Ex. 1 Standard redox potential — Lead-acid battery

The overall chemical reaction in a lead-acid battery (car) is:

$$\mathrm{Pb} + \mathrm{PbO_2} + 2\ \mathrm{H_2SO_4} \Leftrightarrow 2\ \mathrm{PbSO_4} + 2\ \mathrm{H_2O}$$

Looking up the thermodynamic data for this reaction (e.g., in CRC Handbook hbcpnetbase.com, NIST.gov website, CRM's form, etc.), you would find the standard-state data at 25°C:

Compound	$\Delta_f\tilde{h}^{\ominus}_{25°C}$ kJ/mol	$\tilde{s}^{\ominus}_{25°C}$ J/(mol·K)
$PbSO_4$	-920.00	148.5
Pb	0	64.80
PbO_2	-274.47	71.78
H_2SO_4 aqueous	-909.00	20.08
H_2O(l)	-285.80	70.00
H^+ aqueous	0 (definition)	0 (definition)

Derive from these the standard redox potential for a lead-acid battery at 25°C.

Solution

Filling in the data for the complete reaction gives:

$\Delta_\mathrm{r}\tilde{h}^{\ominus}_{25°\mathrm{C}} = -318.86\ \mathrm{kJ/mol}$ and $\Delta_\mathrm{r}\tilde{s}^{\ominus}_{25°\mathrm{C}} = 260.25\ \mathrm{J/(mol \cdot K)}$

The Gibbs free enthalpy for 0°C and 40°C is then computed using the usual linearization:

$\Delta_\mathrm{r}\tilde{g}^{\ominus}_{0°\mathrm{C}} = -389.909\ \mathrm{kJ/mol}$ and $\Delta_\mathrm{r}\tilde{g}^{\ominus}_{40°\mathrm{C}} = -400.319\ \mathrm{kJ/mol}$

With 2 electrons exchanged, the standard redox potential is hence:

$E^{\ominus}_{0°\mathrm{C}} = 2.021\ \mathrm{V}$ and $E^{\ominus}_{40°\mathrm{C}} = 2.075\ \mathrm{V}$

Another way would be to compute $E^{\ominus}$ for each half-reaction (electrode). Below for 25°C:

Cathode (discharge): $\mathrm{PbO_2 + 2H^+ + 2e^- + H_2SO_4 \Leftrightarrow PbSO_4 + 2H_2O}$ $E^{\ominus} = 1.685$ V

Anode (discharge): $\mathrm{Pb + H_2SO_4 \Leftrightarrow PbSO_4 + 2H^+ + 2e^-}$ $E^{\ominus} = -0.356$ V

The (standard) potential difference between both electrodes is then 2.041 V (25°C).

Ex. 2 Standard redox potential – Influence of temperature and gases

The table below gives the standard molar enthalpy-change of formation and the standard molar entropy for some compounds, at 1 bar and 25°C.

Compound	$\Delta_f \tilde{h}^{\ominus}_{25°C}$	$\tilde{s}^{\ominus}_{25°C}$
	kJ/mol	J/(mol·K)
H_2	0	130.6
O_2	0	205.0
H_2O *(l)*	-285.8	69.9
H_2O *(g)*	-241.8	188.7
CH_4	-74.85	186.2
CO_2	-393.5	213.6

1. Compute the *standard* redox potential, $E^{\ominus}$, for the electrochemical oxidation of:
   a) hydrogen at 25°C;
   b) methane at 25°C.

2. Write the *standard* redox potential as a function of *temperature*, $E^{\ominus}(T)$.
   a) Plot $E^{\ominus}(T)$ in the interval $T = [25, 1000]$°C, for hydrogen and for methane.
   b) Draw conclusions regarding the influence of temperature and of gases on $E^{\ominus}$.

Solution

Reminder & nomenclature:

Standard redox potential $E^{\ominus}_{(T)}$ = potential difference between both electrodes where each chemical participating in the reaction is considered at its reference *standard-state* ($\ominus$).[1] Therefore, it doesn't account for specific concentrations, which typically occur when the fuel cell is operating (net external electrical current).

The relation between the standard redox potential $E^{\ominus}$ and thermodynamics is:[2]

$$\Delta_{\mathrm{r}}\tilde{g}^{\ominus}_{(T)} = -\nu_{\mathrm{e}}\mathcal{F}E^{\ominus}_{(T)}$$

The standard molar Gibbs free enthalpy-change of reaction $\Delta_{\mathrm{r}}\tilde{g}^{\ominus}_{(T)}$ is given by the fundamental relation:

$$\Delta_{\mathrm{r}}\tilde{g}^{\ominus}_{(T)} = \Delta_{\mathrm{r}}\tilde{h}^{\ominus}_{(T)} - T\Delta_{\mathrm{r}}\tilde{s}^{\ominus}_{(T)}$$

Caution: *T must be taken in Kelvin!*

The enthalpies ($\Delta_{\mathrm{r}}\tilde{h}^{\ominus}_{(T)}$) and entropies ($\Delta_{\mathrm{r}}\tilde{s}^{\ominus}_{(T)}$ of a reaction are determined thanks to the Hess' law, using the enthalpies of formation, $\Delta_{\mathrm{f}}\tilde{h}_k$, respectively entropies ($\tilde{s}_k$), of the *k* reactants and products. This law holds true for standard or non-standard states, as long as state is consistent.

Hess' law:

$\Delta_{\mathrm{r}}\tilde{h}^{\ominus}_{(T)}) = \sum_j \nu_j \, \Delta_{\mathrm{f}}\tilde{h}_j - \sum_i \nu_i \, \Delta_{\mathrm{f}}\tilde{h}_i$ for a reaction such as: $\sum_i \nu_i \, \mathrm{Reactant}_i \Leftrightarrow \sum_j \nu_j \, \mathrm{Product}_j$

The validity of this law extends to both $\Delta_{\mathrm{r}}\tilde{s}^{\ominus}_{(T)}$ and $\Delta_{\mathrm{r}}\tilde{g}^{\ominus}_{(T)}$.

The stoichiometric coefficients are determined by writing the redox reactions:

- hydrogen: $H_2 + \frac{1}{2} O_2 \Rightarrow H_2O$
- methane: $CH_4 + 2 O_2 \Rightarrow 2 H_2O + CO_2$

The number of electrons that are exchanged are determined by writing the half-reactions. For the case of methane, they are:

- $CH_4 \Rightarrow C^{4+} + 4 e^- + 4 H^+ + 4 e^-$ and $2 O_2 + 8 e^- \Rightarrow 4 O^{2-}$

Standard redox potential $E^{\ominus}$ at 25°C

The thermodynamic data in the provided table are given for 25°C and 1 bar. Therefore, the standard Gibbs free enthalpy of the reaction at 25°C can be computed directly from these values.

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[1] Although standard state is often marked with (^{0}) for convenience, the original symbol $\ominus$ is purposefully used here to highlight the non-zero nature of standard-state (see "thinking further").

[2] Note that this relation holds in non-standard conditions, too: $\Delta_{\mathrm{r}}\tilde{g} = -\nu_{\mathrm{e}}\mathcal{F}E = \Delta_{\mathrm{r}}\tilde{g}^{\ominus} + \mathcal{R}T\ln(Q)$.

Hydrogen at 25°C :

$H_2 + ½ O_2 => H_2O(l)$

Applying Hess' law:

$$\Delta_r\tilde{h}^{\ominus}_{25°C} = 1\,\Delta_f\tilde{h}^{\ominus}_{H_2O(l)} - 0.5\,\Delta_f\tilde{h}^{\ominus}_{O_2} - 1\,\Delta_f\tilde{h}^{\ominus}_{H_2} = -285.8\cdot 10^3 - 0 - 0 = -285'800\text{ J/mol}$$

$$\Delta_r\tilde{s}^{\ominus}_{25°C} = 1\,\tilde{s}^{\ominus}_{H_2O(l)} - 0.5\,\tilde{s}^{\ominus}_{O_2} - 1\,\tilde{s}^{\ominus}_{H_2} = 69.9 - 0.5 * 205.0 - 130.6 = -163.2\text{ J/(mol}\cdot\text{K)}$$

Gibbs:

$$\Delta_r\tilde{g}^{\ominus}_{25°C} = \Delta_r\tilde{h}^{\ominus}_{25°C} - T\Delta_r\tilde{s}^{\ominus}_{25°C} = -285'800 + 298.15\cdot 163.2 = -237'142\text{ J/mol}$$

$$E^{\ominus}_{25°C} = -\frac{\Delta_r\tilde{g}^{\ominus}_{25°C}}{\nu_e\mathcal{F}} = \frac{237'142}{2\cdot 96485.3} = 1.229\text{ V}$$

Methane at 25°C :

$CH_4 + 2\,O_2 => 2\,H_2O(l) + CO_2$ Caution: $\nu_e = 8$

A similar calculation as for (a) gives:

$$\Delta_r\tilde{h}^{\ominus}_{25°C} = -890'250\text{ J/mol}$$

$$\Delta_r\tilde{s}^{\ominus}_{25°C} = -242.8\text{ J/(mol}\cdot\text{K)}$$

$$\Delta_r\tilde{g}^{\ominus}_{25°C} = \Delta_r\tilde{h}^{\ominus}_{25°C} - T\Delta_r\tilde{s}^{\ominus}_{25°C} = -817'919\text{ J/mol}$$

$$E^{\ominus}_{25°C} = -\frac{\Delta_r\tilde{g}^{\ominus}_{25°C}}{\nu_e\mathcal{F}} = 1.060\text{ V}$$

Standard redox potential as a function of *temperature*, $E^{\ominus}(T)$

$$E^{\ominus}(T) = -\frac{\Delta_r\tilde{g}^{\ominus}_{(T)}(T)}{\nu_e\mathcal{F}}$$

In this relation, only $\Delta_r\tilde{g}^{\ominus}_{(T)}$ is function of the temperature. It can be expressed as:

$$\Delta_r\tilde{g}^{\ominus}_{(T)}(T) = \Delta_r\tilde{h}^{\ominus}_{(T)}(T) - T\Delta_r\tilde{s}^{\ominus}_{(T)}(T)$$

As long as there is no phase change, the dependency of $\Delta_r\tilde{h}^{\ominus}_{(T)}$ and $\Delta_r\tilde{s}^{\ominus}_{(T)}$ with temperature is usually relatively low compared to the (direct) linear dependency of $\Delta_r\tilde{g}^{\ominus}_{(T)}$ with temperature. Hence, a good approximation is:

$$\frac{\partial \Delta_{\mathrm{r}}\tilde{g}^{\ominus}_{(T)}(T)}{\partial T} \cong -\Delta_{\mathrm{r}}\tilde{s}^{\ominus}_{(T)}$$

It follows:

$$\frac{\partial E^{\ominus}(T)}{\partial T} \cong \frac{\Delta_{\mathrm{r}}\tilde{s}^{\ominus}_{(T)}}{\nu_{\mathrm{e}}\mathcal{F}}$$

Note that the second term is the slope of $E^{\ominus}$ *near* $T = T_{\mathrm{ref}}$, with T_{ref} referring to the temperature for which the standard entropy of the reaction was computed.
Integrating this relation gives:

$$E^{\ominus}(T) \cong E^{\ominus}_{T_{\mathrm{ref}}} + \left.\frac{\partial E^{\ominus}(T)}{\partial T}\right|_{\mathrm{T}_{ref}} (T - T_{\mathrm{ref}}) = \frac{\Delta_{\mathrm{r}}\tilde{g}^{\ominus}_{T_{\mathrm{ref}}} + \Delta_{\mathrm{r}}\tilde{s}^{\ominus}_{T_{\mathrm{ref}}}(T - T_{\mathrm{ref}})}{\nu_{\mathrm{e}}\mathcal{F}}$$

In case more accurate values are necessary, the variation of $\Delta_{\mathrm{r}}\tilde{h}^{\ominus}_{(T)}$ and $\Delta_{\mathrm{r}}\tilde{s}^{\ominus}_{(T)}$ with temperature should be taken into account. They can be expressed in function of temperature thanks to Kirchhoff's law.

Kirchhoff's law:

$$\frac{\partial \Delta_{\mathrm{r}}\tilde{h}^{\ominus}_{(T)}(T)}{\partial T} = \Delta\tilde{c}_p(T)$$

Integration of this equation permits the evaluation of the heat of reaction at one temperature from measurements at another temperature. It can be decomposed such as to integrate the heat-capacities for individual compounds. $\Delta\tilde{c}_p(T)$ can be found in tables of reference, typically in the form of polynomials.

<u>Evolution of $E^{\ominus}$ with temperature for hydrogen and for methane</u>

Hydrogen:

Starting at 25°C with liquid H_2O, the standard entropy of reaction is retrieved from (a):

$$\Delta_{\mathrm{r}}\tilde{s}^{\ominus}_{25°\mathrm{C}} = -163.2\ \mathrm{J/(mol \cdot K)}$$

So the slope is:

$$\left.\frac{\partial E^{\ominus}(T)}{\partial T}\right|_{25°\mathrm{C}} \cong -846\ \mathrm{\mu V/K}$$

Note that it represent less than 1‰ change per degree.

Above 100°C, the product is steam, for which the enthalpy of formation and entropy are different from those for water (discontinuity). Nevertheless, pay attention that even if the standard-state of the compound is not gaseous at, e.g., 25°C, data is often virtually reported to an equivalent gaseous standard-state at 25°C, as is the case here.

$\Delta_r\tilde{h}^{\ominus}_{25°\mathrm{C}\,(g)} = -241'800\ \mathrm{J/mol}$ $\Delta_r\tilde{s}^{\ominus}_{25°\mathrm{C}\,(g)} = -44.4\ \mathrm{J/(mol\cdot K)}$

Gibbs:

$\Delta_r\tilde{g}^{\ominus}_{25°\mathrm{C}\,(g)} = -228'562\ \mathrm{J/mol}$ $E^{\ominus}_{25°\mathrm{C}\,(g)} = 1.184\ \mathrm{V}$

$$\left.\frac{\partial E^{\ominus}(T)}{\partial T}\right|_{25°\mathrm{C}\,(g)} \cong -230\ \mu\mathrm{V/K}$$

This slightly deviates from the linear regression value obtained (275 µV/K) from "correct" data tabulated below and represented in figure 1.

The value at 1000°C can be computed in one step, from **25°C *(g)*** → 1000°C *(g)*:

$$E^{\ominus}_{1000°\mathrm{C}} = 1.184 - 230\cdot 10^{-6}\cdot(1000-25) = 0.960\ \mathrm{V}$$

Or in two steps (piecewise bi-linear), from **25°C *(l)*** → 100°C *(l/g)* → 1000°C *(g)*:

$$E^{\ominus}_{1000°\mathrm{C}} = 1.229 - 846\cdot 10^{-6}\cdot(100-25) - 230\cdot 10^{-6}\cdot(1000-100) = 0.958\ \mathrm{V}$$

Rigorously correct calculations —involving integration of Kirchhoff's law— gave 0.920 V, hence the error of the approximation at 1000°C is around 4%.

Methane:

Following the same procedure as for hydrogen above:

In the liquid phase, reusing the value $\Delta_r\tilde{s}^{\ominus}_{25°\mathrm{C}} = -248.2\ \mathrm{J/(mol\cdot K)}$, the slope is computed:

$$\left.\frac{\partial E^{\ominus}(T)}{\partial T}\right|_{25°\mathrm{C}} \cong -322\ \mu\mathrm{V/K}$$

Note that again it represent less than 1‰ change per degree.

In the (virtually) gaseous phase:

$\Delta_r\tilde{s}^{\ominus}_{25°\mathrm{C}\,(g)} = -5.17\ \mathrm{J/(mol\cdot K)}$ $\Delta_r\tilde{g}^{\ominus}_{25°\mathrm{C}\,(g)} = -801\ \mathbf{k}\mathrm{J/mol}$ $E^{\ominus}_{25°\mathrm{C}\,(g)} = 1.037\ \mathrm{V}$

$$\left.\frac{\partial E^{\ominus}(T)}{\partial T}\right|_{25°\mathrm{C}\,(g)} \cong -6.7\ \mu\mathrm{V/K}$$

The value at 1000°C is computed in one step, from **25°C *(g)*** → 1000°C *(g)*:

$E^{\ominus}_{1000°\mathrm{C}} = 1.037 - 6.7\cdot 10^{-6}\cdot(1000-25) = 1.030\ \mathrm{V}$ (drop by 7 mV)

Rigorously correct calculations —involving integration of Kirchhoff's law— gave 1.037 V, hence the error of the approximation at 1000°C is less than 1%.

Conclusions regarding the influence of temperature and of gases on $E^{\ominus}$

In the following tables, the variation of $\Delta_\mathrm{r}\tilde{h}^{\ominus}_{(T)}$ and $\Delta_\mathrm{r}\tilde{s}^{\ominus}_{(T)}$ with temperature was taken into account. This variation is quite small as can be seen, within either the liquid or vapor phase. The difference is however significant at the phase-change.

The standard redox potential for the electrochemical oxidation of methane is practically independent of temperature (contrary to H_2), due to the fact that entropy of reaction is close to zero throughout the vapor phase. In the gaseous phase, thermodynamic efficiency is basically ≈ 1 ($\Delta_\mathrm{r}\tilde{g}^{\ominus}_{(T)}/\Delta_\mathrm{r}\tilde{h}^{\ominus}_{(T)}$, see table 2).

For H_2 oxidation, however, thermodynamic losses at high temperature become important, e.g., at 1000°C they amount to $1 - (\Delta_\mathrm{r}\tilde{g}^{\ominus}_{1000°\mathrm{C}}/\Delta_\mathrm{r}\tilde{h}^{\ominus}_{25°\mathrm{C}\,(\mathrm{g})}) = 27\%$ (LHV; 38% for HHV, 25°C *(l)*).

Table 1 — Standard redox potential for oxidation of hydrogen between 25°C and 1’000°C

H_2	T_{ref}	T_{ref}	$\Delta_{\mathrm{r}}\tilde{h}^{\ominus}_{T_{\mathrm{ref}}}$	$\Delta_{\mathrm{r}}\tilde{s}^{\ominus}_{T_{\mathrm{ref}}}$	$\Delta_{\mathrm{r}}\tilde{g}^{\ominus}_{T_{\mathrm{ref}}}$	$E^{\ominus}_{T_{\mathrm{ref}}}$
	°C	K	J/mol	J/(mol·K)	J/mol	V
	25	298.15	-285’840	-163.2	-237’192	1.229
	50	323.15	-285’042	-160.6	-233’146	1.208
H_2O *(l)*	100	373.15	-283’461	-156.0	-225’233	1.167
H_2O *(g)*	100	373.15	-242’562	-46.6	-225’182	1.167
	200	473.15	-243’506	-48.8	-220’407	1.142
	300	573.15	-244’407	-50.5	-215’435	1.116
	400	673.15	-245’263	-51.9	-210’309	1.090
	500	773.15	-246’071	-53.0	-205’059	1.063
	600	873.15	-246’831	-54.0	-199’706	1.035
	700	973.15	-247’543	-54.7	-194’270	1.007
	800	1’073.15	-248’207	-55.4	-188’762	0.978
	900	1’173.15	-248’821	-55.9	-183’194	0.949
	1’000	1’273.15	-249’387	-56.4	-177’576	0.920

Table 2 — Standard redox potential for oxidation of methane between 25°C and 1’000°C

CH_4	T_{ref}	T_{ref}	$\Delta_{\mathrm{r}}\tilde{h}^{\ominus}_{T_{\mathrm{ref}}}$	$\Delta_{\mathrm{r}}\tilde{s}^{\ominus}_{T_{\mathrm{ref}}}$	$\Delta_{\mathrm{r}}\tilde{g}^{\ominus}_{T_{\mathrm{ref}}}$	$E^{\ominus}_{T_{\mathrm{ref}}}$
	°C	K	J/mol	J/(mol·K)	J/mol	V
	25	298.15	-890’340	-242.7	-817’970	1.0597
	50	323.15	-888’005	-235.2	-811’997	1.0520
H_2O *(l)*	100	373.15	-883’390	-221.9	-800’578	1.0372
H_2O *(g)*	100	373.15	-801’593	-3.0	-800’476	1.0371
	200	473.15	-800’748	-1.0	-800’285	1.0368
	300	573.15	-800’105	0.3	-800’255	1.0368
	400	673.15	-799’694	0.9	-800’319	1.0369
	500	773.15	-799’530	1.2	-800’426	1.0370
	600	873.15	-799’620	1.1	-800’539	1.0371
	700	973.15	-799’969	0.7	-800’628	1.0373
	800	1’073.15	-800’579	0.1	-800’668	1.0373
	900	1’173.15	-801’453	-0.7	-800’638	1.0373
	1’000	1’273.15	-802’592	-1.6	-800’524	1.0371

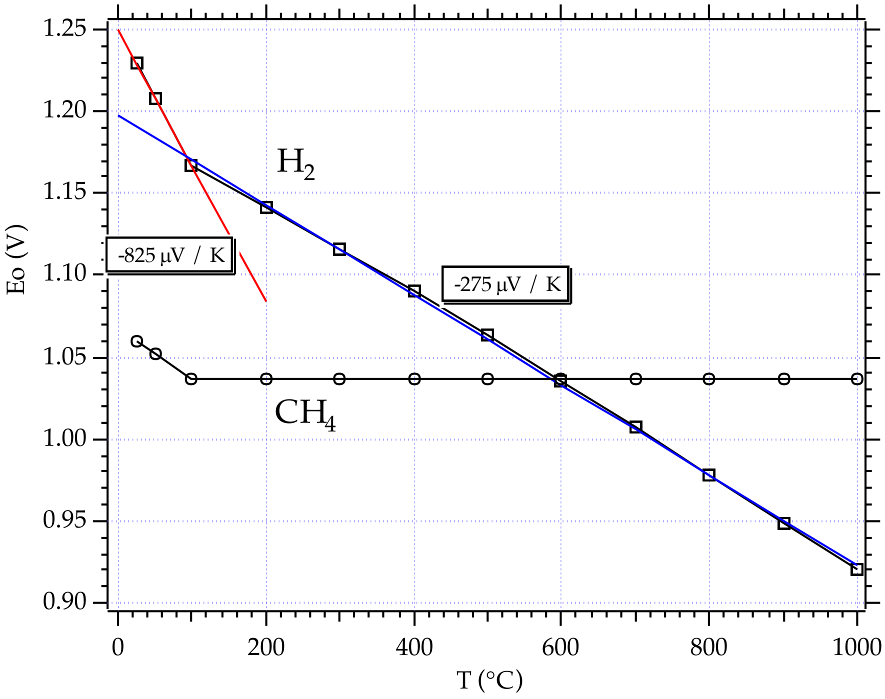

Figure 1 — Standard redox potential as a function of temperature for hydrogen and methane