

## Handin 8: Thermochemistry; Entropy, Temperature, and Heat Transfer; Entropy Applications

1. Nitrous oxide,  $\text{N}_2\text{O}$ , can act as a ligand in transition metal complexes. The infrared stretching frequencies for  $\text{N}_2\text{O}$  are used to judge the strength of coordination to the metal. Nitrous oxide is also an important component of the atmosphere. The isotopic composition of nitrous oxide is a useful marker in atmospheric photochemistry. Nitrous oxide can be thought of as a resonance hybrid among:  $\text{N}^-\text{N}^+=\text{O} \leftrightarrow \text{N}\equiv\text{N}^+-\text{O}^- \leftrightarrow \text{N}^--\text{N}\equiv\text{O}^+$ .  $\text{N}_2\text{O}$  is isoelectronic with carbon dioxide. As such  $\text{N}_2\text{O}$  is linear and has a symmetric ( $\tilde{\nu}_1 = 1285 \text{ cm}^{-1}$ ) and an asymmetric ( $\tilde{\nu}_3 = 2223.5 \text{ cm}^{-1}$ ) stretching mode and two degenerate bending modes ( $\tilde{\nu}_2 = 588 \text{ cm}^{-1}$ ). Using valence force field techniques, the force constants for the NN and NO bonds in nitrous oxide have been estimated to be  $1790 \text{ N m}^{-1}$  and  $1140 \text{ N m}^{-1}$ , respectively. (a). Use these bond force constant estimates and MatLab, Mathematica, or the “eigen” Web applet to calculate the frequencies for the symmetric and asymmetric stretches for nitrous oxide. Your calculation will be very similar to the  $\text{CO}_2$  example in Sec. 8.10. Restrict the motions to just the x-axis (e.g. neglect the bending vibrations) and estimate the force constants in a similar way. You should end up, again, with a  $3 \times 3$  mass weighted force constant matrix. [Hint:  $k_{xx}^{22}$  won't be equal to  $2 k_{xx}^{11}$  in this case because there is a nitrogen on one side and an oxygen on the other side of the central atom, atom 2] (b). Which of the three resonance structures is most representative of the true bonding in  $\text{N}_2\text{O}$ , based on the NN and NO force constants?

*Answer:* (a). Assume that  $k_{xx}^{22} = k(\text{NN}) + k(\text{NO})$ , since moving the central N simultaneously stretches the NN bond and compresses the NO bond. The mass weighted force constant matrix is:

$$\begin{array}{c} \text{N}_1 \\ \text{N}_2 \\ \text{O}_3 \end{array} \begin{array}{c} \text{N}_1 \\ \text{N}_2 \\ \text{O}_3 \end{array} \begin{array}{c} \text{O}_3 \end{array} = \begin{array}{ccc} \begin{pmatrix} \frac{1790}{\sqrt{14}\sqrt{14}} & -\frac{1790}{\sqrt{14}\sqrt{14}} & 0 \\ -\frac{1790}{\sqrt{14}\sqrt{14}} & \frac{2930}{\sqrt{14}\sqrt{14}} & -\frac{1140}{\sqrt{14}\sqrt{16}} \\ 0 & -\frac{1140}{\sqrt{16}\sqrt{14}} & \frac{1140}{\sqrt{16}\sqrt{16}} \end{pmatrix} & \begin{pmatrix} -127.86 & 127.86 & 0 \\ 127.86 & -209.29 & 76.17 \\ 0 & 76.17 & -71.25 \end{pmatrix} \end{array}$$

The output from the “eigen” applet with units conversion using Eq. 8.10.24 is:

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Eigenvector 1: E=318.506                or  $\tilde{\nu} = 2325. \text{ cm}^{-1}$  (or 4.6% high)
-0.539616
0.804598
-0.247865
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Eigenvector 2: E=89.8936                or  $\tilde{\nu} = 1235.2 \text{ cm}^{-1}$  (or 3.9% low)
-0.625007
-0.185588
0.758237
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Eigenvector 3: E=0.0000830617          center of mass translation
0.564075
0.564074
0.603026
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The agreement is amazing given the approximations. (b). The resonance structure  $\text{N}\equiv\text{N}^+-\text{O}^-$  is most representative of the bonding, because the NN force constant is larger than the NO force constant.

2. Evapotranspiration is the process of conversion of liquid water into vapor by the earth's surface. Evapotranspiration is the sum of evaporation and transpiration. Evaporation is the direct vaporization of water from water bodies, plant surfaces, and the soil. Transpiration is the conversion of liquid water into water vapor by movement of water within plants and the subsequent loss of water vapor through stomata in the leaves. Approximately 60% of the energy available from the solar flux in a forest is consumed by evapotranspiration. The solar flux at the equator at midday is about  $1000 \text{ W m}^{-2}$ . The evaporation of water results in a large increase in entropy in vegetated areas. Evapotranspiration also moderates the surface temperature and maintains the local humidity. To provide a very rough model, consider a flat surface that is heated to the boiling point of water by the sun. Assume that 60% of the solar flux is available for the vaporization of water on this surface. Calculate the rate of the production of entropy from the vaporization of water per second per  $\text{m}^2$  at midday at the equator for a forest. The enthalpy of vaporization of water at the normal boiling point is  $\Delta_{\text{vap}}H = 40.7 \text{ kJ mol}^{-1}$ .

*Answer:* Using Eq. 10.2.19 and the normal boiling point of water,  $T_b = 373.15 \text{ K}$  at 1 atm, the molar entropy of vaporization is:

$$\Delta_{\text{tr}}S_m = \frac{\Delta_{\text{tr}}H}{T_{\text{tr}}} = \frac{40.7 \text{ kJ mol}^{-1} (1000 \text{ J/1 kJ})}{373.15 \text{ K}} = 108. \text{ J K}^{-1} \text{ mol}^{-1}$$

With 60% of the solar flux utilized for evapotranspiration, the energy flux is given by:

$$J_{\text{ET}} = 1000 \text{ W m}^{-2} (1 \text{ J s}^{-1}/1 \text{ W})(0.60) = 600. \text{ J s}^{-1} \text{ m}^{-2}$$

and the evapotranspiration rate in moles of water per unit area is then

$$R_{\text{ET}} = J_{\text{ET}}/\Delta_{\text{vap}}H = \frac{600. \text{ J s}^{-1} \text{ m}^{-2}}{40.7 \text{ kJ mol}^{-1}(1000 \text{ J/1 kJ})} = 0.0147 \text{ mol s}^{-1} \text{ m}^{-2}$$

and the entropy production is the product of the evapotranspiration rate and the molar entropy of vaporization. A common symbol for the entropy production is  $\sigma$ :

$$\sigma = R_{\text{ET}} \Delta_{\text{tr}}S_m = 0.0147 \text{ mol s}^{-1} \text{ m}^{-2}(108 \text{ J K}^{-1} \text{ mol}^{-1}) = 1.59 \text{ J K}^{-1} \text{ s}^{-1} \text{ m}^{-2}$$

Much of the sun's energy is used for entropy production by evapotranspiration over vegetated areas. The deforestation of rainforests has the potential to greatly alter the energy balance in tropical regions, which may result in higher temperatures and the loss of productivity because of water scarcity. The humidity above rainforests is recycled as rain.

We used the flat surface at  $100^\circ\text{C}$  because at this point, we haven't discussed how to calculate entropy change for irreversible processes. Please see Chapters 11 and 13.

3. Given that  $dH = TdS + VdP$ , prove that:  $\left(\frac{\partial S}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_S \left(\frac{\partial S}{\partial H}\right)_P = -\frac{V}{T}$

*Answer:* The “misplaced” variable, in the sense of Section 9.7, is that the enthalpy is held constant in  $\left(\frac{\partial S}{\partial P}\right)_H$ . Working through the total differential of H(S,P) and setting dH = 0:

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP \quad (1)$$

Setting this last equation equal to zero, for constant H, and dividing by dP at constant H:

$$0 = \left(\frac{\partial H}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_H + \left(\frac{\partial H}{\partial P}\right)_S \left(\frac{\partial P}{\partial P}\right)_H \quad (2)$$

and solving for  $(\partial S/\partial P)_H$ :

$$\left(\frac{\partial S}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_S \left(\frac{\partial S}{\partial H}\right)_P \quad (3)$$

This result is an example of the Euler chain relationship. Comparing Eq. 1 and dH = TdS + VdP:

$$\left(\frac{\partial H}{\partial P}\right)_S = V \quad \left(\frac{\partial H}{\partial S}\right)_P = T \quad (4)$$

and inverting the last partial derivative:  $\left(\frac{\partial S}{\partial H}\right)_P = \frac{1}{T}$  (5)

Substitution of Eqs. 4 and 5 into Eq. 3 gives the final result:  $\left(\frac{\partial S}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_S \left(\frac{\partial S}{\partial H}\right)_P = -\frac{V}{T}$

When does this derivative arise? This result holds for the Joule-Thompson expansion, which is a constant enthalpy process from high pressure  $P_1$  to low pressure  $P_2$ :

$$\Delta S = - \int_{P_1}^{P_2} \frac{V}{T} dP$$

Assuming an ideal gas,  $V/T = nR/P$ , giving:  $\Delta S = - nR \int_{P_1}^{P_2} \frac{1}{P} dP = - nR \ln P_2/P_1$

as expected for an ideal gas, since an ideal gas doesn't change temperature for a Joule-Thompson expansion. For a real gas the temperature changes during the expansion. For a real gas V/T is determined from the equation of state, and then integrated.

4. Use normal mode analysis to decide whether propane or 2-methylpropane has a higher absolute entropy. You can use any convenient normal mode analysis program based on molecular mechanics or molecular orbital theory.

*Answer:* The results of a normal mode analysis using Spartan at the am1 level is given in the table below. You didn't need to get the thermodynamic analysis, but it is included for comparison.

Table: Normal Mode Analysis for Several Hydrocarbons

Compound	translation	rotation	vibration	total	literature	$\tilde{\nu} < 500 \text{ cm}^{-1}$
methane	143.3	42.8	0.4	186.6	186.26	
acetylene	149.4	45.4	2.7	197.5	200.94	
ethylene	150.3	66.4	2.4	219.1	219.56	
ethane	151.2	68.1	10.9	230.3	229.60	204
cyclopropane	155.4	75.8	4.8	236.0	237.55	
propane	156.0	89.0	32.8	277.7	269.91	79, 190, 414(b)
2-methylpropane	159.4	93.5	44.4	297.3	294.64	149, 191x2, 398x2, 478
butane	159.4	96.7	45.4	301.4	310.23	103, 196, 206, 302, 473
cyclohexane	164.0	95.2	36.8	296.0	298.19	214x2, 331, 467x2
benzene	163.1	86.7	19.1	268.9	269.31	371x2

Notice that 2-methylpropane has six low frequency normal modes, while propane has three. The lower the frequency of the normal mode the bigger the contribution to the entropy and heat capacity. From the table above, propane has the smallest frequency normal mode. However, the overall result for 2-methylpropane is a larger vibrational contribution to the entropy.

The normal modes for propane, using MOPAC are a little different:

142.40391    187.97537    412.50857

The normal modes for 2-methylpropane, using MOPAC are:

144.44885    182.36068    199.92640    395.61601    398.93565    477.33557

The thermodynamic analysis is at the bottom of the output for Spartan, GAMESS, Gaussian, and MOPAC. The thermodynamic analysis for propane from MOPAC, with the THERMO keyword, at 300 K is:

CALCULATED THERMODYNAMIC PROPERTIES						
*						
TEMP. (K)	PARTITION FUNCTION	H.O.F. KCAL/MOL	ENTHALPY CAL/MOLE	HEAT CAPACITY CAL/K/MOL	ENTROPY CAL/K/MOL	
300	VIB.	4.226	1173.47287	8.68840	6.77570	
	ROT.	.200E+05	894.267	2.981	22.664	
	INT.	.846E+05	2067.740	11.669	29.439	
	TRA.	.286E+27	1490.445	4.968	37.291	
	TOT.		-24.224	3558.1849	16.6374	66.7306

The thermodynamic analysis for 2-methylpropane from MOPAC at 300 K is:

CALCULATED THERMODYNAMIC PROPERTIES						
*						
TEMP. (K)	PARTITION FUNCTION	H.O.F. KCAL/MOL	ENTHALPY CAL/MOLE	HEAT CAPACITY CAL/K/MOL	ENTROPY CAL/K/MOL	
300	VIB.	9.160	1911.82988	13.87179	10.77417	
	ROT.	.517E+05	894.267	2.981	24.547	
	INT.	.473E+06	2806.097	16.853	35.321	
	TRA.	.433E+27	1490.445	4.968	38.114	
	TOT.		-29.325	4296.5419	21.8208	73.4355

The vibrational frequencies for torsional modes are very sensitive to the level of the calculation. You will see large differences, especially for the lowest frequency normal modes, from program

to program. However, the number of low frequency normal modes will be reproducible. There is another problem with this approach. The normal mode analysis assumes that the vibrations are purely harmonic oscillators. We will see in the vibrational spectroscopy chapter that torsions are strongly anharmonic. Normal mode analysis does a poor job, quantitatively, in predicting the frequencies of these vibrations. For now, just counting low frequency normal modes will help you to visualize the vibrational contribution to the entropy. We will argue later about how to get good quantitative predictions.