

## **REDUNDANCY IN THERMOCHEMICAL DATA**

## Statement

Thermochemical data tables give  $h_{f^{\oplus}}$ ,  $g_{f^{\oplus}}$  and  $s^{\oplus}$ , but they have a redundancy, to be analysed here for ethanol. In particular:

- a) Indicate the reaction of formation, and compute the standard enthalpy, Gibbs function, and absolute entropy for this reaction.
- b) Find the uncertainty in the tabulated values as the quotient of the residue in  $g_r^{\oplus} = h_r^{\oplus} T^{\oplus} s_r^{\oplus}$  with say  $h_r^{\oplus}$ .
- c) Find the thermochemical values corresponding to the ideal vapour state of ethanol from its standard values, and compare with tabulated values.

Los datos termoquímicos tabulados contienen cierta redundancia que se desea comprobar. En particular, para el etanol, se pide:

- a) Indicar la reacción de formación y calcular la entalpía, función de Gibbs y entropías de la reacción de formación en condiciones estándar.
- a) Calcular la incertidumbre de los datos tabulados, comparando el residuo de la ecuación  $g_r^{\oplus} = h_r^{\oplus} T^{\oplus} s_r^{\oplus}$  con el valor de  $h_r^{\oplus}$ .
- b) Calcular los datos termoquímicos del etanol gaseoso a partir de los datos del etanol líquido, y cotejar con los datos tabulados.

Solution. The tabulated standard thermochemical data for ethanol and its constitutive elements are:

Substance	Formula	$h_{\mathrm{f}}^{\oplus}$ [kJ/mol]	$g_{\mathrm{f}}^{\oplus}$ [kJ/mol]	$s^{\oplus} [J/(mol \cdot K)]$
Ethanol (ideal vapour state)	$C_2H_6O(v)$	-235.4	-168.6	282
Ethanol	$C_2H_6O(l)$	-277.7	-174.9	160.7
Carbon	C(s)	0	0	5.74
Hydrogen	$H_2(g)$	0	0	130.57
Oxygen	$O_2(g)$	0	0	205.04

a) The stoichiometric reaction of formation of ethanol is  $2C+3H_2+\frac{1}{2}O_2=C_2H_6O$ . First question may be why there are two entries for ethanol in that tabulation. The answer is that the entry for 'ideal vapour state' is not the proper standard but a convenient shortcut to facilitate calculations in some problems; the proper standard is  $C_2H_6O(1)$  because ethanol at the standard state ( $T^{\oplus}=25$ °C and  $p^{\oplus}=100$  kPa) is a liquid, as can be checked from its boiling point ( $\underline{T}_b=351$  K=78 °C > $T^{\oplus}$ ). The entry for  $C_2H_6O(v)$  refers to ethanol being in the virtual state (not real) of pure vapour at 25 °C and 100 kPa, which can be computed from the real standard state as later explained.

From the tabulated values for ethanol, one may conclude that:

- The standard enthalpy of formation, h<sub>f</sub>⊕=-277.7 kJ/mol, means that the formation reaction, 2C+3H<sub>2</sub>+<sup>1</sup>/<sub>2</sub>O<sub>2</sub>=C<sub>2</sub>H<sub>6</sub>O, would be exothermic if it occurred (might need special catalysts), i.e. would release about 278 kJ of heat for each mol of ethanol formed from two moles of carbon plus three moles of hydrogen plus half a mole of oxygen, all at 25 °C and 100 kPa (i.e. solid graphite, gaseous hydrogen and oxygen, and liquid ethanol).
- The standard Gibbs function of formation,  $g_f^{\oplus} = -174.9 \text{ kJ/mol}$ , means that the formation reaction would not require an exergy source if it occurred; in fact, it might yield up to 174.9 kJ of work per mole of ethanol.
- The standard entropy of ethanol, s<sup>⊕</sup>=160.7 J/(mol·K), is positive because it is the sum of positive terms, basically s<sup>⊕</sup>=∫(c<sub>p</sub>(T,p<sup>⊕</sup>)T)dT from T→0 to T<sup>⊕</sup>. But notice that this is not the standard entropy of formation, s<sub>r</sub><sup>⊕</sup>.
- The standard entropy of formation is sr<sup>⊕</sup>=Σvisi<sup>⊕</sup> for the formation reaction, 2C+3H<sub>2</sub>+½O<sub>2</sub>=C<sub>2</sub>H<sub>6</sub>O, i.e. sr<sup>⊕</sup>=Σvisi<sup>⊕</sup>=s<sup>⊕</sup>(C<sub>2</sub>H<sub>6</sub>O)-2⋅s<sup>⊕</sup>(C) -3⋅s<sup>⊕</sup>(H<sub>2</sub>) -½⋅s<sup>⊕</sup>(O<sub>2</sub>) =160.7-2⋅5.74-3⋅130.57-½⋅205.04=-345 J/(mol⋅K), showing that it is negative and large, because three and a half moles of gas condense to one mol of liquid (the two moles of solid add little).
- Further notice that, for a chemical element (e.g. C), the reaction of formation would imply no change, e.g. C(s,graphite)→ C(s,graphite), and consequently h<sub>f</sub><sup>⊕</sup>=0, g<sub>f</sub><sup>⊕</sup>=0, and s<sub>f</sub><sup>⊕</sup>=0, but s<sup>⊕</sup>≠0 (i.e. the standard entropy of graphite is s<sup>⊕</sup>=5.74 kJ/mol, but the standard entropy of formation of graphite is s<sub>f</sub><sup>⊕</sup>=5.74–5.74=0). On the other hand, even if g<sub>f</sub><sup>⊕</sup>=0 for the formation of graphite, g<sup>⊕</sup>≠0, since, from the definition of the Gibbs function, G=H-TS, g<sup>⊕</sup>=h<sup>⊕</sup>-T<sup>⊕</sup>s<sup>⊕</sup>=0-298 ⋅ 5.74≠0.
- b) For any kind of reaction at equilibrium, it must be verified  $g_r^{\oplus} = h_r^{\oplus} T^{\oplus} s_r^{\oplus}$ . Defining the residue as  $R \equiv h_r^{\oplus} - T^{\oplus} s_r^{\oplus} - g_r^{\oplus}$ , we see from the data above for C<sub>2</sub>H<sub>6</sub>O(1) that  $R = -277.7 - 298.15 \cdot (-0.345) - (-174.9) = 62$  J/mol; hence, the uncertainty, defined as  $|R/h_r^{\oplus}|$ , is 0.062/277.7 = 0.02%, due to rounding or experimental uncertainty.
- c) We start from the standard thermochemical data from ethanol (that at 25 °C and 100 kPa is a liquid):  $h_{\rm f}^{\oplus}$ =-277.7 kJ/mol,  $g_{\rm f}^{\oplus}$ =-174.9 kJ/mol, and  $s^{\oplus}$ =160.7 J/(mol·K). To find the values for the ideal vapour state at 25 °C and 100 kPa, we cannot directly add the vaporization values because the vaporization 'reaction' C<sub>2</sub>H<sub>6</sub>O(l) $\rightarrow$ C<sub>2</sub>H<sub>6</sub>O(v) is not at equilibrium at 25 °C, but we can follow a series of equilibrium processes:
  - Step 1: decrease pressure of liquid ethanol to its equilibrium vapour pressure at 25 °C. Using Antoine correlation (or Clapeyron equation), we find that for ethanol, *p*<sub>v,25</sub>=7.9 kPa, and using the perfect liquid model for this process, Δ*h*=*c*Δ*T*+Δ*p*/*ρ*=Δ*p*/*ρ*≈0 and Δ*s*=*c*ln(*T*/*T*)=0. From that, Δ*g*=Δ*h*-*T*<sup>⊕</sup>Δ*s*≈0.
  - Step 2: vaporization of liquid ethanol at equilibrium (25 °C, 7.9 kPa). For this process,  $\Delta h = h_{1v,25}, \Delta s = s_{1v,25} = h_{1v,25}/T^{\oplus}$ , and  $\Delta g = 0$ . The vaporization enthalpy at 25 °C can be obtained with the perfect substance model as  $h_{1v,25} = h_{1v,b} - (c-c_p)(T^{\oplus} - T_b) =$

860–(2.44–1.52)(298–352)=910 kJ/kg, having obtained from the <u>liquid</u>'s table the boiling enthalpy and liquid thermal capacity ( $h_{lv,b}$ =860 kJ/kg, c=2440 J/(kg·K), and from the <u>gas</u>'s the vapour thermal capacity ( $c_p$ =1520 J/(kg·K)). And  $\Delta s = s_{lv,25} = h_{lv,25}/T^{\oplus}$ =910/298=3051 J/(kg·K).

Step 3: increase pressure from the *p*<sub>v,25</sub>=7.9 kPa to *p*<sup>⊕</sup>=100 kPa in an idealized process without condensation. With the perfect gas model for this isothermal compression, Δ*h*=*c*<sub>p</sub>Δ*T*=0 and Δ*s*=*c*<sub>p</sub>ln(*T*/*T*)-*R*ln(*p*<sup>⊕</sup>/*p*<sub>v,25</sub>)=0-(8.3/0.046)·ln(100/8.9)=-459 J/(kg·K), where *M*=0.046 kg/mol is the molar mass of ethanol. From that, Δ*g*= Δ*h*-*T*<sup>⊕</sup>Δ*s*=0-298·(-0.459)=137 kJ/kg.

Adding the three processes, for the 'reaction' C<sub>2</sub>H<sub>6</sub>O(l) $\rightarrow$ C<sub>2</sub>H<sub>6</sub>O(v) we have  $hr=0+h_{1v,25}+0=910$  kJ/kg=41.9 kJ/mol,  $s_r=0+h_{1v,25}/T^{\oplus}-R\ln(p^{\oplus}/p_{v,25})=3051-459=2592$  J/(kg·K)=119.3 J/(mol·K), and  $g_r=0+0+137=137$  kJ/kg=6.3 kJ/mol (otherwise,  $g_r^{\oplus}=h_r^{\oplus}-T^{\oplus}s_r^{\oplus}=41.9-298\cdot0.119=6.4$  kJ/mol).

And finally, adding these vaporization 'reaction' values to the standard thermochemical values of liquid ethanol we conclude:  $h_{\rm f}^{\oplus}(v)=h_{\rm f}^{\oplus}(1)+h_{\rm r,vap}^{\oplus}=(-277.7)+41.9=-235.8$  kJ/mol,  $g_{\rm f}^{\oplus}(v)=g_{\rm f}^{\oplus}(1)+g_{\rm r,vap}^{\oplus}=(-174.9)+6.3=-168.6$  kJ/mol, and  $s^{\oplus}(v)=s^{\oplus}(1)+s_{\rm r,vap}^{\oplus}=160.7+119.2=280$ J/(mol·K), which coincide up to rounding uncertainty) with the tabulated values for ethanol as a virtual gas at 25 °C and 100 kPa.

Back