No Analytical crib available

September 22, 2007

Written by Professor Simpson

Biochemistry Cumulative Exam

Title: Transcription and Translation

September 22, 2007

1. (20 points). What are the functions of the following?

(a) EF-Tu

Bacterial elongation factor EF-Tu helps the correct aa-tRNA insert into site A. EF-Tu is a GTPase.

(b) EF-Ts

EF-Ts is an exchange factor for EF-Tu. It helps exchange GDP to GTP.

(c) t-RNA synthetase

An enzyme catalyzing the linkage of a transfer ribonucleic acid (tRNA) molecule to its corresponding amino acid during protein synthesis.

(d) mRNA

RNA that serves as a template for protein synthesis.

2. (5 points) What are the approximate transcription and translation rates in *E. coli*?

30-85 bases/sec
18-20 amino acids/sec

3. (10 points). What is the role of sigma subunit? Why is it advantageous to have sigma subunits?

Answer: σ subunit is responsible for initiating transcription. By controlling the expression of different σ subunits, cells can easily control gene expression.

4. (10 points) Provide any two differences between promoters and enhancers.

    1. Location relative to transcription site is not fixed for enhancers. They can be upstream, downstream or even in the midst of the transcribed genes. Enhancers can be several thousand base pairs away.
    2. A particular enhancer is effective in only certain cells, in which appropriate regulatory proteins are expressed.
    3. Enhancers can stimulate transcription by perturbing chromatin structure.

5. (15 points) Provide any three major identity elements of t-RNA?

Anticodon
Clover leaf like structure
3' end has CCA terminal that couples to its cognate amino acid.

6. (20 points) Define the following terms in two to three sentences:
   (a) Anticodon

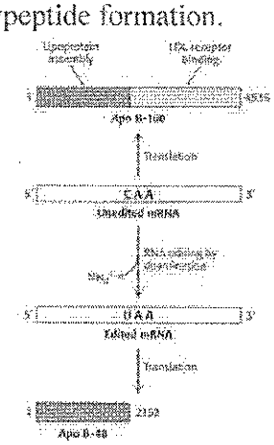
A three nucleotide sequence which is present in the anticodon loop of t-RNA. This sequence is responsible for recognizing codons on mRNA.

(b) Shine Dalgarno sequence

- Ribosome-binding sites at the 5' end of mRNA for several *E. coli* proteins
- S-D sequences occur immediately upstream of initiation codons.
- SD sequence is complementary to a pyrimidine rich sequence at the 3' end of 16S rRNA molecule.

(c) RNA editing

A base change occurs in mRNA, such as conversion of C to U, resulting in a different polypeptide formation.



(d) RNAi

A gene silencing phenomenon whereby double-stranded RNAs trigger the specific degradation of a homologous mRNA. The specific dsRNAs are processed into small interfering RNA (siRNA) which serves as a guide for cleavage of the homologous mRNA in the RNA- induced silencing complex (RISC). Useful as an application for specific suppression of an individual gene.

7. (15 points) What are the three major differences between prokaryotic and eukaryotic mRNA?

Answer: Polyadenylation of the tail of mRNA in eukaryotes
Capping of mRNA in eukaryotes
Splicing
Polycitronic versus monocistronic.

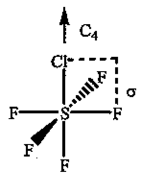
8. (5 points) What is the biggest difference between a typical protein enzyme and ribosome?

Answer: Protein enzyme has the active site made of amino acids. In ribosome, catalytic site is made of RNA and all the reactions in the active site are catalyzed by RNA itself.

Inorganic Cumulative Exam

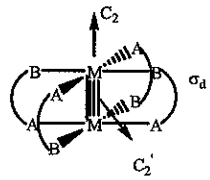
September 22, 2007

1 (25 pt) Assign symmetry point groups for the following molecules/objects (mark symmetry *elements* clearly)



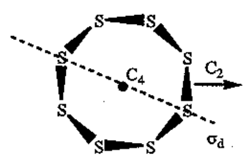
1a

C_{4v}



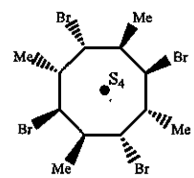
1b

D_{2d}



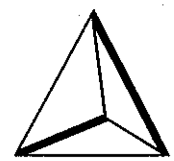
1c

D_{4d}



1d

S_4



1e

(tetrahedron with one pair of opposite edges painted bold)

D_{2d}

S_4 axis linking the midpoints of two painted edges

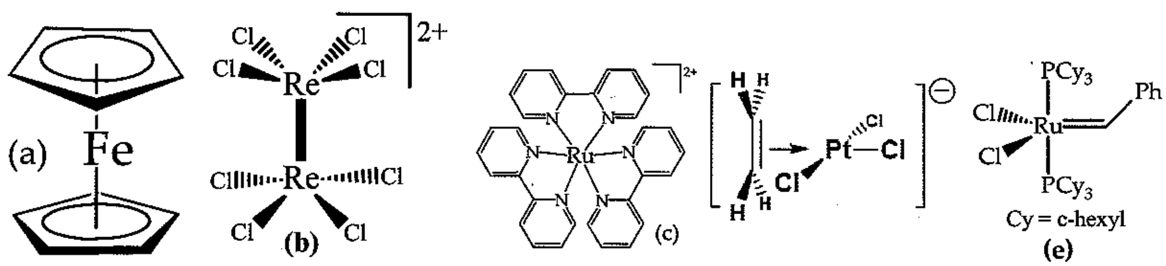
2 (25pt) Use a two dimensional lattice to prove that the only rotation symmetry allowed by lattice translation are C_2, C_3, C_4 and C_6. (See next page)

3 (30 pt) (i) Use the symmetry and LCAO (linear combination of atomic orbitals) to analyze the σ-bonding MOs in $PtCl_4^{2-}$ (use XY plane as the molecular plane) and determine which of Pt valence orbitals are involved in the σ-bonding. Character table can be found from the following page. (ii) By further considering the π-type lone pairs on the Cl^- ligands, sketch *qualitatively* the energy levels of the Pt *d*-orbitals (symmetry unnecessary for this part).

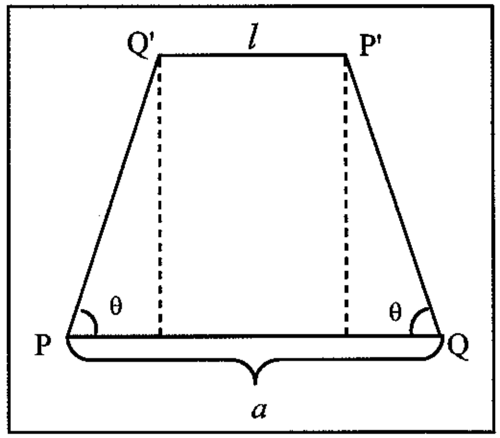
4 (20 pt) Sketch the structures of the following "famous" inorganic compounds (complex ions).

(a) ferrocene (b) $[Re_2Cl_8]^{2-}$ (c) $[Ru(bipy)_3]^{2+}$ (d) Zeiss's salt

(e) Grubbs first generation catalyst



2. On a two dimensional lattice, choose two adjacent lattice points, P and Q, which are related by a *unit* translation *a*.



Should a C_n (rotation $\theta = 2\pi/n$) be permitted on the lattice, then the rotation of PQ about **P** by θ counter clockwise will result in a new lattice point Q'; Similarly, the rotation of PQ about **Q** by θ clockwise will result in a new lattice point P'.

Since both P' and Q' are also lattice points, and P'Q' parallels PQ, Q'P' must be a translation that is a multiple of *a*. Namely,

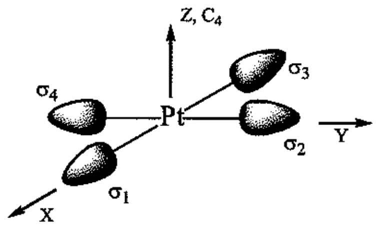
$l = ma$ (*m* is an integer)
$= a - 2a\cos\theta$ (from trigonometry)

Hence, $m = 1 - 2\cos\theta$;

Since $-1 \le \cos\theta \le 1$, then $-1 \le m \le 3$
Since *m* must be an integer, the following table list the possible *m*s, from which the allowed *n* can be derived.

m	θ	*n*
-1	0	1 (trivial)
0	60	6
1	90	4
2	120	3
3	180	2

3. (1) The reducible representation Γ_σ can be derived using the schematic below,



D_{4h}	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	-	x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	-
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	-	x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	-	xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	-	-
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	-
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	-	-
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	-	-
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	-
Γ_σ	4	0	0	2	0	0	0	4	2	0		

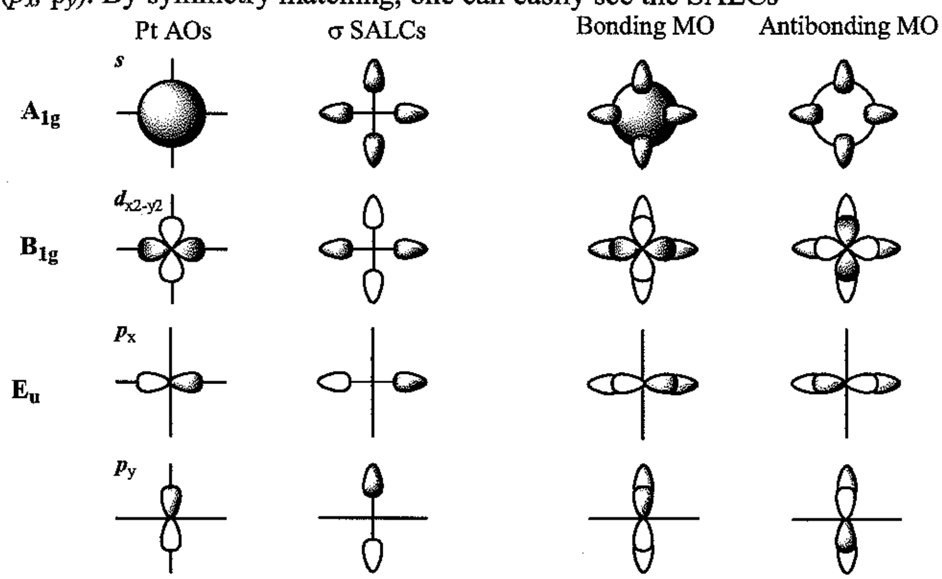
$a_{A1g} = (4 + 4 + 4 + 4)/16 = 1 = a_{B1g}$ $a_{Eu} = (8 + 8)/16 = 1$

$\Gamma_\sigma = A_{1g} + B_{1g} + E_u$;

From character table: possible Pt valence orbitals are s, d_{z2} (A_{1g}); d_{x2-y2} (B_{1g}); and p_x & p_y (E_u)

There are two possible approaches to construct σ-MOs

<u>A Inspection method</u> - Notice that a square planar Pt use dsp^2 hybrid orbitals, where d is d_{x2-y2} and p^2 are (p_x, p_y). By symmetry matching, one can easily see the SALCs



B Projection method (rigorous)

$D_{4h} \rightarrow C_{4v}$: $\Gamma_\sigma = A_{1(g)} + B_{1(g)} + E_{(u)}$

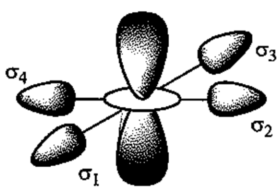
C_{4v}	E	C_4	$C_4^2 = C_2$	C_4^3	σ_v	σ_v'	σ_d	σ_d'
A_1	1	1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1	-1	-1
B_1	1	-1	1	-1	1	1	-1	-1
B_2	1	-1	1	-1	-1	-1	1	1
E	2	0	-2	0	0	0	0	0
σ_1	σ_1	σ_2	σ_3	σ_4	σ_1	σ_3	σ_2	σ_4

$\Phi_{A1} = (\sigma_1+\sigma_2+\sigma_3+\sigma_4)/2$; s; d_{z2}

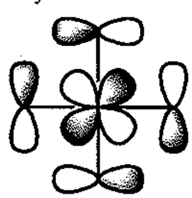
$\Phi_{B1} = (\sigma_1-\sigma_2+\sigma_3-\sigma_4)/2$ d_{x2-y2}

$\Phi'_{Ea} = (\sigma_1-\sigma_3)/\sqrt{2}$; $\Phi'_{Eb} = (\sigma_2-\sigma_4)/\sqrt{2}$; p_x, p_y

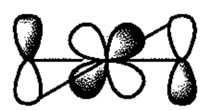
(2) From the discussion above, it is clear that d_{x2-y2} is the most destabilized, while there is no effect on d_{xy}, d_{xz}, d_{yz}. Pt d_{z2} is also destabilized as shown below, but not as drastic as that of d_{x2-y2}. This give rise to the σ-only ligand field diagram. The Cl lone pairs main engage in antibonding interactions with the $d\pi$ orbitals as shown below. Both d_{xz} and d_{yz} are destabilized by interacting with two lone pairs. d_{xy} is destabilized by four lone pairs and thus of higher energy than the (d_{xz}, d_{yz}) pair.

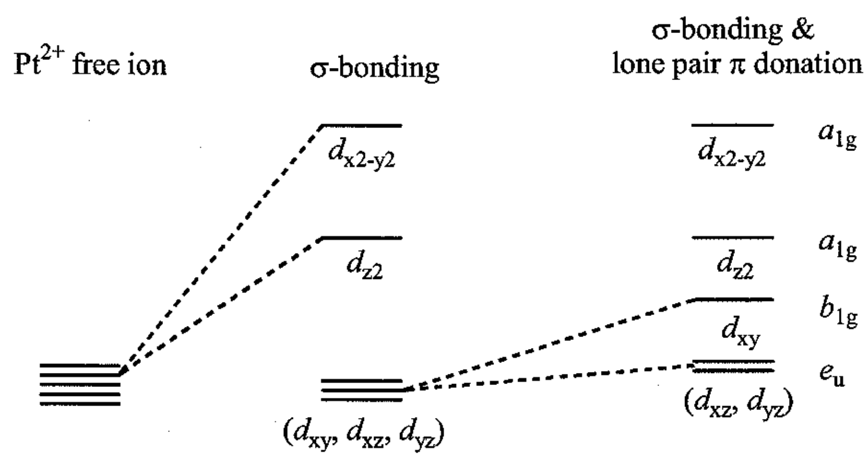


d_{xy} + lone pairs



d_{xz} + lone pairs





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Written by Professor Wei

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Physical Chemistry
Cumulative Exam Solutions

Part A.

a. If $T_{1f} \neq T_{2f}$ ($P_{1f} \neq P_{2f}$) heat (work) energy would be transferred between 1 and 2 and the system would not be in equilibrium. Only if $T_{1f} = T_{2f}$ and $P_{1f} = P_{2f}$ is the system in equilibrium.

b.

(i) Find T_f.

Note $dU = dU_1 + dU_2 = 0$ (system isolated) so that $dU_1 = -dU_2$

or

$$C_{V_1}\, dT_1 = -C_{V_2}\, dT_2 \Rightarrow C_{V_1}(T_{1f} - T_{1i}) = -C_{V_2}(T_{2f} - T_{2i}) \quad (A\cdot 1)$$

or since $T_{1f} = T_{2f} = T_f$,

$$C_{V_1}(T_f - T_{1i}) = -C_{V_2}(T_f - T_{2i}). \quad (A\cdot 2)$$

Solving Eq. (A·2) gives

$$T_f = \frac{C_{V_2} T_{2i} + C_{V_1} T_{1i}}{C_{V_1} + C_{V_2}}. \quad (A\cdot 3)$$

However $C_{V_1} = (3/2 R)(\frac{3}{4} n)$; $C_{V_2} = (5/2\, R)(\frac{1}{4} n)$, $T_{1i} = 5/4\, T_i$, $T_{2i} = T_i$ so

Eq (A·2) becomes

$$\boxed{T_f = \frac{65}{56} T_i}. \quad (A\cdot 4)$$

(A.2)

(ii) Find P_f. First since in the final state $P_1 = P_2$ and $T_1 = T_2$

$P = \frac{nRT}{V} \Rightarrow \frac{V_{1f}}{V_{2f}} = \frac{n_{1f}}{n_{2f}} = \frac{n_{1i}}{n_{2i}} = \frac{3/4\,n}{1/4\,n} = 3$. Thus since

$V_{1f} + V_{2f} = V_{1i} + V_{2i} = \frac{1}{4}V + \frac{3}{4}V = V$, then

$$V_{1f} = \frac{3}{4}V \quad \text{and} \quad V_{2f} = \frac{1}{4}V \qquad (A.5)$$

To find P_f we use (A.6)

$$P_{1f}V_{1f} = n_{1f}RT_{1f} \Rightarrow (P_f)\left(\frac{3}{4}V\right) = \frac{3}{4}nRT_f$$

or

$$\boxed{P_f = \frac{nRT_f}{V} \overset{\text{Eq (A.4)}}{=} \frac{65}{56}\left(\frac{nRT_i}{V}\right)} \qquad (A.7)$$

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Physical Chemistry
Cumulative Exam Solutions

Part B.

(i) What is the final temperature T_f?

$$dU = dq + dw = dw = -P_{ext}\,dV. \qquad (B.1)$$

Also

$$dU = C_v\,dT. \qquad (B.2)$$

Equating gives $C_v\,dT = -P_{ext}\,dV$ or

$$C_v\,(T_f - T_i) = -P_{ext}\,(V_f - V_i). \qquad (B.3)$$

But from ideal gas law

$$V_f - V_i = \frac{RT_f}{P_f} - \frac{RT_i}{P_i} = \frac{R}{P_{ext}}\left(T_f - \frac{T_i}{5}\right). \qquad (B.4)$$

Combining Eqs. (B.3) and (B.4) gives

$$C_v\,(T_f - T_i) \simeq -R\left(T_f - \frac{1}{5}T_i\right)$$

Solving above eqn for T_i and using $C_v = \frac{3}{2}R$ gives

$$\boxed{T_f = \frac{17}{25}T_i \quad \text{(adiabatic cooling)}} \qquad (B.5)$$

(ii) What is the final volume V_f?

$$\boxed{V_f = \frac{RT_f}{P_f} = \frac{RT_f}{P_{ext}} = \frac{17}{25}\frac{RT_i}{P_{ext}}} \qquad (B.6)$$

(iii) What is the work w? From Eq. (B.3)

$$\boxed{w = C_v(T_f - T_i) = \frac{3}{2}R\left(\frac{17}{25} - 1\right)T_i = -\frac{12}{25}RT_i} \qquad (B.7)$$

(iv) What is ΔU?

Eq. (B.7)

$$\boxed{\Delta U = q + w = w = -\frac{12}{25} R T_i} \quad (B.8)$$

(v) What is ΔH? Since $H = U + PV$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + R \Delta T \quad (B.9)$$

But from Eq. (B.7)

$$\Delta T = T_f - T_i = \frac{w}{C_v} = -\frac{12}{25}\,\frac{2}{3}\,\frac{R T_i}{R} = -\frac{8}{25} T_i \quad (B.10)$$

Combining above with Eq. (B.8) gives

$$\boxed{\Delta H = -\frac{4}{5} R T_i} \quad B.11$$