

Table 1. Molar exergy,  $\psi_i$ , of pure species relative to a reference atmosphere at  $p_0=100$  kPa,  $T_0=25$  °C, and 60% RH;  $\psi_i=\mu_i(T_0,p_0,1)-\mu_{i0}(T_0,p_0,x_{i0})$ .

Substance	Formula (state)	Molar fraction in ref. atm. $x_i$	Molar exergy $\psi_i$ [kJ/mol]
Nitrogen	N <sub>2</sub> (g)	0.7651	0.66
Oxygen	O <sub>2</sub> (g)	0.2062	3.9
Water	H <sub>2</sub> O(l)	0.0190	1.3
Argon	Ar(g)	0.0094	12
Carbon dioxide	CO <sub>2</sub> (g)	0.0003	20
Carbon monoxide	CO(g)	NA	275
Hydrogen	H <sub>2</sub> (g)	NA	236
Methane	CH <sub>4</sub> (g)	NA	831
Ethane	C <sub>2</sub> H <sub>6</sub> (g)	NA	1500
Ethylene	C <sub>2</sub> H <sub>4</sub> (g)	NA	1360
Acetylene	C <sub>2</sub> H <sub>2</sub> (g)	NA	1265
Propane	C <sub>3</sub> H <sub>8</sub> (g)	NA	2150
n-Butane	C <sub>4</sub> H <sub>10</sub> (l)	NA	2800
Carbon (graphite)	C(s)	NA	410
Nitrogen monoxide	NO(g)	NA	89
Nitrogen dioxide	NO <sub>2</sub> (g)	NA	56
Ammonia	NH <sub>3</sub> (g)	NA	340
Methanol	CH <sub>3</sub> OH(l)	NA	720
Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH(l)	NA	1400

NA, not available in the model atmosphere.

## EXERGY AND THE ENVIRONMENT

Exergy is the minimum work that must be given to an isolated system at equilibrium to force it to a non-equilibrium state, or the maximum work obtainable from an isolated non-equilibrium system, and it is a state function. Instead of isolated systems out of equilibrium, exergy usually refers to a system in internal equilibrium in the presence of another much larger system: the environment; in this case, exergy is a state function of the combination system+environment. The problem with this environment-dependent exergy concept is how to model a realistic environment (temperature, pressure, and composition), since it is a fact that there is not a universal uniform environment of interest: there are people living at the sea side, others in cold continental climates; climate variables change seasonally; there are places full of natural resources, and others deprived, etc.

But the concept of exergy as the general currency to compare the relative efficiency of engineering achievements is so important that it is better a crude model than none at all. The simplest choice for a terrestrial environment is just a model atmosphere of infinite extent, at constant temperature, pressure, and composition, with the following values:

- Reference temperature is usually taken to be 25 °C (298.15 K), from Chemistry tradition, although the global mean sea-level value of 15 °C might be more appropriate. More realistic exergy

analyses should consider a time and space variation of temperature (e.g. 10 °C for winter, 30 °C for summer, –50 °C for cruising aircraft...).

- Reference pressure is usually taken to be 100 kPa (formerly 101.325 kPa), but other values might be more realistic in underwater or aeronautical applications. Contrary to temperature-reference choice, this small difference in reference pressure has no significant effect.
- Reference composition is usually taken to be that of air with some humidity. Besides the major constituents, N<sub>2</sub> and O<sub>2</sub>, one has to include minor components that add all the variety of atoms of interest; for chemical reactions involving only C, H, O, and N atoms, the H<sub>2</sub>O and CO<sub>2</sub> constituents of air are enough (argon is added in Table 1 to avoid dropping a component more abundant than those retained). If a larger variety of atoms and chemical reactions is needed, this simple reference environment should be enlarged to include other atoms in the atmosphere (e.g. He), the hydrosphere (dissolved species, but then air should be assumed in equilibrium with water), and the lithosphere (e.g. one may take SiO<sub>2</sub> as a source of Si, Al<sub>2</sub>O<sub>3</sub> as a source of Al in spite of silicates being more abundant, CaCO<sub>3</sub> as a source of Ca...), but the problem gets entangled because it becomes unrealistic to assume such a complex system in thermodynamic equilibrium, and thus, no zero exergy level can be ascribed to it.

The exergy of a system (relative to the assumed reference environment) depends on system temperature, pressure, and composition; the first two contribute to [thermo-mechanical exergy](#), and the effect of composition to chemical exergy. For the general case of a control volume, the exergy balance is:

$$\Delta\Phi = \Delta(E + p_0V - T_0S)_{n_i} + \sum n_i (\mu_i - \mu_{i0})_{T_0, p_0} = W_u + \int \left(1 - \frac{T_0}{T}\right) dQ - T_0 S_{gen} + \sum_{\text{openings}} \int \psi_e \dot{n}_e dt \quad (1)$$

with the molar exergy of flow through the system openings:

$$\psi \equiv (h - T_0s)_{n_i} + \sum x_i (\mu_i - \mu_{i0})_{T_0, p_0} \quad (2)$$

The molar chemical exergy (i.e. the system exergy per unit amount of substance),  $\psi = \sum x_i (\mu_i - \mu_{i0})_{T_0, p_0}$ , depends on the molar fraction of every species in the system,  $x_i$ , their chemical potential at the reference temperature and pressure,  $\mu_i(T_0, p_0, x_i, x_j)$  (or  $\mu_i(T_0, p_0, x_i)$  for ideal mixtures), and the chemical potential of each species in the reference environment,  $\mu_{i0}(T_0, p_0, x_{i0})$ . Table 2 presents the effect of two different choices for the reference atmosphere.

Table 2. Molar exergy of species separation for two choices of the reference atmosphere, at 100 kPa.

Component	At 288 K and 60%RH		At 298 K and 60%RH	
	Molar fraction $x_i$	Molar exergy $\psi_i$	Molar fraction $x_i$	Molar exergy $\psi_i$
N <sub>2</sub>	0.7720	0.62 kJ/mol <sub>N<sub>2</sub></sub>	0.7651	0.66 kJ/mol <sub>N<sub>2</sub></sub>
O <sub>2</sub>	0.2080	3.8 kJ/mol <sub>O<sub>2</sub></sub>	0.2062	3.9 kJ/mol <sub>O<sub>2</sub></sub>
H <sub>2</sub> O	0.0102	1.2 kJ/mol <sub>H<sub>2</sub>O</sub>	0.0190	1.3 kJ/mol <sub>H<sub>2</sub>O</sub>
Ar	0.0095	11 kJ/mol <sub>Ar</sub>	0.0094	12 kJ/mol <sub>Ar</sub>
CO <sub>2</sub>	0.0003	20 kJ/mol <sub>CO<sub>2</sub></sub>	0.0003	20 kJ/mol <sub>CO<sub>2</sub></sub>

## Computing chemical exergy

If we take as reference atmosphere air at 25 °C and 100 kPa with the composition given in Table 1 (25 °C), then this kind of air has zero exergy by definition, but any other air composition would have  $\psi > 0$ .

For substances in the reference atmosphere (Table 1), it can be shown (see [Exergy of demixing](#)) that the molar exergy of the pure component, at  $T_0, p_0$ , and if in gaseous state, is  $\psi_i = -R_u T^\oplus \ln x_{i0}$ , where  $R_u = 8.314$  J/(mol·K),  $T^\oplus = 298.15$  K, and  $x_{i0}$  its molar fraction in the environment (e.g. for argon,  $\psi_{Ar} = -R_u T^\oplus \ln x_{Ar} = -8.3 \cdot 298 \cdot \ln 0.0095 = 11.5$  kJ/mol). The case of H<sub>2</sub>O is different because water is not a gas at 25 °C and 100 kPa, and  $\psi_{H_2O} = -R_u T^\oplus \ln(x_{H_2O} p^\oplus / p^*(T^\oplus)) = -R_u T^\oplus \ln \phi$  must be used, with  $\phi$  being ambient air relative humidity (per unit, not percent; i.e.  $\psi_{H_2O} = -8.3 \cdot 298 \cdot \ln 0.6 = 1.26$  kJ/mol in Table 1).

For substances not in the reference atmosphere (but with all of its different atoms represented in the environment), e.g. for CO, a [chemical reaction](#) must be set to produce it from the existing species in the environment, e.g.  $CO_2 = CO + (1/2)O_2$ , and the process arranged as in Fig. 1.

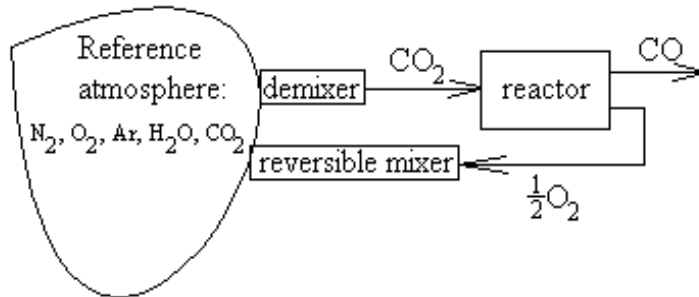


Fig. 1. Example of synthesising a substance out of the reference atmosphere.

In general, the exergy of synthesising a component  $M_1$  from species  $M_i$  in the atmosphere is:

$$\psi_{M_1}^\oplus = \psi_r^\oplus - \sum_{i=2}^C v_i \psi_{M_i}^\oplus = g_{f,M_1}^\oplus + \sum_{i=2}^C v_i (g_{f,M_i}^\oplus - \psi_{M_i}^\oplus) \quad \text{for } 0 = M_1 + \sum_{i=2}^C v_i M_i \quad (3)$$

where  $\psi_r^\oplus$  is the exergy to produce the synthesis reaction at standard conditions (the Gibbs function of reaction):

$$\psi_r^\oplus = g_r^\oplus = \sum_{i=1}^C v_i g_{f_i}^\oplus \quad (4)$$

e.g. for  $CO_2 = CO + (1/2)O_2$   $\psi_r^\oplus = g_{f,CO}^\oplus + (1/2)g_{f,O_2}^\oplus - g_{f,CO_2}^\oplus = (-137) + 0 - (-394) = 257$  kJ/mol<sub>CO<sub>2</sub></sub> = 257 kJ/mol<sub>CO</sub>. Finally in the mixer one may get an exergy (maximum obtainable work) contrary to the one for demixing, i.e.  $(1/2) \cdot 3.9$  kJ/mol<sub>CO</sub>. Thus, to produce CO from the atmosphere one has to spend a minimum work of  $20 + 257 - 2 = 275$  kJ/mol<sub>CO<sub>2</sub></sub> that is thence the chemical exergy of CO.

Notice the difference between exergy of a substance and exergy of reaction, because it is sometimes confused in combustion reactions. For instance, when one carelessly says the 'available energy of a fuel',

one usually refers to the exergy of reaction with pure oxygen and not really to fuel exergy, similarly as when one says carelessly 'the heating power of a fuel', one usually refers to the heating power of the combustion reaction of that fuel with oxygen, pure or in a mixture.

Example. Find the exergy of methane at 100 kPa and 25 °C, and the exergy of its standard combustion reaction.

Sol.: Methane is not a constituent of the reference atmosphere in Table 2. To make it, we have to extract CO<sub>2</sub> for the C-atoms and H<sub>2</sub>O for the H-atoms, and carry out the synthesis-reaction CO<sub>2</sub>+2H<sub>2</sub>O=CH<sub>4</sub>+2O<sub>2</sub>, returning the unneeded constituent (O<sub>2</sub>) to the environment to recover its exergy. From Table 2, extracting CO<sub>2</sub> costs 20 kJ/mol<sub>CO<sub>2</sub></sub>, extracting H<sub>2</sub>O costs 1.3 kJ/mol<sub>H<sub>2</sub>O</sub>, but returning O<sub>2</sub> recovers 3.9 kJ/mol<sub>O<sub>2</sub></sub>. All these processes are theoretical in the sense that they correspond to limiting thermodynamic process which may be far from the present engineering state of the art.

The exergy needed to perform the synthesis-reaction CO<sub>2</sub>+2H<sub>2</sub>O=CH<sub>4</sub>+2O<sub>2</sub> (equal and of opposite sign to the exergy of the standard 'combustion-reaction' CH<sub>4</sub>+2O<sub>2</sub>=CO<sub>2</sub>+2H<sub>2</sub>O), is  $\psi_r^\oplus = g_{f,\text{CH}_4}^\oplus + 2g_{f,\text{O}_2}^\oplus - g_{f,\text{CO}_2}^\oplus - 2g_{f,\text{H}_2\text{O}}^\oplus = (-50) + 2 \cdot 0 - (-394) - 2 \cdot (-237) = 818$  kJ/mol, so that the exergy of methane is  $\psi_{\text{CH}_4}^\oplus = \psi_{\text{CO}_2}^\oplus + 2\psi_{\text{H}_2\text{O}}^\oplus + \psi_r^\oplus - 2\psi_{\text{O}_2}^\oplus = 20 + 2 \cdot 1.3 + 818 - 2 \cdot 3.9 = 831$  kJ/mol. The inverted commas used above in 'combustion-reaction' are intended to point out that this reaction should be carried out under reversible conditions, i.e. as can be approached in a fuel cell, but not in an actual combustion process, with its associated irreversible thermal rushing.

In conclusion, the standard 'combustion-reaction' of methane might yield 818 kJ per mol of methane reacted; otherwise, it takes 818 kJ to generate 1 mol of CH<sub>4</sub> (and 2 mol of O<sub>2</sub> as subproduct) from 1 mol of CO<sub>2</sub> and 2 mol of H<sub>2</sub>O. But it takes 831 kJ (as a thermodynamic limit) to generate 1 mol of CH<sub>4</sub> from the atmosphere.

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