \exp \left[ -\frac{mC^2}{2kT} \right] C^3 dC = \left( \frac{8RT}{\pi M} \right)^{1/2}
\]

- Root-Mean-Square speed \( C_{\text{rms}} \):

\[
\langle C^2 \rangle^{1/2} = \left[ 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_{0}^{\infty} \exp \left[ -\frac{mC^2}{2kT} \right] C^4 dC \right]^{1/2} = \left( \frac{3RT}{M} \right)^{1/2}
\]

- Most probable C: \( C_{mp} \)

\[
C_{mp} = \left( \frac{2RT}{M} \right)^{1/2}
\]

Q. Which is greater?

\[ \text{dP(C)/dC} = 0 \]

**Kinetic Theory of Gas**

An ideal gas of \( N \) molecules (mass \( m \)) is enclosed in a cubic box of length \( L \)

\[
F = \sum_{k=1}^{N} m\nu_{x_k}^2 / L
\]

By \( N \) molecules,

\[
F = mN \left( \frac{1}{N} \sum_{k=1}^{N} \nu_{x_k}^2 \right) / L = mN \left( \frac{1}{N} \sum_{k=1}^{N} \nu_{x_k}^2 \right) / L
\]

\[
\text{By N molecules,}
\]

\[
P = F/L^2 \rightarrow P = mN\langle \nu_x^2 \rangle / L^3 = Nk_B T / L^3 = nRT/V
\]
Internal Energy of Translation, Rotation, Vibration (Text Ch23 p600)

Translational Energy for N molecules

\[ U_T = \frac{3Nk_B T}{2} = \frac{3nRT}{2} \]

Rotational Energy

- \[ U_R = Nk_B T = nRT \] (linear)
- \[ U_R = \frac{3Nk_B T}{2} = 3nRT/2 \] (non-linear)
- \[ U_R = [Q1] \] (atomic)

Vibrational Energy

- \[ U_V = \frac{Nhc \bar{\nu}}{\exp(hc \bar{\nu} / kT) - 1} \]

Ch. 2

• First law of Thermodynamics:

The internal energy, \( U \), of an isolated system is constant.

In other words, if the surrounding exchanges energy with the system, the total energy of the surrounding and the system should not change.

\[ 0 = \Delta U_{\text{Total}} = \Delta U_{\text{system}} + \Delta U_{\text{surrounding}} \]

\[ \Delta U_{\text{system}} = -\Delta U_{\text{surrounding}} \]

In a closed system: \(-\Delta U_{\text{surrounding}} = q(\text{heat}) + w(\text{work})\)

\[ \Delta U = q + w \]
Work by pressure

Pressure: \( P = \frac{F}{A} \), where \( A \) is area

\[ F = P_{\text{external}}A \]

The work done by the system:

\[ w = \int F \, dL \]

\[ = -\int P_{\text{external}}A \, dz = -\int P_{\text{external}} \cdot (Adz) \]

\[ = -\int P_{\text{external}} \cdot d(V) \]

Note: In general, \( P_{\text{external}} \neq P_{\text{system}} \)

For a constant \( P_{\text{ext}} \)

\[ w = -P_{\text{external}} \Delta V \]

The sign of \( w \) (Q. Which process gives us a positive work?)

\[ \Delta U = w \]

\[ \Delta U = w \]
Sample Question (Ex. 2.1 p18)

- Calculate the work involved when a human adult exhales. Assume that an adult expels 0.5 L of air at 1 atm.
  
  \[ P_{\text{external}} = 1 \text{ atm} \]
  
  \[ \Delta V = 0.5 \text{ L} \]
  
  \[ W = -P_{\text{external}} \Delta V = -1 \text{ atm} \times 0.5 \text{ L} \]
  
  \[ = -1 \times 1.01 \times 10^5 \text{ Pa} \times 0.5 \times 10^{-3} \text{ m}^3 \]
  
  \[ = -50.0 \text{ J} \approx -0.2 \text{ kcal} \]

Math in Expansion of Gas

- **Case [1]** If \( P_{\text{external}} = \text{const} \) (p24)
  
  \[ w = -\int P_{\text{external}} dV \]
  
  \[ = -P_{\text{external}} \int_{V_{\text{ini}}}^{V_{\text{fin}}} dV \]
  
  \[ = -P_{\text{external}} \left[ V^{V_{\text{fin}}}_{V_{\text{ini}}} \right] = -P_{\text{external}} (V_{\text{fin}} - V_{\text{ini}}) \]

- **Case [2]** Reversible Expansion \( P_{\text{external}} = P_{\text{int}} \)
  
  \[ w = -\int P_{\text{int}} (V,T) dV \]

- **Case [3]** Isothermal Reversible Expansion. \( P_{\text{external}} = P_{\text{int}} = nRT/V \) & \( T = \text{const} \) (see p27)
  
  \[ w = -\int_{V_{\text{ini}}}^{V_{\text{fin}}} (nRT/V) dV \]
  
  \[ = -nRT \int_{V_{\text{ini}}}^{V_{\text{fin}}} \left( \frac{1}{V} \right) dV \]
  
  \[ = -nRT \left[ \ln(V) \right]_{V_{\text{ini}}}^{V_{\text{fin}}} \]
  
  \[ = -nRT \{ \ln(V_{\text{fin}}) - \ln(V_{\text{ini}}) \} \]
  
  \[ = -nRT \{ \ln(V_{\text{fin}}/V_{\text{ini}}) \} \]
Work by Electrostatics

The work required for transporting charge $q$ across the electrical potential $\phi$

- $W_{\text{electrical}} = q\phi$

Using a current $I$ and ($q = It$),

- $W_{\text{electrical}} = IVt$ [A V sec] = [W sec] = [J]

<table>
<thead>
<tr>
<th>Types of Work</th>
<th>Variables</th>
<th>Equation for Work</th>
<th>Conversional Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work expansion</td>
<td>Pressure ($P$), volume ($V$)</td>
<td>$w = \int P , dV$</td>
<td>$\text{Pa m}^3 = \text{J}$</td>
</tr>
<tr>
<td>Straining</td>
<td>Tension ($F$), length ($L$)</td>
<td>$w = \int F , dl$</td>
<td>$\text{N m} = \text{J}$</td>
</tr>
<tr>
<td>Surface creation</td>
<td>Surface tension ($\sigma$)</td>
<td>$w = \int \sigma , dA$</td>
<td>$\text{N m}^{-1} = \text{J}$</td>
</tr>
<tr>
<td>Volume creation</td>
<td>Volume ($V$)</td>
<td>$w = \int \rho , dV$</td>
<td>$\text{kg m}^{-3} \text{m}^3 = \text{J}$</td>
</tr>
<tr>
<td>Transport (Diffusion)</td>
<td>Temperature ($T$), activity ($a$), the activity of a species in solution is proportional to the concentration, as well be discussed in Section 9 11.</td>
<td>$w = \int kF , dx$</td>
<td>$\text{J}$</td>
</tr>
</tbody>
</table>

$\int F \, dx = (kx) \, dx$

(Ch 9.1)

2.3 Heat

- Heat is defined as the quality of energy that flows across the boundary between the system and the surrounding because of a temperature difference

When $w = 0$

$\Delta U = \delta q_{\text{sys}}$

$\delta q_{\text{sys}} < 0$

$T_{\text{surrounding}} < T_{\text{sys}}$

$\delta q_{\text{sys}} > 0$

$T_{\text{surrounding}} > T_{\text{sys}}$
2.4 Heat Capacity

- Assume that the work $w$ of $I \phi t$ is done by a heating coil in a system and the work is completely converted to heat $q$ (ie. $q = I \phi t$)

$\rightarrow$ We expect temperature change from $T_{ini}$ to $T_{fin}$

The response of the system to a heat flow is described by heat capacity $C$

$$C = \lim_{\Delta T \to 0} \frac{q}{T_{fin} - T_{ini}} = \frac{Dq}{dT}$$

[D is denoted as $\phi$ in the text. The meaning will be discussed in a later section.]

$\rightarrow$ $C$ denotes heat needed to increase $T$ by 1K

$C_m = C/n$: molar heat capacity

Heat Capacity Depends on the Conditions ($V, P, T$)

- $C_V$: Heat capacity for a constant volume
- $C_P$: Heat capacity for a constant pressure

$C_V \neq C_P$

$C_P$ and $C_V$ also depend on temperature and phase in general.

Q. How much heat is needed to increase $T$ by 2K for 1 mol of $Cl_2$ at $T = 100, 200, 300K$?
Solution

\[
q = \int_{T_{\text{ini}}}^{T_{\text{fin}}} C(T) \, dT
\]

If \( C(T) \) is invariant within \( T_{\text{ini}} \leq T \leq T_{\text{fin}} \)

\[
q = -\int_{T_{\text{ini}}}^{T_{\text{fin}}} C(T) \, dT
\]

\[
= C(T)(T_{\text{fin}} - T_{\text{ini}})
\]

At 100 K, \( C_m(T) \sim 43 \text{ Jmol}^{-1} \)
At 200 K, \( C_m(T) \sim 68 \text{ Jmol}^{-1} \)
At 200 K, \( C_m(T) \sim 29 \text{ Jmol}^{-1} \)

2.5 State Functions and Path Functions

- An alternate statement of first law:
  \( \Delta U \) is independent of the path between the initial and final states.

\( \Delta U \) only depends only on the initial and final states as

\[
\Delta U = \int_{U_{\text{ini}}}^{U_{\text{fin}}} dU = U_{\text{fin}} - U_{\text{ini}}
\]

Any function that satisfies this condition is called a state function.

\( dU \) is called an “exact differential”, the integration of which \((U)\) is a state function. \((Dq \) is not an exact differential).
Work and Heat Are “Path Functions” (not “State Function”)

• W and q are not state functions, but path functions.

\[ q = \int_{\text{ini}}^{\text{fin}} Dq \neq q_{\text{fin}} - q_{\text{ini}} \]

\[ w = \int_{\text{ini}}^{\text{fin}} Dw \neq w_{\text{fin}} - w_{\text{ini}} \]

W + q = \Delta U are actually a state function

Q. Calculate the work performed along the path in the right. Assume (P_{\text{ext}} = P)

\[ W = -P^2(V^2 - V_1) - P_1(V_1 - V_2) = (P_1 - P_2)(V_2 - V_1) \]

2.6 Equilibrium, Change, Revers

Reversible? If a infinitely small mass is placed at one side of the top figure, a weight can be moved in either direction.

• Quasi-static process: The system changes by going through a series of equilibrium states.

• Reversible Process: In a reversible process, you can change the direction of the process by increasing any of P, V, T by infinitely small quantity. (P_{\text{ext}} = P_{\text{ini}})

• Irreversible Process: Infinitely small change in variable does not change the direction of the process.
Heat Capacity Depends on the Conditions 
(V, P, T)

- \( C_V \): Heat capacity for a constant volume
- \( C_P \): Heat capacity for a constant pressure

\( C_V \neq C_P \)

\( C_P \) and \( C_V \) also depend on temperature and phase in general.

Q. How much heat is needed to increase \( T \) by 2K for 1 mol of \( \text{Cl}_2 \) at \( T = 100, 200, 300\text{K} \)?

Solution

\[ q = \int_{T_{\text{ini}}}^{T_{\text{fin}}} C(T) \,dT \]

If \( C(T) \) is invariant within \( T_{\text{ini}} \leq T \leq T_{\text{fin}} \)

\[ q = -\int_{T_{\text{ini}}}^{T_{\text{fin}}} C(T) \,dT \]

\[ = C(T)(T_{\text{fin}} - T_{\text{ini}}) \]

At 100 K, \( C_m(T) \sim 43 \text{ Jmol}^{-1} \)
At 200 K, \( C_m(T) \sim 68 \text{ Jmol}^{-1} \)
At 200 K, \( C_m(T) \sim 29 \text{ Jmol}^{-1} \)
5.8 Absolute Entropies and The Third Law of Thermodynamics

- The entropy of an element or a compound is experimentally determined from
  \[ dS = \frac{Dq_{\text{reversible}}}{T} = \frac{(C_p/T)dT}{T} \]

**Molar Entropy for Gas**

\[
S_m(T) = S_m(0K) + \int_0^T \frac{C_{p,m}^{\text{solid}}}{T'}dT' + \frac{\Delta H_{\text{fusion,m}}}{T_f} + \int_{T_f}^{T_b} \frac{C_{p,m}^{\text{liquid}}}{T}dT + \frac{\Delta H_{\text{vaporization,m}}}{T_b} + \int_{T_b}^{T^"} \frac{C_{p,m}^{\text{gas}}}{T^"}dT^" 
\]

Third Law of thermodynamics - What is \( S_m(0K) \)?

The entropy of a pure, perfectly crystalline substance (element or compound) is zero at 0K.

2.5 State Functions and Path Functions

- An alternate statement of first law:
  \( \Delta U \) is independent of the path between the initial and final states.
  \( \Delta U \) only depends only on the initial and final states as
  \[
  \Delta U = \int_{U_{\text{ini}}}^{U_{\text{fin}}} dU = U_{\text{fin}} - U_{\text{ini}}
  \]

Any function that satisfies this condition is called a state function.

\( dU \) is called an “exact differential”, the integration of which \( U \) is a state function. (\( Dq \) is not an exact differential).
Work and Heat Are “Path Functions” (not “State Function”)

- W and q are not state functions, but path functions.

\[ q = \int_{\text{ini}}^{\text{fin}} Dq \neq q_{\text{fin}} - q_{\text{ini}} \]

\[ w = \int_{\text{ini}}^{\text{fin}} Dw \neq w_{\text{fin}} - w_{\text{ini}} \]

W + q = ΔU are actually a state function

Q. Calculate the work performed along the path in the right. Assume (P_{ext} = P)

\[ W = -P_2(V_2 - V_1) - P_1(V_1 - V_2) = (P_1 - P_2)(V_2 - V_1) \]

Additional Questions

W + q = ΔU: a state function

Q2. How much heat is needed for this cycle?

\[ q = \Delta U - w = -w \]

Q3. How much work is needed for the reverse cycle?
### 2.7 Work for Reversible Process

- In reversible process, \( P = P_{\text{ext}} \)

\[
w = - \int_{V_{\text{ini}}}^{V_{\text{fin}}} P_{\text{ext}} \, dV = - \int_{V_{\text{ini}}}^{V_{\text{fin}}} P_{\text{int}} \, dV
\]

For isothermal reversible process,

\[
w = - \int_{V_{\text{ini}}}^{V_{\text{fin}}} (nRT/V) \, dV
\]

\[
= -nRT \int_{V_{\text{ini}}}^{V_{\text{fin}}} (1/V) \, dV
\]

\[
= -nRT \ln(V_{\text{fin}}/V_{\text{ini}})
\]

\[
= -nRT \{ \ln(V_{\text{fin}}) - \ln(V_{\text{ini}}) \} = -nRT \{ \ln(V_{\text{fin}}/V_{\text{ini}}) \}
\]

#### Question:

Q. How much \( w \) is needed for the cycle \( P_i \to P_f \to P_i \)?

### 2.9 Calculating \( q, w, \Delta U, \Delta H \) for Ideal Gas

(Note: all the equations in this section of the text are valid only for Ideal Gas)

\[
\Delta U = q_v = \int_{T_{\text{ini}}}^{T_{\text{fin}}} C_v(T) \, dT = C_v(T_{\text{fin}} - T_{\text{ini}})
\]

\[
\Delta H = \Delta U + \Delta(PV)
\]

\[
= \Delta U + \Delta(nRT) = \Delta U + nR\Delta T = C_v \Delta T + nR\Delta T
\]

\[
= (C_v + nR) \Delta T = C_p \Delta T
\]

\[
q_p = \int_{T_{\text{ini}}}^{T_{\text{fin}}} C_p(T) \, dT = C_p(T_{\text{fin}} - T_{\text{ini}}) = \Delta H
\]
HW3

- **P2.3)** 3.00 moles of an ideal gas are compressed isothermally from 60.0 to 20.0 L using a constant external pressure of 5.00 atm. Calculate \( q, w, \Delta U, \) and \( \Delta H. \)

**Q. How can we calculate \( \Delta U \) and \( \Delta H? \)**

Which equation should we use?

\[
\Delta U = q_V = C_V (T_{\text{fin}} - T_{\text{ini}}) \quad \Delta H = \Delta U + P_{\text{ext}} \Delta V
\]

\[
\Delta H = q_P = C_P (T_{\text{fin}} - T_{\text{ini}}) \quad \Delta U = w + q
\]

**Q2. How can we calculate \( w \) and \( q? \)**

\[
\Delta H = \Delta U + P_{\text{int}} \Delta V
\]

\[
w = -P_{\text{ext}} \Delta V
\]

---

**HW 3**

- **P2.7** For 1.00 mol of an ideal gas, \( P_{\text{external}} = P = 200.0 \times 10^3 \text{ Pa}. \) The temperature is changed from 100.0\(^\circ\) C to 25.0\(^\circ\) C, and \( C_{V,m} = 3/2R. \) Calculate \( q, w, \Delta U, \) and \( \Delta H. \)

**Q. Which equation should we use first?** → First obtain \( U \) and then \( H. \)

\[
\Delta U = q_V = C_V (T_{\text{fin}} - T_{\text{ini}}) \quad \Delta H = \Delta U + P_{\text{ext}} \Delta V
\]

\[
\Delta H = q_P = C_P (T_{\text{fin}} - T_{\text{ini}}) \quad \Delta U = w + q
\]

\[
R = C_P - C_V \\
\Delta H = \Delta U + P_{\text{int}} \Delta V
\]

→ \( \Delta H = (C_V + R) \Delta T \)

\[
w = -P_{\text{ext}} \Delta V
\]
HW 3

• **P2.7** For 1.00 mol of an ideal gas, $P_{\text{external}} = P = 200.0 \times 10^3 \text{ Pa}$. The temperature is changed from $100.0^\circ \text{ C}$ to $25.0^\circ \text{ C}$, and $C_{V,m} = 3/2R$. Calculate $q$, $w$, $\Delta U$, and $\Delta H$.

\[ \Delta U = q_V = C_V (T_{\text{fin}} - T_{\text{ini}}) \quad \rightarrow \text{Note } \Delta U < 0 \]

\[ nR = C_P - C_V \]

\[ \Delta H = \Delta U + P_{\text{ext}} \Delta V \]

\[ \Delta H = C_P (T_{\text{fin}} - T_{\text{ini}}) = \Delta U + nR \Delta T \]

\[ q_p = \Delta H \quad \text{(Reversible)} \]

\[ \Delta U = w + q \]

\[ w = \Delta U - q \]

---

2.8 Determining $\Delta U$ & Introduction of Enthalpy $H$: a New State Function

(1) **Relationship between $U$ and $q$ under a constant $V$**

• If $w = PdV = 0$, $\Delta U = q$

\[ \Delta U \text{ can be determined by heat under a constant } V \text{ as } \]

\[ \Delta U_V = q_v \]

(2) What about it if $P = \text{const}$?

\[ \Delta U = q + w = \Delta U = q - P_{\text{ext}} \Delta V \quad \rightarrow \quad q = \Delta U + P_{\text{ext}} \Delta V \]

(3) Let us define $H$ as

\[ H \equiv U + P_{\text{int}}V \]

(4) **Relationship between $H$ and $q$ under a constant $P_{\text{int}}$**

\[ \Delta H_p = \Delta U + P \Delta V = q_p \quad \text{(for reversible process)} \]
2.10 Reversible Adiabatic Expansion (for an ideal gas) (Derivation)

- **Adiabatic process** \(\rightarrow q = 0\)
- \(\Delta U = w \rightarrow C_VdT = -P_{ext}dV\)

For a reversible process \(P_{ext} = P_{int}\)
- \(C_VdT = -P_{int}dV\)
- \(C_VdT = -nRT/VdV\)
- \(C_V(1/T)dT = -nR(1/V)dV\)

\[
C_V \int_{T_{ini}}^{T_{fin}} (1/T) dT = -nR \int_{V_{ini}}^{V_{fin}} (1/V) dV
\]

\[
C_V \ln(T_{fin} / T_{ini}) = -nR \ln(V_{fin} / V_{ini})
\]

\[
\frac{C_V \ln(T_{fin} / T_{ini})}{C_V \ln(T_{fin} / T_{ini})} = -nR \ln(V_{fin} / V_{ini})
\]

\[
\ln\left(\frac{T_{fin}}{T_{ini}}\right) = -(nR/C_V)\ln\left(\frac{V_{fin}}{V_{ini}}\right) = -\frac{C_p - C_V}{C_V} \ln\left(\frac{V_{fin}}{V_{ini}}\right) = (1 - \gamma) \ln\left(\frac{V_{fin}}{V_{ini}}\right)
\]

\[
\frac{T_{fin}}{T_{ini}} = \left(\frac{V_{fin}}{V_{ini}}\right)^{(1-\gamma)}
\]

\[
\frac{P_{fin}V_{fin}}{P_{ini}V_{ini}} = \left(\frac{V_{fin}}{V_{ini}}\right)^{(1-\gamma)}
\]

\[
P_{ini}V_{ini}^\gamma = P_{fin}V_{fin}^\gamma
\]
Calculated Change in Enthalpy (continued)

- Case 3 (3'). Reversible change in T for a fixed V

\[ \Delta S = \int \frac{Dq_{\text{reversible}}}{T} = \int \frac{nC_{v,m}dT}{T} = nC_{v,m} \ln(T_f/T_i) \]

- Case 4 (4'). Reversible change in T for a fixed P

\[ \Delta S = \int \frac{Dq_{\text{reversible}}}{T} = \int \frac{nC_{P,m}dT}{T} = nC_{P,m} \ln(T_f/T_i) \]

- Case 5 (reversible) & 5'(irreversible) process: \((T_i, V_i) \rightarrow (T_p, V_f)\)

By calculating \(S\) for \((T_i, V_i) \rightarrow (T_i, V_f) \rightarrow (T_p, V_f)\)

\[ \Delta S = nR \ln(V_f/V_i) + nC_{v,m} \ln(T_f/T_i) \]

- Case 6 & 6' (\(T_i, P_i) \rightarrow (T_p, P_f)\)

By calculating \(S\) for \((T_i, P_i) \rightarrow (T_i, P_f) \rightarrow (T_p, P_f)\) \((P_i/P_f = V_f/V_i)\)

\[ \Delta S = nR \ln(V_f/V_i) + nC_{P,m} \ln(T_f/T_i) = -nR \ln(P_f/P_i) + nC_{P,m} \ln(T_f/T_i) \]

5.4 Calculating Changes in Entropy for Ideal Gas

\[ dS = \frac{Dq_{\text{reversible}}}{T} \]

| V = 1L | P = 1 bar | T = 300 K |
| V = 1L | P' = P bar |

- Case 1. Adiabatic reversible process

\[ dS = \frac{Dq_{\text{reversible}}}{T} = 0 \rightarrow \Delta S = 0 \]

- Case 2. Isothermal reversible process \((V_i, T_i) \rightarrow (V_f, T_i)\)

\[ q_{\text{reversible}} = -w_{\text{reversible}} = \int P dV = \int \frac{nRT}{V} dV = nRT \ln(V_f/V_i) \]

\[ \Delta S = \int \frac{Dq_{\text{reversible}}}{T} = \frac{q_{\text{reversible}}}{T} = nR \ln(V_f/V_i) \]

Q. What is the sign of \(\Delta S\) for isothermal reversible compression?
## w & q in various process for ideal gas

<table>
<thead>
<tr>
<th>Type of work</th>
<th>w</th>
<th>q</th>
<th>( \Delta U )</th>
<th>( \Delta T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expansion for ( P_{ext} = ) const</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>isotherm</td>
<td>(-P_{ext}\Delta V)</td>
<td>-w</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>adiabatic</td>
<td>(-P_{ext}\Delta V)</td>
<td>0</td>
<td>(-P_{ext}\Delta V)</td>
<td>(\Delta U/C_v)</td>
</tr>
<tr>
<td>Reversible expansion/ compression</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>isotherm</td>
<td>(-nRT \ln(V_{fin}/V_{ini}))</td>
<td>-w</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>adiabatic</td>
<td>(C_v\Delta T)</td>
<td>0</td>
<td>(C_v\Delta T)</td>
<td>(T_{ini}{(V_{fin}/V_{ini})^a - 1})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

- **P2.19** 3.50 moles of an ideal gas are expanded from 450. K and an initial pressure of 5.00 bar to a final pressure of 1.00 bar, and \(C_{p,m} = 5/2R\). Calculate \(w\) for the following two cases: **a.** The expansion is isothermal and reversible. **b.** The expansion is adiabatic and reversible.

- **b.** \(q = 0 \Rightarrow w = \Delta U = C_v(T_{fin} - T_{ini})\)
- \(C_v = C_p - nR \Rightarrow\) So the question is how to get \(T_{fin}\)?

\[
\frac{T_{fin}}{T_{ini}} = \left(\frac{V_{fin}}{V_{ini}}\right)^{(1-\gamma)}
\]

\[
P_{ini} V_{ini}^\gamma = P_{fin} V_{fin}^\gamma
\]

\[
\Rightarrow \left(\frac{P_{fin}}{P_{ini}}\right)^{1/\gamma} = \left(\frac{V_{ini}}{V_{fin}}\right)
\]
P2.20) An ideal gas described by $T_i = 300$ K, $P_i = 1.00 \text{ bar}$, and $V_i = 10.0 \text{ L}$ is heated at constant volume until $P = 10.0 \text{ bar}$. It then undergoes a reversible isothermal expansion until $P = 1.00 \text{ bar}$. It is then restored to its original state by the extraction of heat at constant pressure. Depict this closed-cycle process in a $P-V$ diagram. Calculate $w$ for each step and for the total process. What values for $w$ would you calculate if the cycle were traversed in the opposite direction?

$(P, V) \quad V = \text{const} \quad T = \text{const} \quad P = \text{const}$

$(1 \text{ bar}, 10 \text{ L}) \rightarrow (10 \text{ bar}, 10 \text{ L}) \rightarrow (1 \text{ bar}, 100 \text{ L}) \rightarrow (1 \text{ bar}, 10 \text{ L})$

- Which process involves work?
- How much work is involved?

Ch3.1 Math Properties of State Function

$$Z(x + dx, y + dy) = Z(x, y) + \left( \frac{\partial Z(x, y)}{\partial x} \right)_y dx + \left( \frac{\partial Z(x, y)}{\partial y} \right)_x dy$$

$$dZ(x, y) = \left( \frac{\partial Z(x, y)}{\partial x} \right)_y dx + \left( \frac{\partial Z(x, y)}{\partial y} \right)_x dy$$

If $Z$ is a state function,

$$\left[ \frac{\partial}{\partial y} \left( \frac{\partial Z(x, y)}{\partial x} \right) \right]_x = \left[ \frac{\partial}{\partial x} \left( \frac{\partial Z(x, y)}{\partial y} \right) \right]_y$$
How to Obtain Partial Derivatives? (text p44)

\[ dP(V, T) = \left( \frac{\partial P}{\partial V} \right)_T dV + \left( \frac{\partial P}{\partial T} \right)_V dT \]

**Step 1:** Rewrite \( P \) as a function of \( T \) and \( V \).

\[ \left( \frac{\partial P}{\partial V} \right)_T = \left( \frac{\partial nRT}{\partial V} \right)_T \]

**Step 2:** Put the constants outside the derivative.

\[ \left( \frac{\partial P}{\partial V} \right)_T = nRT \left( \frac{\partial 1}{\partial V} \right)_T \quad \text{T is considered to be a constant for this partial derivative.} \]

**Step 3:** Perform the derivative with respect to \( V \)

\[ \left( \frac{\partial P}{\partial V} \right)_T = nRT \left[ \frac{-1}{V^2} \right] \quad \left( \frac{\partial P}{\partial T} \right)_V = ? \]

---

**Total Differential, Exact Differential, & the Test for Exactness**

d\( Z \) is called **total differential of \( Z \)**

\[ dZ(x, y) = \left( \frac{\partial Z(x, y)}{\partial x} \right)_y dx + \left( \frac{\partial Z(x, y)}{\partial y} \right)_x dy = f(x, y)dx + g(x, y)dy \]

d\( Z \) is called **“an exact differential”** if

\[ \left[ \frac{\partial}{\partial y} \left( \frac{\partial Z(x, y)}{\partial x} \right) \right]_x = \left[ \frac{\partial}{\partial x} \left( \frac{\partial Z(x, y)}{\partial y} \right) \right]_y \quad \text{or} \quad \left[ \frac{\partial}{\partial y} f(x, y) \right]_x = \left[ \frac{\partial}{\partial x} g(x, y) \right]_y \]

When \( dZ \) is exact, \( Z \) is a state function. Namely, the change in \( Z \) does not depend on a path of \( (x, y) \).

\[ \Delta Z = Z(x_{\text{fin}}, y_{\text{fin}}) - Z(x_{\text{ini}}, y_{\text{ini}}) \]
Sample Question
(Test of inexactness of $Dw = -PdV$)

We define work as $Dw = -PdV$.
Show $Dw$ is an *inexact* differential with respect to $V$ and $T$ for an ideal gas.

$$Dw = -PdV + 0\,dT.$$  

$$\frac{\partial}{\partial T}P(V,T)\bigg|_V = \frac{\partial}{\partial V}0(V,T)\bigg|_T$$  

$$\frac{\partial}{\partial T}P(V,T)\bigg|_V = \frac{\partial}{\partial T}nRT/V\bigg|_V = nR/V$$

Sample Questions about Rules in Partial Differentials

Q. Which is a correct equation? Choose all correct ones.

(a) $$\frac{\partial x}{\partial y}\bigg|_z = 1/\left(\frac{\partial y}{\partial x}\bigg|_z\right)$$  
(b) $$\frac{\partial x}{\partial y}\bigg|_z = 1/\left(\frac{\partial y}{\partial x}\bigg|_z\right)$$

(c) $$\left(\frac{\partial x}{\partial y}\bigg|_z\right)\left(\frac{\partial y}{\partial z}\bigg|_x\right)\left(\frac{\partial z}{\partial x}\bigg|_y\right) = 1$$  
(d) $$\left(\frac{\partial x}{\partial y}\bigg|_z\right)\left(\frac{\partial y}{\partial z}\bigg|_x\right)\left(\frac{\partial z}{\partial x}\bigg|_y\right) = -1$$

(e) $$\left(\frac{\partial z}{\partial x}\bigg|_y\right)\left(\frac{\partial x}{\partial y}\bigg|_z\right)\left(\frac{\partial y}{\partial z}\bigg|_x\right) = -1$$  
(f) $$\left(\frac{\partial y}{\partial z}\bigg|_x\right)\left(\frac{\partial z}{\partial x}\bigg|_y\right) = -1/\left(\frac{\partial x}{\partial y}\bigg|_z\right)$$

(g) $$\left(\frac{\partial y}{\partial z}\bigg|_x\right)\left(\frac{\partial z}{\partial x}\bigg|_y\right) = -\left(\frac{\partial y}{\partial x}\bigg|_z\right)$$

(h) $$\left(\frac{\partial x}{\partial z}\bigg|_y\right)\left(\frac{\partial x}{\partial y}\bigg|_z\right)\left(\frac{\partial y}{\partial z}\bigg|_x\right) = -1$$
Sample Questions about Rules in Partial Differentials

Q. Which is a correct equation? Choose all correct ones.

(a) \( \frac{\partial x}{\partial y} = \frac{\partial y}{\partial x} \) \( \frac{\partial y}{\partial z} \) \( \frac{\partial z}{\partial x} \)

(b) \( \frac{\partial x}{\partial y} = \frac{\partial y}{\partial x} \)

(c) \( \frac{\partial x}{\partial y} \frac{\partial y}{\partial z} \frac{\partial z}{\partial x} \)

(d) \( \frac{\partial x}{\partial y} \frac{\partial y}{\partial z} \frac{\partial z}{\partial x} = 1 \)

(e) \( \frac{\partial z}{\partial x} \frac{\partial x}{\partial y} \frac{\partial y}{\partial z} = -1 \)

(f) \( \frac{\partial y}{\partial z} \frac{\partial z}{\partial x} \frac{\partial x}{\partial y} = -1 \)

(g) \( \frac{\partial x}{\partial z} \frac{\partial z}{\partial y} \frac{\partial y}{\partial x} = -1 \)

(h) \( \frac{\partial x}{\partial z} \frac{\partial z}{\partial y} \frac{\partial y}{\partial x} = -1 \)

3.2 Dependence of U on V and T

- U varies by changing V and T as
  \[ dU(V, T) = \left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT \]

Using \( dU = q + w = Dq - P_{ext} dV \)

\[ Dq - P_{ext} dV = \left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT \]

When \( dV = 0 \) \( \implies Dq_v = \left( \frac{\partial U}{\partial T} \right)_V dT \)

\[ \frac{\partial U}{\partial T} \frac{dU}{dT} = C_v \]

To be derived in Sec. 6.3
Heat Capacity & \((\partial U / \partial V)_T\)

\[
\left( \frac{\partial U}{\partial T} \right)_v = \frac{Dq_v}{dT} \equiv C_v \quad \Rightarrow \quad \Delta U_v = \int_{T_1}^{T_2} C_v(T) dT = n \int_{T_1}^{T_2} C_{mv}(T) dT
\]

\[
\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \quad \Rightarrow \quad \Delta U_T = \int_{V_{ini}}^{V_{fin}} \left\{ T \left( \frac{\partial P}{\partial T} \right)_V - P \right\} dV
\]

In general,

\[
\Delta U = \int_{T_1}^{T_2} C_v(T) dT + \int_{V_{ini}}^{V_{fin}} \left\{ T \left( \frac{\partial P}{\partial T} \right)_V - P \right\} dV
\]

Isn’t it true that \(\Delta U = 0\) at constant \(T\)?

---

3.3 Does the Internal Energy Depend More Strongly on \(V\) or \(T\)?

\((\partial U / \partial V)_T\) for an Ideal Gas (text p50)

Isn’t it true that \(\Delta U = 0\) for an ideal gas at constant \(T\)?

For an ideal gas,

\[
\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P = T \left( \frac{\partial nRT / V}{\partial T} \right)_V - P = \frac{nRT}{V} - P = 0
\]

\[
\Rightarrow \quad dU = C_v dT + 0 \; dV = C_v \; dT
\]

\[
\Delta U = \int_{T_{ini}}^{T} C_v(T) dT
\]
(\partial U/\partial V)_T for van der Waals Gas
Example Problem 3.4 (text p51) (HW4 P3.21)

• For a gas described by the van der Waals eq of state, \(P = RT/(V_m - b) - a/V_m^2\).

(a) Calculate \((\partial U/\partial V)_T\) using \((\partial U/\partial V)_T = T(\partial P/\partial T)_V - P\).

(b) Derive an expression for the change in internal energy,

\[ \Delta U_T = \int_{V_{\text{ini}}}^{V_{\text{fin}}} \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV \]

in compressing a van der Waals gas from an initial molar volume \(V_M\) to a final molar volume \(V_m\) at constant temperature.

Solution

(a) vdW eq: \(P = RT/(V_m - b) - a/V_m^2\)

\[
\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P = T \left( \frac{\partial RT}{\partial T} \right)_V \left( \frac{V_m - b - a/V_m^2}{V_m} \right) - P
\]

\[ = \frac{RT}{(V_m - b)} - P = a/V_m^2 \]

\(\Rightarrow\) This term represents inter-molecular interaction

(b) \(\Delta U_{Tm} = \int_{V_{\text{ini}}}^{V_{\text{fin}}} T \left( \frac{\partial P}{\partial T} \right)_V - P \) \(dV_m = \int_{V_{\text{ini}}}^{V_{\text{fin}}} a/V_m^2 \) \(dV_m\)

\[= \left[ -a \right]_{V_{\text{ini}}}^{V_{\text{fin}}} V_m \]

\[= a \left( \frac{1}{V_{\text{ini}}} - \frac{1}{V_{\text{fin}}} \right) \]
3.4 H as a function of \( P \) & \( T \)

- \( H \) varies by changing \( P \) and \( T \) as

\[
dH(P, T) = \left( \frac{\partial H}{\partial P} \right)_T dP + \left( \frac{\partial H}{\partial T} \right)_P dT
\]

When \( dP = 0 \) (\& \( P = P_{\text{ext}} \))

\[
Dq_P = dH_p = \left( \frac{\partial H}{\partial T} \right)_P dT
\]

\[
\left( \frac{\partial H}{\partial T} \right)_P = \frac{Dq_P}{dT} \equiv C_P
\]

\[
\left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P
\]

Q. What is this \((\partial H/\partial P)_T\) value for an ideal gas?

\( \rightarrow \) For non-ideal gas: \((\partial H/\partial P)_T = -C_P \mu_f(T) \) (Ch 3.7)

3.5 How Are \( C_P \) and \( C_v \) Related?

(General case)

- \( dU = Dq - P_{\text{ext}} dV \rightarrow Dq = dU + P_{\text{ext}} dV \)

For a reversible case \( (P_{\text{ext}} = P) \) and \( P = \text{const} \),

\[
Dq_P = dU + P dV = \left\{ T \left( \frac{\partial P}{\partial T} \right)_V \right\} dV + C_v dT
\]

\[
dU = \left\{ T \left( \frac{\partial P}{\partial T} \right)_V \right\} dV + C_v dT
\]

When \( P \) is const \( \rightarrow Dq = Dq_P = C_P dT \)

\[
C_P dT_p = C_v dT_p + \left\{ T \left( \frac{\partial P}{\partial T} \right)_V \right\} dV_p
\]

\[
C_P = C_v + T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P = C_v + TV \beta^2 \kappa
\]
• **P3.10)** Starting with the van der Waals equation of state, find an expression for the total differential \( dP \) in terms of \( dV \) and \( dT \). By calculating the mixed partial derivatives \( \left( \frac{\partial}{\partial T} \left( \frac{\partial P}{\partial V} \right) \right)_T \) and \( \left( \frac{\partial}{\partial V} \left( \frac{\partial P}{\partial T} \right) \right)_P \) determine if \( dP \) is an exact differential.

- Van der Waals equation:
  \[
P = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2}
\]

Note: The second term vanishes (you should show why).

\[
\left( \frac{\partial}{\partial V} \frac{RT}{(V_m - b)} \right)_T = \left( \frac{\partial}{\partial V} \frac{nRT}{(V - nb)} \right)_T = -\frac{nRT}{(V - nb)^2}
\]

---

**Sample Question (Ch 3.6)**

Q. Prove this

\[
\left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P
\]

From definition \( H = U + PV \)

\[
dH = dU + PdV + V \quad [Q1]
\]

\[
C_\rho dT + C_v dT + \left[ Q2 \right] dP = C_v dT + \left( \frac{\partial U}{\partial V} \right)_T dV + PdV + VdP
\]

For isothermal process \( dT = 0 \),

\[
\left( \frac{\partial H}{\partial P} \right)_T dP = \left\{ \left( \frac{\partial U}{\partial V} \right)_T + P \right\} dV + VdP
\]

\[
\therefore \left( \frac{\partial H}{\partial P} \right)_T = \left\{ \left( \frac{\partial U}{\partial V} \right)_T + P \right\} \left( \frac{dV}{dP} \right)_T + V
\]
• **P3.16** A mass of 35.0 g of H2O(s) at 273 K is dropped into 180.0 g of H2O(l) at 325 K in an insulated container at 1 bar of pressure. Calculate the temperature of the system once equilibrium has been reached. Assume that $CP_m$ for H2O is constant at its values for 298 K throughout the temperature range of interest.

  - Heat to H2O(s) is $n \Delta H_{fus} + C_{pm}^{\text{water}} n(T - 273K)$
  - Heat to H2O(l) to ice $C_{pm}^{\text{water}} m(325 - T)$

→ For P3.16 Use enthalpy of fusion for Ice (6008 Jmol⁻¹)

---

**HW4**

• **P3.19** Because $(\partial H/\partial P)_T = -C_P \mu_{J,T}$ the change in enthalpy of a gas expanded at constant temperature can be calculated. To do so, the functional dependence of $\mu_{J,T}$ on $P$ must be known.

  - Q1. Treating Ar as a van der Waals gas, calculate $\Delta H$ when 1 mol of Ar is expanded from 400. to 1.00 bar at 300. K. Assume that $\mu_{J,T}$ is independent of pressure and is given by $\mu_{J,T} = [(2a/RT) - b]/C_{Pm}$, and $C_{Pm} = 5/2R$ for Ar.

  - Q2. What value would $\Delta H$ have if the gas exhibited ideal gas behavior?

Q1. $dH = (\partial H/\partial P)_T dP + C_p dT$

What is $dT$ in this case?

How do you obtain $\Delta H$?

• For an ideal gas, $\mu_{J,T} = 0$. This means $(\partial H/\partial P)_T = 0$  

[Q3]
Heat Capacity $C_V$ of Various Gas

**Q.** What defines $C_V$ for He, CO, & $C_2H_4$ at 200K?

**Hint:** $R \sim 8\text{ J K}^{-1}\text{ mol}^{-1}$

\[
\frac{d(E_{\text{trans}} + E_{\text{rot}})}{dT} = 3R
\]

\[
\frac{d(E_{\text{trans}} + E_{\text{rot}})}{dT} = \frac{5R}{2}
\]

\[
\frac{dE_{\text{trans}}}{dT} = \frac{3R}{2}
\]

---

**Ch 4. Standard Partial Molar Enthalpy**

(Raff p105)

For a molecule $A$,

\[dH_A = C_pA dT + (\frac{\partial H}{\partial P})dP + \Delta n_A \overline{H}_A\]

$\overline{H}_A = \left(\frac{\partial H}{\partial n_A}\right)_{T,P}$ is the partial molar enthalpy of $A$.

- At the standard condition ($T = 298.15\text{ K, P =1bar}$)
  \[dH_A = \overline{H}_A \Delta n_A \Rightarrow \Delta H_A = \overline{H}_A \Delta n_A\]

If we have more than one type of molecule,

\[\Delta H = \Delta n_A \overline{H}_A + \Delta n_B \overline{H}_B + \Delta n_C \overline{H}_C + \ldots = \sum X \Delta n_X \overline{H}_X\]
Standard Formation Enthalpy

- Consider a reaction from pure elements that are most stable at 29815 K and 1 bar, which results in the formation of one mole of a molecule of your interest.
  - C(s, graphite) + O₂(g) → CO₂(g) + q_{sur}(393.5 kJ)
  - 1/2N₂(g) + 3/2H₃ → NH₃(g) + q_{sur}(45.9 kJ)
  - 1/2N₂(g) → N(g) + q_{sur}(-472.7 kJ)

Note, the only product should be the molecule of your interest.

- Assume that q is the heat generated for the reaction when P = 1 bar and T = 298.15K (Standard State). The energy is described as a standard formation enthalpy $\Delta H_f^0$ for CO₂(g) and NH₃(g) as
  - $\Delta H_f^0$ for CO₂ = −393.5 kJmol⁻¹
  - $\Delta H_f^0$ for NH₃ = −45.9 kJmol⁻¹
  - $\Delta H_f^0$ for N(g) = +472.7 kJmol⁻¹

Reaction Enthalpy

- For a reaction that takes place at constant P and T, the heat flow needed for a chemical reaction is $\Delta H_{\text{reaction}}$.
  - $v_A A + v_B B \rightarrow v_X X + v_Y Y$
  - $\Delta H_{\text{reaction}} = [Q1]$

- In general,
  
  $\Delta H_{\text{reaction}} = \sum_{i=X} v_i \Delta H_{f_i}^{\text{Product}} - \sum_{k=A} v_k \Delta H_{f_k}^{\text{Reactant}}$

  or
  
  $\Delta H_{\text{reaction}} = \sum_i v_i \Delta H_{f_i}^0$

  (Note use $v_i > 0$ for products and $v_i < 0$ for reactants)
Sample Question
Ex. 4.1 (p67)

\[ \Delta H_f^0(C_{12}H_{22}O_{11}(s)) = -2226 \text{ kJmol}^{-1} \]
\[ \Delta H_f^0(CO_2(aq)) = -412.9 \text{ kJmol}^{-1} \]
\[ \Delta H_f^0(H_2O(l)) = -258.8 \text{ kJmol}^{-1} \]

• How much is the reaction enthalpy for the following reaction?
\[ C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(aq) + 11H_2O(l) \]

\[ \Delta H_{\text{reaction}} = \nu_X H_f^0 + \nu_Y H_f^0 - \nu_A H_f^0 - \nu_B H_f^0 \]
\[ = 12H_f^0(CO_2(aq)) + 11H_f^0(H_2O(l)) - H_f^0(C_{12}H_{22}O_{11}(s)) - H_f^0(O_2(g)) \]
\[ = 12 \times (-412.9 \text{ kJ}) + 11 \times (-258.8 \text{ kJ}) - (-2226 \text{ kJ}) = -5873 \text{ kJ} \]

Bond Energy: \( \Delta U \) for Reactions for a Bond Formation (P69)

The average bond enthalpy of the O—H bond in water is defined as one-half of the enthalpy change for the reaction \( H_2O(g) \rightarrow 2H(g) + O(g) \). The formation enthalpies, \( \Delta H_f^0 \), for \( H(g) \) and \( O(g) \) are 218.0 and 249.2 kJ mol\(^{-1} \), respectively, at 298.15 K, and \( \Delta H_f^0 \) for \( H_2O(g) \) is -241.8 kJ mol\(^{-1} \) at the same temperature.

a. Use this information to determine the average bond enthalpy of the O—H bond in water at 298.15 K.

\( \Delta H_{\text{bond}}^0 = \Delta H_{\text{reaction}}^0 \)
\[ \Delta H_{\text{reaction}}^0 = 2\Delta H_f^0(H(g)) + \Delta H_f^0(O(g)) - \Delta H_f^0(H_2O(g)) \]
\[ = 218.0 \times 2 \text{ kJ} + 249.2 \text{ kJ} - (-241.8 \text{ kJ}) = 927 \text{ kJ} \]

b. Determine the average bond energy, \( \Delta U \), of the O—H bond in water at 298.15 K. Assume ideal gas behavior.

\[ \Delta U_{\text{reaction}}^0 = \Delta H_{\text{reaction}}^0 - \Delta (PV) = \Delta H_{\text{reaction}}^0 - RT \Delta (n) \]

Q. What is \( \Delta n \)?
4.4 The Temperature Dependence of Reaction Enthalpies

Suppose we would like to perform a reaction at a higher temperature than 298.15 K, the enthalpy can be calculated from

\[ H^0_T = H^0_{298.15 \text{ K}} + \int_{298.15 \text{ K}}^{T} C_P(T')dT' \]

For a reaction

\[ \Delta H^0_{\text{reaction}, T} = \Delta H^0_{\text{reaction}, 298.15 \text{ K}} + \int_{298.15 \text{ K}}^{T} \Delta C_P(T')dT' \]

\[ \Delta C_P(T') = \sum \nu_j C_{p,j}(T') \]

HW5 Q1

- Using \( dH_A = C_{pA}dT + (\partial H/\partial P)_Tdn + (\partial H/\partial n)_Tpdn_A \) (\( A = B, X, \) or \( Y \)), prove that the reaction enthalpy \( \Delta H_{\text{reaction}}(T) \) is given by eq. (4.27) in the text. Specify the path of (P, T, n) you would like to use. Assume a reaction \( B \rightarrow X + Y \).

\[ \Delta H^0_{\text{reaction}, T} = \Delta H^0_{\text{reaction}, 298.15 \text{ K}} + \int_{298.15 \text{ K}}^{T} \Delta C_P(T')dT' \]

(1) \( B(T) \rightarrow B(298K) \quad \Delta H(1) = [Q1] \)

(2) \( B(298K) \rightarrow X(298K) + Y(298K) \quad \Delta H(2) = [Q2] \)

(3) \( X(298K) + Y(298K) \rightarrow X(T) + Y(T) \quad \Delta H(3) = [Q3] \)
Ch 4.5 How to convert $\Delta U$ to $\Delta H$?

For ideal gas,

$$\Delta H_{\text{reaction}}^{0} = \Delta U_{\text{reaction}}^{0} + \Delta (PV) = \Delta U_{\text{reaction}}^{0} + RT(\Delta n)$$

For liquid/solid,

$$\Delta H_{\text{reaction}}^{0} = \Delta U_{\text{reaction}} + \Delta (PV) \sim \Delta U_{\text{reaction}}$$

Overall,

$$\Delta H_{\text{reaction}}^{0} = \Delta U_{\text{reaction}}^{0} + RT(\Delta n_{\text{gas}})$$

Q. What is $\Delta n_{\text{gas}}$ for this reaction?

**Ex.**

$$\text{NH}_2\text{CONH}_2(s) + \frac{3}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l) + \text{N}_2(g)$$

$$\Delta H_{\text{reaction}} = \Delta U_{\text{reaction}} + \Delta (PV) = \Delta U_{\text{reaction}} + RT\Delta n$$

$$= -6.37 \times 10^5 \text{ J mol}^{-1} + \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}{2}$$

$$= -635 \text{ kJ mol}^{-1}$$

Ch 5.3 Introducing Entropy (Lec. 19)

Entropy: $S \equiv \frac{Dq_{\text{reversible}}}{T}$ [5.12]

S is a new state function

$$\int dS = \int \frac{Dq_{\text{reversible}}}{T} = 0$$

For a “natural” process $\Delta S \geq 0$ in an isolated system

So our world’s entropy is always increasing!

Second Law of Thermodynamics:

It is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat into the system from a heat reservoir and the performance of an equivalent amount of work by the system on the surroundings.
Ch 5.1 The Universe has a natural direction of change

A

\[ V = 1 \text{L} \quad P = 1 \text{bar} \quad T = 300 \text{K} \]

B

\[ V = 2 \text{L} \quad P = \frac{1}{2} \text{bar} \quad T = 300 \text{K} \]

C

Adiabatic expansion

V = 1L \quad P' = 0 \text{bar}

D

Q. Why cannot we expect B \rightarrow A or D \rightarrow C in a spontaneous way?

5.4 Calculating Changes in Entropy for Ideal Gas

\[ dS \equiv \frac{Dq_{\text{reversible}}}{T} \]

\[ \begin{array}{l}
V = 1 \text{L} \quad P = 1 \text{bar} \\
T = 300 \text{K}
\end{array} \]

\[ \begin{array}{l}
V = 1 \text{L} \quad P' = P \text{bar}
\end{array} \]

• Case 1. Adiabatic reversible process
  \[ dS = \frac{Dq_{\text{reversible}}}{T} = 0 \rightarrow \Delta S = 0 \]

• Case 2. Isothermal reversible process \((V_i, T_i) \rightarrow (V_f, T_f)\)
  \[ q_{\text{reversible}} = -w_{\text{reversible}} = \int_{V_i}^{V_f} PdV = \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \ln(V_f/V_i) \]

\[ \Delta S = \int \frac{Dq_{\text{reversible}}}{T} = q_{\text{reversible}} = nRT \ln(V_f/V_i) \]

Q. What is the sign of \(\Delta S\) for isothermal reversible compression?
5.5 Using Enthalpy to Calculate the Natural Direction of a Process in an Isolated System

- \( dS_L = -\frac{Dq}{T_L} = C_v dT_L / T_L \)
- \( dS_R = \frac{Dq}{T_R} = C_v dT_R / T_R \)
- \( dS = Dq \left( \frac{1}{T_R} - \frac{1}{T_L} \right) \)

\[ dS > 0 \rightarrow dS > 0 \text{ or } dS < 0? \]

\[ \Delta S = \int_{300K}^{400K} \frac{C_v}{T_L} dT_L + \int_{400K}^{500K} \frac{C_v}{T_R} dT_R \]
\[ = C_v \ln \left( \frac{400K}{300K} \right) + C_v \ln \left( \frac{500K}{400K} \right) \]
\[ = C_v \ln \left( \frac{16}{16 - 1} \right) > 0 \]

Q. How much is \( \Delta S \) for B \( \rightarrow \) A? Is \( \Delta S \) positive?

5.6 Clausius Inequality (p95)
\[ dU = Dq - P_{ext} dV \] (5.29)
- For a reversible change,
\[ dU = Dq_{\text{reversible}} - P_{ext} dV = TdS - P_{ext} dV \] (5.30)
- When \( dU \) and \( dV \) for (5.29) and (5.30) are common,
\[ TdS - P_{ext} dV = Dq_{\text{reversible}} - P_{ext} dV \]

\[ \Rightarrow TdS = Dq_{\text{reversible}} - P_{ext} dV \] (5.31)
- If \( P - P_{ext} > 0 \rightarrow \) The system will expand or \( dV > 0 \).
- If \( P - P_{ext} < 0 \rightarrow \) The system will shrink or \( dV < 0 \).

Namely, \( TdS - Dq > 0 \) when \( P \neq P_{ext} \) (when 5.29 is irreversible)
\[ \Rightarrow dS > \frac{Dq_{\text{reversible}}}{T} \]

\[ dS > \frac{Dq_{\text{irreversible}}}{T} = 0 \]

For an irreversible process in an isolated system
Calculated Change in Enthalpy (continued)

• Case 3 (3'). Reversible change in T for a fixed V

\[ \Delta S = \int \frac{Dq_{\text{reversible}}}{T} = \int nC_{v,m} \frac{dT}{T} = nC_{v,m} \ln \left( \frac{T_f}{T_i} \right) \]

• Case 4 (4'). Reversible change in T for a fixed P

\[ \Delta S = \int \frac{Dq_{\text{reversible}}}{T} = \int nC_{p,m} \frac{dT}{T} = nC_{p,m} \ln \left( \frac{T_f}{T_i} \right) \]

• Case 5 (reversible) & 5'(irreversible) process: \((T_i, V_i) \rightarrow (T_p, V_f)\)

By calculating S for \((T_i, V_i) \rightarrow (T_p, V_i) \rightarrow (T_p, V_f)\)

\[ \Delta S = nR \ln \left( \frac{V_f}{V_i} \right) + nC_{v,m} \ln \left( \frac{T_f}{T_i} \right) \]

• Case 6 & 6' (Ti, Pi) \rightarrow (T_p, P_f)

By calculating S for \((T_i, P_i) \rightarrow (T_p, P_i) \rightarrow (T_p, P_f)\) \((P_i/P_f = V_f/V_i)\)

\[ \Delta S = nR \ln \left( \frac{V_f}{V_i} \right) + nC_{p,m} \ln \left( \frac{T_f}{T_i} \right) = -nR \ln \left( \frac{P_f}{P_i} \right) + nC_{p,m} \ln \left( \frac{T_f}{T_i} \right) \]

HW6

• P5.5) Calculate \(\Delta S\) if the temperature of 1 mol of an ideal gas with \(C_v = \frac{3}{2} R\) is increased from 150. to 350. K under conditions of (b) constant volume and (a) constant pressure. Choose the correct one.

(1) \(\frac{3R}{2} \ln(150K/350K)\)  (2) \(2R \ln(150K/350K)\)

(b) \(\frac{3R}{2} \ln(350K/150K)\)  (4) \(2R \ln(350K/150K)\)

(a) \(\frac{5R}{2} \ln(350K/150K)\)  (6) \(\frac{5R}{2} \ln(150K/350K)\)

\(\Delta S = nR \ln \left( \frac{V_f}{V_i} \right) + nC_{v,m} \ln \left( \frac{T_f}{T_i} \right)\)

\(\Delta S = -nR \ln \left( \frac{P_f}{P_i} \right) + nC_{p,m} \ln \left( \frac{T_f}{T_i} \right)\)

\(C_p = C_v + nR\)
**Equations to be memorized for ideal gas**

(0) For constant $C_{v,m}$ or $C_{p,m}$
- $\Delta U = n C_{v,m} \Delta T$ \[1\]
- $\Delta H = n C_{p,m} \Delta T = n(C_{v,m} + R) \Delta T$ \[2\]

(1) For a reversible isothermal process,
- $\Delta U = \Delta H = 0$  
  $\Delta S = n R \ln(V_f/V_i)$
- $w = -q = -n R T \ln(V_f/V_i)$

(2) For a reversible adiabatic process (for $C_{p,m}, C_{v,m}$ const)

$$\frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right)^{1-\gamma} \left( \frac{p_i}{p_f} \right)^{1-\gamma} \rightarrow \text{Useful for } \Delta H \text{ & } \Delta U \text{ calc. in [1] & [2]}$$

$$\Delta S = n R \ln(V_f/V_i) + n C_{v,m} \ln(T_f/T_i) = 0$$

$$\Delta S = -n R \ln(P_f/P_i) + n C_{p,m} \ln(T_f/T_i) = 0$$

---

**P5.13** One mole of an ideal gas with $C_{v,m} = 5/2 \ R$ undergoes the transformations described in the following list from an initial state described by $T_i = 250 \ \text{K}$ and $P_i = 1.00 \ \text{bar}$. Calculate $q$, $w$, $\Delta U$, $\Delta H$, and $\Delta S$ for each process.

**a.** The gas undergoes a reversible adiabatic expansion until the final pressure is half its initial value.
- (a) $q_{rev} = 0$. 
  $dS = Dq_{rev}/T = 0$

$$\frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right)^{1-\gamma} = \left( \frac{p_i}{p_f} \right)^{1-\gamma} \rightarrow \left( \frac{T_f}{T_i} \right)^{\gamma} = \left( \frac{p_i}{p_f} \right)^{\gamma}$$

Use $X = Y^a$ \rightarrow $X = Y^{\sigma a}$ **Obtain** $T_f$

$$w = \Delta U = n C_{v,m} \Delta T; \ \Delta H = n C_{p,m} \Delta T$$

**[Q1]**

**[Q2]**
(3) For an ideal gas in a reversible adiabatic process for T-dependent $C_v(T)$ or $C_p(T)$ (Memorize)

$$
\Delta U = \int nC_v,m(T)dT \quad \Delta H = \int nC_p,m(T)dT
$$

$$
\Delta S = -nR\ln(P_f/P_i) + \int \frac{nC_p,m(T)dT}{T}
$$

$$
\Delta S = nR\ln(V_f/V_i) + \int \frac{nC_v,m(T)dT}{T}
$$

(4) For an ideal gas in an irreversible adiabatic process at a constant external pressure ($C_v, C_p$ const)

$$
\Delta U = nC_v,m\left(T_f - T_i\right) = -nRp_{\text{external}}\left(\frac{T_f}{p_f} - \frac{T_i}{p_i}\right) = W \rightarrow \text{Solve this for } T_f
$$

$$
\Delta H = nC_p,m\Delta T
$$

$$
\Delta S = -nR\ln(P_f/P_i) + nC_p,m\ln(T_f/T_i)
$$

Q. What are $\Delta U$, $\Delta H$, $\Delta S$ for $P_{\text{ext}} = 0$?

$$
\Delta S = nR\ln(V_f/V_i) + nC_v,m\ln(T_f/T_i)
$$

---

**P5.6** One mole of $N_2$ at 20.5°C and 6.00 bar undergoes a transformation to the state described by 145°C and 2.75 bar. Calculate $\Delta S$ if

$$
\frac{C_{p,m}}{\text{J mol}^{-1}\text{K}^{-1}} = 30.81 - 11.87 \times 10^{-3} \frac{T}{\text{K}} + 2.3968 \times 10^{-5} \frac{T^2}{\text{K}^2} - 1.0176 \times 10^{-8} \frac{T^3}{\text{K}^3}
$$

$$
\Delta S = -nR \ln \frac{p_f}{p_i} + n \int_{T_i}^{T_f} \frac{C_{p,m}}{T} dT
$$
P5.13) One mole of an ideal gas with $C_v,m = \frac{5}{2} R$ undergoes the transformations described in the following list from an initial state described by $T = 250. \text{ K}$ and $P = 1.00 \text{ bar}$. Calculate $q$, $w$, $\Delta U$, $\Delta H$, and $\Delta S$ for each process.

b. The gas undergoes an adiabatic expansion against a constant external pressure of 0.500 bar until the final pressure is half its initial value.

$$\Delta U = n \ C_v,m \ (T_f - T_i) = -n \ R \ p_{\text{external}} \ (\frac{T_f}{P_f} - \frac{T_i}{P_i}) = w$$

$$\Delta H = n C_{p,m} \Delta T \quad \Rightarrow \text{Solve this for } T_f$$

Q. Which equation should we use for $\Delta S$?

$$\Delta S = -nR \ln\left(\frac{P_f}{P_i}\right) + n C_{p,m} \ln\left(\frac{T_f}{T_i}\right)$$

---

5.10 Entropy Change in Chemical Reaction

At 298.15 K and 1 bar

A + 2B $\rightarrow$ 2C + D

- $\Delta S_{\text{reaction}}^0 = 2S_C^0 + S_D^0 - S_A^0 - 2S_B^0$

In general

$$\Delta S_R^0 (T) = \sum \nu X S_{X,m}^0$$

- A(T) + 2B(T) $\rightarrow$ 2C(T) + D(T)

For a constant pressure

$$\Delta S(T) = \Delta S(298K) + \int_{298}^{T} \frac{\Delta C_p^0 dT'}{T'}$$

$$\Delta C_p^0 = \sum \nu X C_{p,m}^0$$

Q. How much is $\Delta C_p^0$ for the above reaction?

$$\Delta C_p^0 = 2C_{p,m_C}^0 + C_{p,m_D}^0 - C_{p,m_A}^0 - 2C_{p,m_B}^0$$
• P5.20) Consider the formation of glucose from carbon dioxide and water, that is, the reaction of the following photosynthetic process: $6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g)$. The following table of information will be useful in working this problem:

<table>
<thead>
<tr>
<th>$T = 298$ K</th>
<th>$\text{CO}_2(g)$</th>
<th>$\text{H}_2\text{O}(l)$</th>
<th>$\text{C}<em>6\text{H}</em>{12}\text{O}_6(s)$</th>
<th>$\text{O}_2(g)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^0_f$ kJ mol$^{-1}$</td>
<td>$-393.5$</td>
<td>$-285.8$</td>
<td>$-1273.1$</td>
<td>$0.0$</td>
</tr>
<tr>
<td>$S^0_f$ J mol$^{-1}$ K$^{-1}$</td>
<td>$213.8$</td>
<td>$70.0$</td>
<td>$209.2$</td>
<td>$205.2$</td>
</tr>
<tr>
<td>$C_{p,m}^0$ J mol$^{-1}$ K$^{-1}$</td>
<td>$37.1$</td>
<td>$75.3$</td>
<td>$219.2$</td>
<td>$29.4$</td>
</tr>
</tbody>
</table>

- Calculate the entropy and enthalpy changes for this chemical system at (a) $T = 298$ K and (b) $T = 330$ K. Calculate also the entropy of the surrounding and the universe at both temperatures.

\[ (a) \Delta S^0 = \sum \nu X \Delta S^0_X \]
\[ (b) \Delta S(T) = \Delta S(298 K) + \int_{298}^{T} \frac{\Delta C_p^0 dT}{T} \]
\[ \Delta C_p^0 = \sum \nu X C_{p,m}^0 \]

---

\[ \Delta S \text{ for liquid & solid (p91)} \]
\[ dS = \left( \frac{\partial P}{\partial V} \right)_T dV + \left( \frac{\partial V}{\partial T} \right)_P dP - \frac{1}{T} C_v dT = \frac{\beta}{\kappa} dV + \frac{C_v}{T} dT \]
\[ \Delta S = \int_{V_i}^{V_f} \frac{\beta}{\kappa} dV + \int_{T_i}^{T_f} \frac{C_v}{T} dT = \frac{\beta}{\kappa} (V_f - V_i) + C_v \ln \left( \frac{T_f}{T_i} \right) \]
\[ \text{Correct for Solid & Liquid} \]

\[ \Delta S = \int_{P_i}^{P_f} \frac{\beta}{\kappa} dP + \int_{T_i}^{T_f} \frac{C_p}{T} dT = V \beta (P_f - P_i) + C_p \ln \left( \frac{T_f}{T_i} \right) \]

Q Is the equation valid for an ideal gas?
\[ \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{T} \quad \kappa = -\frac{1}{V} \left( \frac{\partial P}{\partial T} \right)_V = \frac{1}{P} \quad \text{so} \quad \frac{\beta}{\kappa} = \frac{P}{T} = \frac{nR}{V} \]