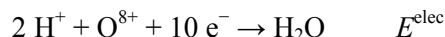


## 1. Connection between QM and Thermodynamics

We have focused to this point on the many approaches and details of calculating the *internal electronic energy* of a single molecule, that is, the energy associated with taking infinitely separated constituent nuclei and electrons at rest and forming a molecule:



We typically calculate  $E^{\text{elec}}$  within the Born-Oppenheimer approximation, i.e. within the approximation that the nuclei of the molecule are all fixed in space. We know that even at 0 K molecules have a *zero-point vibrational energy* (ZPVE), and the 0 K internal energy of a molecule is thus:

$$E^0 = E^{\text{elec}} + \text{ZPVE}$$

ZPVE can be calculated pretty reliably within the harmonic approximation, according to

$$\text{ZPVE} = \frac{1}{2} h \sum_{i=1}^{3n-6} \nu_i$$

where  $\nu_i$  are the harmonic vibrational frequencies, obtained from a vibrational frequency analysis.  $E^{\text{elec}}$  is not directly observable;  $U^0$  in principle is.

$U^0$  is the minimum energy a molecule can have. Higher energies are possible by electronic excitation, or vibrational excitation, or due to rotational motion, or translational motion. If we assume that they are *separable*:

$$E = E^0 + E^{\text{elec}} + E^{\text{vib}} + E^{\text{rot}} + E^{\text{trans}}$$

To fully describe *microscopic* state of a molecule, we would have to specify all these quantities.

Macroscopically, though, what we are typically interested in is the equilibrium value of internal energy,  $U$  (or some other thermodynamic quantity, like  $S$  or  $H$ ) at some specified, externally imposed thermodynamic conditions, like temperature  $T$  or pressure  $P$ . These equilibrium values are obtained by *averaging* over all the possible states of an *ensemble* of molecules. The way this average is constructed is the realm of *statistical thermodynamics*.

Most important for us is the *canonical ensemble*, in which the free variables are  $N$ ,  $V$ , and  $T$ . We'll generally choose  $N$  to be 1 mole, so we can talk about molar values of quantities.

The relative probability of a molecule being in a particular state  $E_i$  above  $E^0$  in the canonical ensemble is given by the Boltzmann factor,

$$P_i \propto e^{-E_i/\beta} = e^{-E_i/k_B T}$$

The sum over all the states is the canonical *partition function*:

$$Q(N, V, T) = \sum_i e^{-E_i/\beta}$$

Good news: all thermodynamic quantities can be defined in terms of this function (see table). Bad news: not so easy to calculate for some general collection of molecules, like a liquid, where  $E_i$  runs over all the states of all the molecules.

## The Equations of the Canonical Ensemble ( $N, V, T$ independent variables)

NOTE: All energies are referenced to  $E^0$ .

$\beta = 1/k_B T$	Full Canonical Ensemble	Distinguishable Particles (e.g., atoms in a crystal lattice)	Indistinguishable Particles (e.g., molecules in a fluid)
Single particle partition function	$Q(N, V, T) = \sum_i e^{-E_i \beta}$	$q(V, T) = \sum_i e^{-\varepsilon_i \beta}$	$q(V, T) = \sum_i e^{-\varepsilon_i \beta}$
Full partition function	$Q(N, V, T) = \sum_i e^{-E_i \beta}$	$Q = q(V, T)^N$	$Q = q(V, T)^N / N!$
Log partition function	$\ln Q$	$N \ln q$	$N \ln q - \ln N!$ $\approx N(\ln q - \ln N + 1)$
Internal Energy ( $U$ )	$-\left(\frac{\partial \ln Q}{\partial \beta}\right)_{NV}$	$-N\left(\frac{\partial \ln q}{\partial \beta}\right)_V$	$-N\left(\frac{\partial \ln q}{\partial \beta}\right)_V$
Pressure ( $P$ )	$\frac{1}{\beta} \left(\frac{\partial \ln Q}{\partial V}\right)_{NT}$	$\frac{N}{\beta} \left(\frac{\partial \ln q}{\partial V}\right)_T$	$\frac{N}{\beta} \left(\frac{\partial \ln q}{\partial V}\right)_T$
Helmholtz Energy ( $A = U - TS$ )	$-\frac{\ln Q}{\beta}$	$-\frac{N \ln q}{\beta}$	$-\frac{N}{\beta} \left(\ln q / N + 1\right)$
Entropy ( $S$ )	$k_B (\beta U + \ln Q)$	$k_B (\beta U + N \ln q)$	$k_B \left\{ \beta U + N \left( \ln q / N + 1 \right) \right\}$
Enthalpy ( $H = U + PV$ )	$U + \frac{V}{\beta} \left(\frac{\partial \ln Q}{\partial V}\right)_{NT}$	$U + \frac{NV}{\beta} \left(\frac{\partial \ln q}{\partial V}\right)_T$	$U + \frac{NV}{\beta} \left(\frac{\partial \ln q}{\partial V}\right)_T$
Gibbs Energy ( $G = A + PV$ )	$-\frac{\ln Q}{\beta} + \frac{V}{\beta} \left(\frac{\partial \ln Q}{\partial V}\right)_{NT}$	$-\frac{N}{\beta} \left\{ \ln q + V \left(\frac{\partial \ln q}{\partial V}\right)_T \right\}$	$-\frac{N}{\beta} \left\{ \ln q / N + 1 + V \left(\frac{\partial \ln q}{\partial V}\right)_T \right\}$
Chemical Potential $\left( \mu = \left( \frac{\partial A}{\partial N} \right)_{VT} \right)$	$-\frac{1}{\beta} \left(\frac{\partial \ln Q}{\partial N}\right)_{VT}$	$-\frac{\ln q}{\beta}$	$-\frac{\ln q / N}{\beta}$

## 2. Ideal Gas Thermodynamics

For a gas of *identical molecules*, though, the partition function can be (nearly exactly) factored:

$$Q(N, V, T) = q(V, T)^N / N!, \quad q(V, T) = \sum_i e^{-\epsilon_i \beta}$$

$q(V, T)$  is the *molecular partition function*, and is calculated by summing over the internal energy states  $\epsilon_i$  of an individual molecule (starting at  $E^0$ ).

Further simplified by factoring into contributions from various ( $3N$ ) degrees of freedom:

$$\begin{aligned} q(V, T) &= \left( \sum_{trans} e^{-\epsilon_{trans} \beta} \right) \left( \sum_{rot} e^{-\epsilon_{rot} \beta} \right) \left( \sum_{vib} e^{-\epsilon_{vib} \beta} \right) \left( \sum_{elec} e^{-\epsilon_{elec} \beta} \right) \\ &= q_{trans} q_{rot} q_{vib} q_{elec} \\ U &= E^0 + U_{trans} + U_{rot} + U_{vib} + U_{elec} \end{aligned}$$

Similarly for other thermodynamic quantities. For example,

$$C_v = \left( \frac{\partial U}{\partial T} \right)_V = C_{v,trans} + C_{v,rot} + C_{v,vib} + C_{v,elec}$$

Have to separately calculate contributions from each DOF:

Translational – 3 degrees of freedom. Assume particle-in-a-box.

$$\Delta \epsilon_{trans} \rightarrow 0 \quad q_{trans} \approx 10^{30}$$

Implies  $PV = nRT$ . Note we have to choose a standard pressure/concentration here! *Gaussian* chooses by default 1 atm as pressure.

Rotational – construct sum for each of 3 rotational degrees of freedom. Assume rigid rotor, means we need moments of inertia from molecular geometry.

$$\Delta \epsilon_{rot} \approx 0.001 \text{ eV} \quad q_{rot} \approx 100$$

Vibrational – construct sum for each of  $3N-6$  normal modes within harmonic approximation. Means we need vibrational spectrum.

$$\Delta \epsilon_{vib} \approx 0.1 \text{ eV} \quad q_{vib} \approx 1$$

Electronic – sum over excited electronic states. At usual temperatures, only ground state is important.

$$\Delta \epsilon_{elec} \approx 1 \text{ eV} \quad q_{elec} = \text{degeneracy of ground state}$$

## The Statistical Thermodynamics of an Ideal Gas

All energies referenced to their 0 K values

All thermodynamic quantities expressed on a per mole basis

### Translational DOFs– 3-D particle in a box model

$$\text{Thermal wavelength } \Lambda = h \left( \frac{\beta}{2\pi m} \right)^{1/2}$$

$$\text{For } \Lambda \ll L, q_{\text{trans}} = V/\Lambda^3 = \left( \frac{k_B T}{P} \right) \frac{1}{\Lambda^3} \text{ (essentially always true)}$$

$$U_{\text{trans}} = \frac{3}{2} RT \quad C_{v,\text{trans}} = \frac{3}{2} R \quad S_{\text{trans}} = R \ln \left( \frac{e^{5/2} V}{N \Lambda^3} \right) = R \ln \left( \frac{e^{5/2} k_B T}{P \Lambda^3} \right)$$

### Rotational DOFs– rigid rotor model

Linear molecule – rotational temperature  $\theta_R = hcB/k_B$

$$q_{\text{rot}} = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)\frac{\theta_R}{T}} \approx \frac{1}{\sigma} \frac{T}{\theta_R}, T \gg \theta_R \quad \sigma = \begin{cases} 1, \text{unsymmetric} \\ 2, \text{symmetric} \end{cases}$$

$$U_{\text{rot}} = RT \quad C_{v,\text{rot}} = R \quad S_{\text{rot}} = R(1 - \ln(\sigma \theta_R/T))$$

Non-linear molecule –rotational temperatures  $\theta_\alpha = hcB_\alpha/k_B$

$$q_{\text{rot}} \approx \frac{1}{\sigma} \left( \frac{\pi T^3}{\theta_A \theta_B \theta_C} \right)^{1/2}, T \gg \theta_{A,B,C} \quad \sigma = \text{rotational symmetry number}$$

$$U_{\text{rot}} = \frac{3}{2} RT \quad C_{v,\text{rot}} = \frac{3}{2} R \quad S_{\text{rot}} = \frac{R}{2} \left( 3 - \ln \frac{\sigma \theta_A \theta_B \theta_C}{\pi T^3} \right)$$

### Vibrational DOFs – harmonic oscillator model

Single harmonic mode – vibrational temperature  $\theta_V = hc\tilde{\nu}/k_B$

$$q_{\text{vib}} = \frac{1}{1 - e^{-\theta_V/T}} \approx \frac{T}{\theta_V}, T \gg \theta_V \text{ (generally must use full form)}$$

$$U_{\text{vib}} = R \frac{\theta_V}{e^{\theta_V/T} - 1} \quad C_{v,\text{vib}} = R \left( \frac{\theta_V}{T} \frac{e^{\theta_V/2T}}{e^{\theta_V/T} - 1} \right)^2 \quad S_{\text{vib}} = R \left[ \frac{\theta_V/T}{e^{\theta_V/T} - 1} - \ln(1 - e^{-\theta_V/T}) \right]$$

Multiple harmonic modes – vibrational temperatures  $\theta_v = hc\tilde{\nu}_v/k_B$

$$q_{\text{vib}} = \prod_v \frac{1}{1 - e^{-\theta_v/T}}$$

$$U_{\text{vib}} = R \sum_v \frac{\theta_v}{e^{\theta_v/T} - 1} \quad C_{v,\text{vib}} = R \sum_v \left( \frac{\theta_v}{T} \frac{e^{\theta_v/2T}}{e^{\theta_v/T} - 1} \right)^2 \quad S_{\text{vib}} = R \sum_v \left[ \frac{\theta_v/T}{e^{\theta_v/T} - 1} - \ln(1 - e^{-\theta_v/T}) \right]$$

### Electronic DOFs

$q_{\text{elec}} \approx \text{spin multiplicity}$

### 3. *Gaussian* thermochemistry output

Vibrational frequency calculation within *Gaussian* calculates all these quantities for you. See Section 3 of Ochterski, “Thermochemistry in *Gaussian*,” for description.

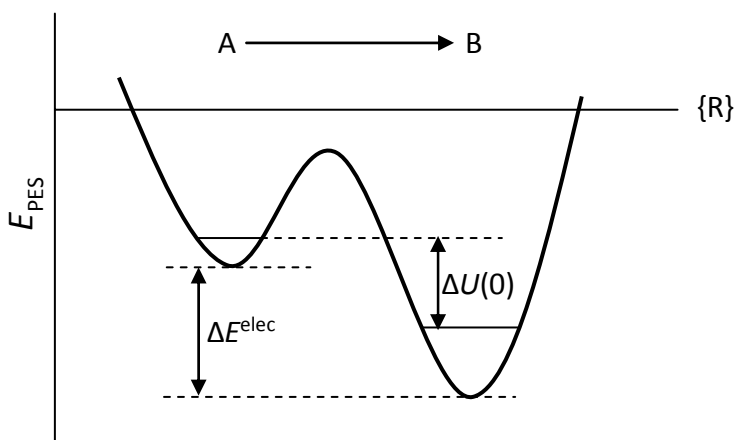
### 4. Reaction thermodynamics

Often interested in changes in thermodynamic quantities accompanying a chemical reaction. Have to calculate differences:

$$\Delta U(T, \bar{V}) = \Delta E_{elec} + \Delta ZPVE + \Delta U_{trans}(T, \bar{V}) + \Delta U_{rot}(T) + \Delta U_{vib}(T)$$

$$\Delta S(T, \bar{V}) = \Delta S_{trans}(T, \bar{V}) + \Delta S_{rot}(T) + \Delta S_{vib}(T)$$

Can do this for any condition you want. If you want a particular standard state (e.g. 273 K, 1 bar), have to choose density/ $\bar{V}$  appropriately.



Equilibrium constants,  $K(T) = e^{-\Delta G(T, \bar{V})}$ . Corresponding concentration units and “standard state” determined by  $\bar{V}$ .

See Section 4 of Ochterski, “Thermochemistry in *Gaussian*,” for description.

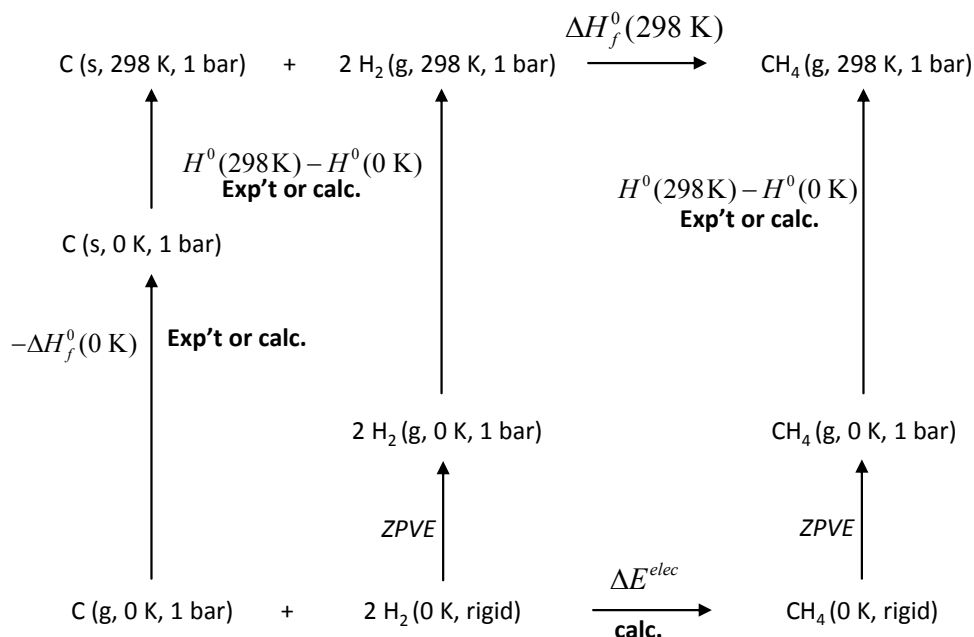
### 5. Mixing electronic structure and experimental thermochemistry

Sometimes want to relate to some experimental standard, like heat (enthalpy) of formation. Recall that this is an enthalpy relative to elemental species, and these are not always easy to calculate with a particular method. Use a thermodynamic cycle, and combine experimental and calculated quantities as necessary.

Note that  $\Delta H_f^0 = 0$  for the elements in their most stable state *at all temperatures* by definition, but that does not mean that the enthalpy of an element is not temperature dependent. Can calculate or measure this quantity depending on convenience.

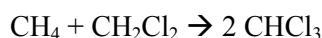
Same approach can be used for  $S$ ,  $G$ .

Sample thermodynamic cycle for calculating the heat of formation of methane:



## 6. Isodesmic reactions

Ultimately reliability depends on ability to calculate electronic energy differences, and these can be difficult, especially for reactions that involve significant changes in electronic structure. Isodesmic reaction is a little trick of the trade that takes advantage of fact that correlation errors are often constant for a given bond type. Write unknown compound in terms of reactions that conserve bond types, for example:



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### Thermochemistry of COF<sub>2</sub> and Related Compounds

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Recent calculations by Montgomery and co-workers<sup>1</sup> suggest that the accepted value for the heat of formation of COF<sub>2</sub> is in error by more than 6 kcal mol<sup>-1</sup>. Additional calculations reported here support this contention. The revised value for Δ<sub>f</sub>H<sup>o</sup><sub>298</sub>(COF<sub>2</sub>) permits a reanalysis of available kinetic and thermodynamic data on the energies of a number of other small fluorine-containing molecules, including CF<sub>3</sub>O radical, CF<sub>3</sub>OF, and CF<sub>3</sub>-OOCF<sub>3</sub>, and resolves a number of discrepancies between previous calculated and experimental results. It also allows a reevaluation of the energetics of HF loss from CF<sub>3</sub>OH, an important reaction in the atmospheric degradation of several HFCs.

Uses CH<sub>2</sub>F<sub>2</sub> + HCHO → CH<sub>4</sub> + COF<sub>2</sub> reaction and known information about first three molecules to calculate thermodynamics of the fourth.

## 7. Reaction Kinetics

Reaction rates more challenging to predict than thermodynamics—the latter is a universal property of a reaction for given conditions, the former depends on the pathway(s) from reactants to products.

Conceive of a reaction as happening in a sequence of “elementary steps.” In general difficult to predict these elementary steps *a priori*. Given them, though, our task is to calculate the rates of the individual steps.

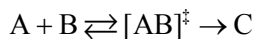


Units?

Conceived of as passage from one well to another. Can be complex dynamical process. *Transition state theory* is a very useful model that is straightforward to apply from computational results.

TST assumptions (in order of degree of approximation):

1. Existence of a PES
2. Existence of a “dividing surface” (“point of no return”)
3. Existence of a critical “transition state” point on dividing surface
4. Existence of a quasi-equilibrium between reactants and transition state



5. Harmonic (quadratic) form of the PES near the TS

Equilibrium and harmonic approximations lead to:

$$k(T) = \frac{k_B T}{h} \frac{q_\ddagger}{q_A q_B} e^{-\Delta E_0 / k_B T} (c^\circ)^{\Delta n}$$

$$\frac{k_B T}{h} : \text{frequency factor, reciprocal time}$$

$q_\ddagger$  : partition function of TS, excluding reaction coordinate mode

$q_A, q_B$  : partition function of reactants

$\Delta E_0$  : zero-point corrected activation energy

$$c^\circ = \frac{P}{N_A k_B T} = \frac{P}{RT} : \text{standard concentration units}$$

$\Delta n$  : changes in number of species from reactants to TS

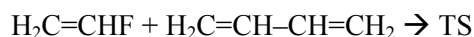
Can equivalently be expressed

$$k(T) = \frac{k_B T}{h} e^{\Delta^\ddagger S^\circ / R} e^{-\Delta^\ddagger H^\circ / RT} (c^\circ)^{\Delta n}$$

$\Delta^\ddagger S^\circ$  : standard entropy of activation

$\Delta^\ddagger H^\circ$  : standard enthalpy of activation

Example: Diels-Alder reaction



	h	6.6261E-34	J s		
	NA	6.0221E+23	/mol		
	R	8.31447	J/mol K		
	kB	1.3807E-23	J/K		
	T	298.15	K		
	P	1.00	atm		
	H <sub>2</sub> C=CHF	H <sub>2</sub> C=CH-CH=CH <sub>2</sub>	TS	Delta (kJ/mol)	
	<i>E</i> <sup>elec</sup>	-177.82	-155.99	-333.77	85.8
	ZPVE	0.04	0.09	0.13	8.5
	delta E0				94.2
1	Boltzmann				3.09E-17
2	<i>q</i>	1.59E+11	1.92E+12	2.07E+14	6.7397E-10
3	kB T/h				6.21E+12 s-1
4	RT/P				24.465428 l/mol
4p	kT/P				4.06E-20 cm^3
		1*2*3*4:	k(298.15)	5.09E-25	l/mol s
		1*2*3*4p:	k(298.15)	5.25E-33	cm3/molecule s

Slow.... What would I have to do to calculate at a higher temperature? Or pressure?

## 8. Special kinetics topics

*Kinetic isotope effect* – partition functions calculated by default for most abundant isotope. Substitution of D for H can significantly impact rate.

*Tunneling correction* – especially for reaction paths involving light atoms, tunneling through barrier can significantly impact rates. Hard to treat quantitatively; simple models available based on knowing curvature at TS.

*Variational transition state theory* – what if a reaction doesn't have an energy barrier? May still have a *free energy* barrier, place where  $\Delta^\ddagger G^\circ$  is maximized. Found by searching along IRC.

*Non-adiabatic dynamics* – incorporate effect of multiple electronic states on reaction rate