ME 370B
Energy Systems II:
Modeling and Advanced Concepts

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Exergy
(*with an emphasis on its chemical component*)

Exergy (a.k.a. *Availability*) is the ability of an energy resource to do work. An energy resource possesses the ability to do work by being in a state of non-equilibrium with its surroundings. By allowing the resource to interact with those surroundings, it may be brought to equilibrium with the surroundings, and in the process, it is possible to extract work. In fact, according to the Gouy-Stodola (a.k.a. *Lost Work*) theorem, the only way to perform this equilibration reversibly is by extracting work during the process.

Understanding exergy—both conceptually and functionally—is arguably the most important requirement for developing (and analyzing) future energy systems. *Energy* is the basis of all of our efforts, and its conservation is critical for both fundamental understanding of what is possible and, in practice, as a tool to quantify what actually happens. But the fact that it is conserved means that a part of the story is missing: If the energy is always there despite what I do, how do I know if I am doing well with my system? How do I know if I could do better? *Entropy* provides the next step in developing an improved understanding. It is not conserved, only transferred and generated (never destroyed), and it explains why there are intrinsic asymmetries in energy (e.g., work is more valuable than heat). The reversible process—no entropy generation—also provides a useful limit that tells how well devices, and sometimes complete systems, can perform. What entropy does *not* tell us is how well our system performed in an absolute sense—relative to all possible systems—and it is only through the Gouy-Stodola theorem that an explicit connection is made between entropy generation and the loss of the ability to obtain work.

Exergy and *exergy analysis* provide the bridge between the first and second law (and therefore energy and entropy) that is lacking. Unlike energy, exergy is not conserved—it can only be transferred or destroyed. Unlike entropy, exergy is a measure of the ability to transfer energy, and the transfer that it measures is the most valuable kind—work. As we will see later in the quarter, exergy is actually a form of *Free Energy*—a general measure of the ability of matter to do work given a specified set of interactions. In particular, exergy is *environmental free energy*—the work that can be done when permitting thermal, mechanical, and chemical interactions with a specified environment.

The reason why we care about exergy—and how to perform exergy analyses—is that it provides the vehicle we need to understand and quantify advanced energy systems, including those that have yet to be conceived. In essence, energy system design is about taking responsibility for an energy resource in a given environment, determining how much work that resource is capable of delivering, and then developing a system that delivers desired energy services from that resource in a way that destroys as little exergy as possible. Stated another way: The problem of energy

system design is actually one of exergy management. Our job as developers of energy systems is to provide the system that best utilizes the exergy of a resource. Note that this does not imply that the system must actually deliver work (i.e., be an engine). Since work is an entropy-free transfer of energy, any other desired transfer (heat, matter, radiation), can be obtained from work without penalty (at least theoretically). All other transfers of energy are "down-hill" from work.

But perhaps the most important, yet unrecognized, aspect of exergy is that—being environmental free energy—it provides a direct, immediate, quantitative measure of the environmental impact of any transfer from an energy system to the environment. Any system that discharges exergy into the environment has the potential to drive change in that environment. Stated more forcefully, any discharge of exergy into the environment *will* cause change, through entropy generation, until complete equilibration. The only type of discharge that does not cause environmental change is one that is not exergetic. Later in the year (ME370C) we will see that this is practically impossible, but also that the amount and types of exergy discharged, coupled with knowledge of the sensitivity of our environment to such discharges, provides what we need to understand how to design energy systems with minimal environmental impact.

In effect, the realization that exergy is environmental free energy will confirm that our responsibility as engineers is not only to develop energy systems that efficiently utilize resources to deliver energy services, but that when we are finished delivering those services, it is our responsibility to manage the re-incorporation of the energy appropriated back into the natural environment. As such we have two jobs to perform—one is to be the best industrialist that we can—helping humankind to improve and develop—and another to be the best environmentalist that we can—helping humankind to incorporate its activities into the natural system in the least disruptive way possible. It is worth your time to understand exergy.

The Exergy of Matter

Energy can be stored within matter or as radiation. In what follows, we will show how to find the exergy of matter. We will set aside the analysis of cavity radiation (i.e., energy storage within an isothermal, evacuated, cavity), and we will not consider non-thermal modes of radiation energy transfer (laser and microwave beams, etc.). While exergy analysis of radiation is an important topic, it is less-well developed and will require significant ancillary discussions. As such we will defer that conversation until later this quarter.

The approach we will take to finding the exergy of matter will be a bit abstract. By that I mean that we will make no attempt to justify *how* the maximum amount of work can be extracted from a resource—for example, via a suitable collection of reversible machines. Instead we will rely on the combination of the first and second laws, and knowledge of the state principle, to tell us how much work is available from a resource. We do this not to disparage the alternative approach—quite the contrary, illustration of idealized systems that are capable of maximum work extraction from complex energy resources or streams is very informative—instead we do this to emphasize that it is not required to be able to conceive of such a system in order to be able to quantify the exergy of a resource; the exergy of a resource can be evaluated even when we have no idea of how to approach its actual extraction. What this approach does is to both provide an easier path to our objective—we cannot be blocked by issues of machine

complexity—but also shows the power of exergy analysis as a metric of energy quality: "I don't know how you are going to improve it, but I can tell you that you have only delivered X% of the work available in your resource." Exergy analysis tells you when a better system is possible, even while it cannot tell you how to design it.

Figure 1 illustrates the system for analysis. It consists of a prescribed sample of matter at a specified thermodynamic state—referred to as the *resource*. For simplicity we will assume that the matter is at rest (no flow work or kinetic energy), has negligible gravitational potential energy, and has negligible electrostatic potential energy (or is charge neutral). None of these restrictions are essential, but our objective is to provide a systematic discussion for a simple system.
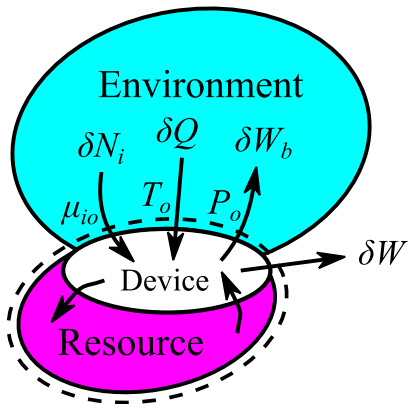

Fig. 1 Illustration of a resource placed in contact with a large-but-finite environment with which it will equilibrate with the aid of a virtual device that does work during the process.

The resource is allowed to equilibrate with an *environment*—a large-but-finite reservoir the properties of which are those of the portion of the natural environment to be utilized in extracting work from the resource. The reservoir with which the resource interacts is sufficiently large that its intensive properties T_o, P_o, μ_{io} remain unaltered due to the interaction. We also postulate that the reservoir has sufficiently rapid internal transport (i.e., relaxation) such that it experiences no internal gradients during the process. This latter assumption may seem odd at first, but recognize that if we did permit gradients to develop within the reservoir then there would be additional entropy generation taking place outside of the system boundary (resource and virtual device) that would be unaccounted for. By asserting that the reservoir can be configured in such a way as to preclude gradients within it, all entropy generation is forced to occur inside the system boundary, and a meaningful assessment of resource exergy will result.[1,2]

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[1] An alternative approach is to allow a portion of the environmental reservoir to be affected during the process, but then to allow the system boundary to extend into the reservoir to the limit of the affected region. This approach is commonly used when considering the assessment of entropy generation due to heat transfer to the environment. Both approaches achieve the same end, and since we are only interested in the reversible limit (no entropy generation anywhere) it seems simpler to set aside the issue in the way done here rather than undertake an extended discussion of boundary extension, but to no ultimate effect.

[2] The role of the virtual device included with the resource inside the system boundary is to enact the reversible transfers and transformations required during equilibration of the resource with the environment. Since the device must have the same state at the beginning and end of the process to achieve maximum work output (it cannot store energy), its presence does not affect the analysis. Note that I am not suggesting that you try to figure out the details

Four energy transfers are permitted during the process of equilibration. The first three are exchanges of heat, work (via boundary displacement), and matter with the environmental reservoir. Note that since we have assumed that the reservoir is capable of fast transport, the values of the corresponding intensive properties of each transfer T, P, μ_i at the boundary correspond to those inside (and throughout) the reservoir, T_o, P_o, μ_{io}. The fourth energy transfer is the work taken from the system δW. Note that this is in addition to the boundary work that takes place at the interface with the reservoir δW_b —which is unavailable—and that δW does not correspond to dilatation or contraction of the system.[3]

Writing extensive energy E and entropy S balances for the system for a differential step in the equilibration process gives

$$[E]: \quad dU = \delta Q - \delta W_b + \sum_k \overline{h}_k \delta N_k - \delta W$$

$$[S]: \quad dS = \frac{\delta Q}{T_o} + \sum_k \overline{s}_k \delta N_k + \delta S_{gen}$$

where k is an index indicating any molecular species that may undergo transfer between the system and the environmental reservoir, and $\overline{h}_k$ and $\overline{s}_k$ are the molar enthalpy and entropy of species k as it crosses the system boundary. These equations can be combined by eliminating δQ between them. Doing this, expressing the boundary work in terms of dilatation $\delta W_b = P_o dV$ and solving for the external work delivered δW gives

$$\delta W = -dU - P_o dV + T_o dS + \sum_k \left(\overline{h}_k - T_o \overline{s}_k \right) \delta N_k - T_o \delta S_{gen}$$

So far no restriction has been applied to the species that may be present in the system or transferred between the system and the environmental reservoir. We know that for transfers into the system, only species that already occur in the environment are available. For transfers in the other direction—out of the system—anything is possible, depending only on the composition of the resource that comprises the system. Moreover, since we explicitly permit the resource to react, any reaction product of the resource formed either on its own, or by virtue of access to species drawn from the environment, is a potential candidate for transfer to the environmental reservoir.

It is at this point that it is helpful to invoke the second law $\delta S_{gen} \geq 0$. Looking at the expression for work above, it is clear that the last term can only result in a loss of work such that setting

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of this machine—that is problematic. Instead, the role of the device is simply to provide some grounding for how it is that the reversible transfers and transformations are brokered during the equilibration process.

[3] Thinking in a concrete way, this is well conceived as a rotating shaft that extends out from the system to deliver work in the form of torque at some rotational speed. Accepting work from such a shaft involves no dilatation of the system, and assuming negligible viscous drag on the shaft once outside of the system, produces no entropy. Note that we prefer not to invoke the notion of "electrical work" at this time since, in reality, that form of work requires the transfer of matter in the form of electrons both in-to and out-of the system.

entropy generation to its reversible limit (zero) is desirable. Invoking this limit requires that all transfers—heat, work, and matter—occur with their conjugate intensive properties set equal to those in the environment. Stated explicitly, to be reversible any heat transfer must occur at T_o, boundary work must be done against P_o, and the chemical potential of all species transferred must be evaluated at the conditions of the environmental reservoir, i.e. at $\mu_{ko} = \overline{h}_{ko} - T_o \overline{s}_{ko}$. Note that this must be true even when a species to be transferred is not present within the environmental reservoir (and as a result, its chemical potential at first introduction is negative infinity).

We will see later that this does not actually present a problem, but for the time being, we will restrict attention to resources that are either composed of species already present in the environment, or that can react with species in the environment (e.g., oxygen) to form species already present in the environment (e.g., carbon dioxide, water). We will return to the more general—but ecologically questionable—case of non-environmental species later on.

With these conditions, the expression for the reversible work obtainable from a resource is then

$$\delta W_{rev} = -dU - P_o dV + T_o dS + \sum_{i=1}^{I} \mu_{io} \delta N_i$$

where the summation has been restricted to include only species that are already present in the environment. Restriction of the matter exchange to species naturally present in the environment is indicated by the use of environmental species index i, and the range of the summation is over all components of the environment (a total of I species).

If the resource consists of a non-reactive species, then the only exergy it possesses is by virtue of its ability to diffuse into the environment, and our work is largely done. The above expression is just integrated from the resource state to the dead state. The more interesting case is where the resource has the ability to react—either with another species present within the resource (for example, molecular hydrogen mixed with hydrogen peroxide) or with species drawn from the environment (for example, pure methane as the resource but using oxygen drawn from the environment). In either case the reaction process is reversible, work is extracted during the process, and the reaction results in only environmental species as products.

In order to pursue this more-general case, what we need is to invoke a reaction balance for each species in the resource that maps its transformation to environmental species. Paralleling the notation chosen for environmental species, we will use j as an index to denote each component of the resource—including those components that might also be environmental species—and we will let the index range across all components of the resource (a total of J species).

A notional reaction balance suitable for transforming hypothetical species A to product species C and D by virtue of reaction with some other species B, may be written as

$$\left[Rxn \text{ of } A \right]: \quad aA + bB \rightarrow cC + dD$$
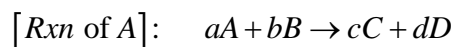
where each "mole of reaction" results in the conversion of a moles of species A to c moles of C and d moles of D, and in the process consumes b moles of B. This balance may be rewritten using a signed stoichiometric coefficient for the reaction partner B as

$$[Rxn \text{ of } A]: \quad aA \rightarrow -bB + cC + dD$$
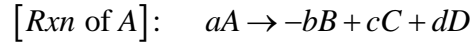
such that role of the reaction in transforming species A is highlighted. This form of reaction balance may be written in a generic form for each resource species M_j (read as *molecule j*) with stoichiometric coefficient v_j as

$$[Rxn \text{ of } M_j]: v_j M_j \rightarrow \sum_{i=1}^{I} v_{ij} M_i \quad \text{(signed coefs.)}$$
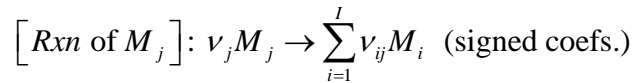
where M_i denotes environmental species involved in the reaction (as either reactants or products), and v_{ij} is the signed stoichiometric coefficient for the reaction of species j to or with environmental species i (*-b, c, d* from before). We reiterate that if the reaction has an environmental species as a product, the environmental species stoichiometric coefficient is positive; if the reaction requires an environmental species as a reactant, the coefficient is negative. (The coefficient of the resource species undergoing reaction M_j is always positive.)

Note that since we will take our summation over all resource species—whether or not they are environmental—it is important to recognize that any environmental species is considered to undergo a chemical transformation that simply maps it to itself as a product.[4]

Using the reaction balance expression, the differential change in amount of j-th resource species $\delta N_{rxn,j}$ due to a differential amount of chemical reaction $\delta \xi_j$ may be written as

$$\delta N_{rxn,j} = -v_j \delta \xi_j$$

And since chemical reaction is the only method by which a change in the amount of species j can occur (unreacted transfer to the environment is not permitted), the differential balance for the amount of species j in the system becomes

$$[N_j]: \quad dN_j = \delta N_{rxn,j} = -v_j \delta \xi_j$$

The amount-of-substance balance for each environmental species i in the system can be written as the sum of two components: the amount due to transfers across the system boundary δN_i, and the amount generated via chemical reaction

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[4] In other words, when species j is present in the environment $v_j = 1$ and $v_{ij} = 1$ when $j = i$ but $v_{ij} = 0$ when $j \neq i$ (e.g., $1H_2O \rightarrow 1H_2O$). Stated another way, water is transformed to water, nothing else, so the stoichiometric coefficients of all species that are not water are equal to zero.

$$[N_i]: \quad dN_i = \delta N_i + \sum_{j=1}^{J} \nu_{ij} \delta \xi_j$$

In this expression, the summation gives the net formation of species *i* resulting from all reactions that transform resource species *j* to environmental species.

Eliminating the change in extent of reaction for each resource species in favor of its change in mole number, and rearranging this expression to solve for the amount of substance transferred to or from the environment yields the transfer terms that we require

$$\delta N_i = dN_i + \sum_{j=1}^{J} \left(\nu_{ij} / \nu_j \right) dN_j$$

What this indicates is that the *transfer* of environmental species can be written as the sum of the change in the species within the system boundary and the (net) amount of the species required by chemical reactions that transform resource species. For example, if during an increment of the process, the oxygen mole number inside the system increased, and oxygen from the environment was also needed for reaction of a resource species, then both terms would make positive contributions to the required oxygen transfer. (Both dN_j and ν_{ij} would be negative in the second term, resulting in a positive contribution from reaction.)

This may be substituted back into our expression for the reversible work so as to eliminate the inexact differentials (due to species transfers) in favor of exact differentials (due to changes in the amount of species):

$$\delta W_{rev} = -dU - P_o dV + T_o dS + \sum_{i=1}^{I} \mu_{io} dN_i + \sum_{i=1}^{I} \mu_{io} \sum_{j=1}^{J} \left(\nu_{ij} / \nu_j \right) dN_j$$

The importance of eliminating the inexact differentials cannot be overstated. What this has done is to leave us in a position where the right side of this expression is exact, and the coefficients of the various differentials are all constants. What this allows us to do is to use any path of our choosing for integration between the initial and final states.

For the sake of both simplicity and compatibility with commonly used terminology, we choose a path for integration that consists of two parts: First, we will integrate to find the reversible work obtainable from a resource as we take it from its original state (*resource state*) to thermal and mechanical equilibrium with the environment (*restricted dead state* or *thermo-mechanical dead state*), but at fixed composition. Second, let's allow the resource to react and diffuse in communication with the environmental reservoir, all the while maintaining thermal and mechanical equilibrium with the environment (*unrestricted dead state* or just *dead state*).

The result of this two-part integration path can be written as

$$W_{max} = \int_{\text{Resource State}}^{\text{T-M Dead State}} \left(-dU - P_o dV + T_o dS \right) \Big|_{\substack{\text{Fixed Composition} \\ \text{No Reaction or Diffusion}}}$$

$$+ \int_{\text{T-M Dead State}}^{\text{Dead State}} \left(-dU - P_o dV + T_o dS + \sum_{i=1}^{I} \mu_{io} dN_i + \sum_{i=1}^{I} \mu_{io} \sum_{j=1}^{J} \left(\nu_{ij} / \nu_j \right) dN_j \right) \Bigg|_{\substack{T=T_o \\ P=P_o}}$$

where the terms in the first integral that correspond to changes in composition have been set to zero. This first integral leads to what is sometimes referred to as the *physical* or *thermo-mechanical exergy*, for which we will use the symbol X_{TM}. The second integral is the usual definition of the *chemical exergy*, which we will denote as X_C. We will denote the combination of these two as the (overall) exergy $X = X_{TM} + X_C$.[5]

The expressions for the thermo-mechanical and chemical exergy may be further simplified. Starting with the thermo-mechanical exergy, since all the coefficients of the differentials are constants, this expression may be immediately integrated to

$$\begin{aligned} X_{TM} &= \left(U - U_{TM} \right) + P_o \left(V - V_{TM} \right) - T_o \left(S - S_{TM} \right) \\ &= \underbrace{\left(U + P_o V - T_o S \right)}_{\equiv \mathcal{A}} - \underbrace{\left(U_{TM} + P_o V_{TM} - T_o S_{TM} \right)}_{= G_{TM}} \end{aligned}$$

The first term on the bottom line is sometimes referred to as the control-mass availability function and is often represented by the symbol $\mathcal{A}$ (or a on a mass-specific basis). The second term is this same function but evaluated at the conditions of the thermo-mechanical dead state. Since the temperature and pressure of that state are T_o, P_o this function is identical to the Gibbs function of the resource evaluated at the temperature and pressure of the dead state. The expression for thermo-mechanical exergy can then be written in the shorthand

$$X_{TM} = \mathcal{A} - \mathcal{A}_{TM} = \mathcal{A} - G_{TM}$$

where $\mathcal{A}$ and G_{TM} are both evaluated using the composition of the original resource, but at each of the two states (that of the resource initially, and that of the environment).

The expression for chemical exergy may be simplified in a similar way

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[5] Since the so-called conservative forms of energy (e.g., kinetic and potential) are completely convertible into work, these must also be included in the overall exergy in situations where they are non-negligible.

$$X_C = \left(U_{TM} - U_o\right) + P_o\left(V_{TM} - V_o\right) - T_o\left(S_{TM} - S_o\right)$$

$$+ \sum_{i=1}^{I} \mu_{io}\left(N_{io} - N_{iTM}\right) + \sum_{i=1}^{I} \mu_{io} \sum_{j=1}^{J}\left(-v_{ij}/v_j\right)\left(N_{jTM} - N_{jo}\right)$$

$$= \underbrace{\left(U_{TM} + P_oV_{TM} - T_oS_{TM}\right)}_{=G_{TM}} - \underbrace{\left(U_o + P_oV_o - T_oS_o\right)}_{\substack{\text{Environmental Intensive State: } T_o, P_o, \{x_{io}\} \\ \text{Unknown Extensive Composition: } \{N_{io}\}}}$$

$$+ \sum_{i=1}^{I} \underbrace{\mu_{io}}_{\substack{\text{Environ.} \\ \text{Intensive} \\ \text{State}}} (\ \underbrace{N_{io}}_{\substack{\text{Unknown} \\ \text{Extensive} \\ \text{Comp.}}} - N_{iTM}) + \sum_{i=1}^{I} \mu_{io} \sum_{j=1}^{J}\left(-v_{ij}/v_j\right)(N_{jTM} - \underbrace{N_{jo}}_{=0})$$

Focusing on the second level of this expression, we see that the first term is the same Gibbs function expression we have just encountered. The second term can also be written as Gibbs function, but it corresponds to the composition and thermomechanical state of the environment (not the resource) since it is post-equilibration. The difficulty with this term is that the amount of each environmental species present inside the system boundary at the end of the process N_{io} is not known. (Another way of saying this is that the size of the system at the end of the process is unknown.) Fortunately this problem is immediately mitigated by viewing the third term. This term gives the change in chemical potential of environmental species in the system. At the beginning of the reaction process the amount of substance for i-type species is represented by the known set of mole numbers N_{iTM}. At the end of the process, however, the set of mole numbers are the unknown values N_{io}. Fortunately, this unknown term exactly cancels the previous unknown term. The result is that we do not need to know that which we do not know, and the essential difficulty in the expression is removed.[6] With regards to the last expression, note that the chemical reaction results in complete transformation of the original j-type species to environmental species such that the amount of substance of any species j at the end of the process N_{jo} is zero.

Employing these observations, the expression for chemical exergy can be simplified to

$$X_C = G_{TM} - \sum_{i=1}^{I} \mu_{io}N_{iTM} - \sum_{i=1}^{I} \mu_{io} \sum_{j=1}^{J}\left(v_{ij}/v_j\right)N_{jTM}$$

Recall that we had previously discussed how a choice must be made with regard to how to treat environmental species that are present in the resource. Recapping, either of two choices can be made: The choice can be made to differentiate between those components of the resource that are environmental species and those that are not, or the choice can be made not to differentiate between components of the resource (i.e., to treat all j equally). If the former choice is made, then environmental species would not be considered to undergo chemical reaction (their stoichiometric coefficients would all be zero), but their existence within the system would need

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[6] Another way of thinking about this is that the equation is trying to tell us that the size of the system is irrelevant. Since the post-equilibration system has identical thermal state and composition as the environment, the ability to differentiate between the two has become artificial (and is therefore immaterial).

to be tracked since their chemical potential in the resource will be different from in the environment. If the latter—which is the choice made here—then environmental species are also considered to react, but the result of the reaction is that they form themselves. The effect of this choice on the expression above is that all components of the resource are considered to be reactive and therefore N_{iTM} is identically zero. (If the alternative choice were made, N_{iTM} would not necessarily be zero, and the summation over reactive species would not include any environmental species.)[7] We also recognize the fact that the composition of the system N_{jTM} is identical to that of the original resource N_j such that the *TM* subscript is not required.

Given this choice of conventions (to treat all *j* equally), our final expression becomes

$$X_C = G_{TM} - \sum_{i=1}^{I} \mu_{io} \sum_{j=1}^{J} \left(\nu_{ij} / \nu_j \right) N_j$$

What this surprisingly simple expression says is that the chemical exergy of a resource is given by the difference between the Gibbs function of the resource evaluated at the thermo-mechanical dead state and the aggregated chemical potential of the species to which the resource will be transformed in the environment. Later in the quarter we will see that this interpretation is in complete agreement with our understanding of the relationship between chemical potential and free energy—as applied to processes that take place while interacting with the environment.

Denoting this last term by the symbol $\mathcal{G}_o$, the expression for chemical exergy can be written as

$$X_C = G_{TM} - \mathcal{G}_o$$

and the expression for the overall exergy can be written as

$$X = X_{TM} + X_C = \left(\mathcal{A} - G_{TM} \right) + \left(G_{TM} - \mathcal{G}_o \right) = \mathcal{A} - \mathcal{G}_o$$

The exergy of a resource is the difference between its control-mass availability function and the chemical potential of what it will leave behind in the environment.

Following the usual convention for thermodynamic properties, we will denote mass-specific and mole-specific exergy by x and $\overline{x}$ respectively. Note that since the expressions of thermo-mechanical exergy and chemical exergy depend only on properties of the system, exergy itself is also a property.[8]

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[7] The reason for making this choice is convenience in computer programming. We will see that it is slightly simpler to not have to distinguish between environmental and non-environmental species in the resource when writing a general function for computing chemical exergy.

[8] A purist will state that exergy is actually a joint property of the system and the specified environment. While this is true, we note that making a choice of environment is really no different than choosing a reference state for computing enthalpy or defining reference species for chemical reaction. Once the choice is made, all values follow unambiguously from the choice of these reference parameters.

Exergy of Matter with Nonenvironmental Products

In our first pass through how to find the exergy of a resource we found it convenient to narrow the discussion to resources comprised solely of environmental species or which upon chemical reaction were capable of forming environmental species. Recall too that the definition of an environmental species was one that was already (i.e., naturally) present in the environment (non-zero mole fraction). It is time to relax those restrictions so as to see what we can learn from the more general case.

In order to accomplish this, several minor modifications are needed to the expressions derived above. The first is that we must now permit the transfer of nonenvironmental species (zero mole fraction in the environment initially). We could do this either by modifying our definition of the index i to include these species, or we could add another summation (with a new index) in order to provide for these terms. For reasons that should be apparent later, we choose the latter. As such, the expression for reversible work becomes

$$\delta W_{rev} = -dU - P_o dV + T_o dS + \sum_{i=1}^{I} \mu_{io} \delta N_i - \sum_{k=1}^{K} \mu_{ko} \delta N_k$$

where k is introduced as the index over nonenvironmental species (a total of K species), and i is retained as the index over species already present in the environment. Note that the list of species indexed by k should include all nonenvironmental species present in the resource itself (since they could be released without reaction) as well as any nonenvironmental products of reaction, and that the sign of the last term has been changed to reflect our expectations about the transfer of these species. (They can only exit the system.)
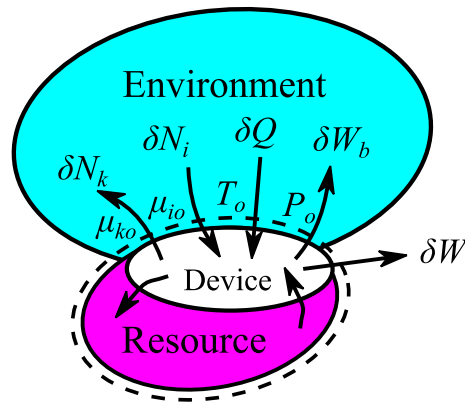

Fig. 2 Inclusion of nonenvironmental species transfers is required to treat the general case for exergy analysis. Since these species (index k) are not initially present in the environmental reservoir, we have reversed the direction of the transfer taken as positive.

The expression for the transformation of resource species to products (or to itself) must now include these species

$$\left[Rxn \text{ of } M_j \right] : \quad v_j M_j \rightarrow \sum_{i=1}^{I} v_{ij} M_i + \sum_{k=1}^{K} v_{kj} M_k \quad \text{(signed coefs.)}$$

The amount of resource destroyed by a differential amount of reaction is unchanged

$$\delta N_{rxn,j} = -v_j \delta \xi_j$$

as is the balance for each resource species (since each is forced to be transformed to a product)

$$\left[N_j \right] : \quad dN_j = \delta N_{rxn,j} = -v_j \delta \xi_j$$

The balance equation for environmental species remains unchanged

$$\left[N_i \right] : \quad dN_i = \delta N_i + \sum_{j=1}^{J} v_{ij} \delta \xi_j$$

but a new set of balances is required for the nonenvironmental species

$$\left[N_k \right] : \quad dN_k = -\delta N_k + \sum_{k=1}^{K} v_{kj} \delta \xi_j$$

Note that just as with environmental species, accumulation within the system boundary, exchange with the environmental reservoir, and generation via chemical transformation are all included in this balance.

These two types of balance equation may be rearranged to show how the transfer terms depend explicitly on reaction and accumulation

$$\delta N_i = dN_i + \sum_{j=1}^{J} \left(v_{ij} / v_j \right) dN_j$$

$$-\delta N_k = dN_k + \sum_{j=1}^{J} \left(v_{kj} / v_j \right) dN_j$$

It was at this point in our prior development that we eliminated the inexact differential transfer terms from the equation for reversible work so as to be able to perform the integration over exact changes in the amount of species contained within the system boundary. This was convenient because the chemical potential of each species transferred was a known constant and therefore there was no need to consider how to relate the kernel of the integral to its differential. Since the environmental reservoir with which we interact is "large-but-finite" the chemical potential for

any species already present in the environment remains constant, and so for these species, we can use the same approach.[9]

This is not true for the nonenvironmental species, however. These species have identically zero mole fraction in our environmental reservoir before the equilibration (and work extraction) process begins, and their initial chemical potentials are therefore negative infinity. Fortunately the singularity at zero mole fraction is integrable, so that a well-defined value of chemical exergy still exists. But what this does mean is that we will have to take a different approach to performing the integration for nonenvironmental species.

Noting that the only way in which nonenvironmental species can begin to accumulate in the environmental reservoir is by transfer (i.e., they cannot be formed in the environment), the balance equation for nonenvironmental species *in the environment* is given by

$$\left[N_{ko}\right]: \quad dN_{ko} = \delta N_k$$

where N_{ko} is the amount of substance k in the environment.

Writing the expression for environmental species as before, but casting the nonenvironmental component in terms of changes in the *environmental reservoir* state yields

$$\delta W_{rev} = -dU - P_o dV + T_o dS + \sum_{i=1}^{I} \mu_{io} \left[dN_i + \sum_{j=1}^{J} \left(v_{ij}/v_j\right) dN_j \right] - \sum_{k=1}^{K} \mu_{ko} dN_{ko}$$

In addition to providing an expression in terms of exact differentials, what we have done is to set up the nonenvironmental transfer term in such a way that it can be integrated. The reason is that the chemical potential of nonenvironmental species in the environment μ_{ko} can be expressed solely as a function of the amount of species k that has accumulated in the environment N_{ko}.

The reason for this last statement again comes back to the fact that our reservoir is large but finite. Under these conditions, all new species additions to the reservoir occur in the *ideally dilute* limit.[10] This is the limit where regardless of the complexity of molecular interactions (i.e., non-ideal effects), any new molecular additions see an environment which is essentially unchanging. As a result, the fugacity of the dilute components is directly proportional to the amount of substance added (and the coefficient of proportionality is Henry's constant). The expression for the chemical potential of species of type k within the (large) environmental reservoir may then be written as

$$\mu_{ko} = \mu_{ko}^o + \bar{R}T_o \ln x_{ko}$$

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[9] In fact it is this requirement that defines what is meant by large-but-finite: The environmental reservoir must be sufficiently large that any change is chemical potential of a species already existing within it is negligible.
[10] See Levine, Ch. 9 for a comprehensive discussion of the chemical potential of real solutions considered in the ideally dilute limit.

Using the fact that the reservoir is finite, and assigning it a total mole number N_o, the chemical potential can be written in terms of the mole number in the reservoir N_{ko} instead of the mole fraction x_{ko} (since $x_{ko} = N_{ko}/N_o$)

$$\mu_{ko} = \mu_{ko}^o - \bar{R}T_o \ln N_o + \bar{R}T_o \ln N_{ko}$$

Again due to our assumption that the reservoir is large, variations in its total mole number N_o are negligible, and as a result, the first two terms in this expression are constants. Substituting into the expression for reversible work gives

$$\delta W_{rev} = -dU - P_o dV + T_o dS$$
$$+ \sum_{i=1}^{I} \mu_{io} \left[dN_i + \sum_{j=1}^{J} \left(v_{ij}/v_j \right) dN_j \right]$$
$$- \sum_{k=1}^{K} \left[\mu_{ko}^o - \bar{R}T_o \ln N_o + \bar{R}T_o \ln N_{ko} \right] dN_{ko}$$

It was at this stage that we took advantage of the exact nature of the right side of this expression so as to choose a convenient, two-part path for integration. Having expressed the last term explicitly in terms of the state of the environmental reservoir, we again have an exact expression which permits the same two-part integration.

$$W_{max} = \int_{\text{Resource State}}^{\text{T-M Dead State}} \left(-dU - P_o dV + T_o dS \right) \Big|_{\substack{\text{Fixed Composition} \\ \text{No Reaction or Diffusion}}}$$
$$+ \int_{\text{T-M Dead State}}^{\text{Dead State}} \left(-dU - P_o dV + T_o dS + \sum_{i=1}^{I} \mu_{io} \left[dN_i + \sum_{j=1}^{J} \left(v_{ij}/v_j \right) dN_j \right] \right) \Bigg|_{\substack{T=T_o \\ P=P_o}}$$
$$+ \int_{\text{T-M Dead State}}^{\text{Dead State}} \left(-\sum_{k=1}^{K} \left[\mu_{ko}^o - \bar{R}T_o \ln N_o + \bar{R}T_o \ln N_{ko} \right] dN_{ko} \right) \Bigg|_{\substack{T=T_o \\ P=P_o}}$$

Following our prior development still further, we see that there are no changes to be made in our expression for thermo-mechanical exergy. All of our adjustments affect only the chemical component of exergy. The result is as before

$$X_{TM} = A - G_{TM}$$

Similarly, the first line of the expression for chemical exergy remains unaltered with all coefficients being known constants. This part of the integration for chemical exergy can be performed immediately yielding

$$X_C = \left(U_{TM} - U_{DS}\right) + P_o\left(V_{TM} - V_{DS}\right) - T_o\left(S_{TM} - S_{DS}\right)$$

$$+ \sum_{i=1}^{I} \mu_{io} N_{iDS} + \sum_{i=1}^{I} \mu_{io} \sum_{j=1}^{J}\left(-\nu_{ij}/\nu_j\right) N_{jTM}$$

$$+ \left. \int_{\text{T-M Dead State}}^{\text{Dead State}} \left(-\sum_{k=1}^{K}\left[\mu_{ko}^o - \bar{R}T_o \ln N_o + \bar{R}T_o \ln N_{ko}\right] dN_{ko} \right) \right|_{\substack{T=T_o \\ P=P_o}}$$

where we have used the more explicit subscript *DS* to indicate a property of the system evaluated at the end of the process (dead state) in lieu of the subscript naught (since that might now become confused with a property of the environmental reservoir).

Performing the integration on the last term in isolation gives

$$\left. \int_{\text{T-M Dead State}}^{\text{Dead State}} \left(-\sum_{k=1}^{K}\left[\mu_{ko}^o - \bar{R}T_o \ln N_o + \bar{R}T_o \ln N_{ko}\right] dN_{ko} \right) \right|_{\substack{T=T_o \\ P=P_o}}$$

$$= -\sum_{k=1}^{K}\left[\mu_{ko}^o - \bar{R}T_o \ln N_o\right]\left(N_{koDS} - N_{koTM}\right)$$

$$-\sum_{k=1}^{K} \bar{R}T_o \left[N_{koDS} \ln N_{koDS} - N_{koDS} - N_{koTM} \ln N_{koTM} + N_{koTM}\right]$$

where we have used the fact that the integral of $\ln x$ is $x \ln x - x$.

Recognizing that
1. there are no nonenvironmental species in the env. reservoir at the *TM* state $\left(N_{koTM} = 0\right)$,
2. that by using L'Hopital's rule the $x \ln x$ term for the *TM* state is zero (since $N_{koTM} = 0$),
3. that $\mu_{ko}^o + \bar{R}T_o \ln\left(N_{koDS}/N_o\right) = \mu_{koDS}$ is the chemical potential of nonenvironmental species in both the system and the environment at the end of the process, and
4. that $\ln x - 1$ goes to $\ln x$ in the limit of small x,

the overall expression can be simplified to:

$$X_C = \left(U_{TM} - U_{DS}\right) + P_o\left(V_{TM} - V_{DS}\right) - T_o\left(S_{TM} - S_{DS}\right)$$

$$+ \sum_{i=1}^{I} \mu_{io} N_{iDS} + \sum_{i=1}^{I} \mu_{io} \sum_{j=1}^{J}\left(-\nu_{ij}/\nu_j\right) N_{jTM} - \sum_{k=1}^{K} \mu_{koDS} N_{koDS}$$

Recognizing that the final system composition includes components from both environmental and nonenvironmental species we can write

$$U_{DS} + P_o V_{DS} - T_o S_{DS} = \sum_{i=1}^{I} \mu_{io} N_{iDS} + \sum_{k=1}^{K} \mu_{koDS} N_{kDS}$$

where N_{kDS} is the mole number of nonenvironmental species inside the system boundary at the end of the process. Using this along with the definition of the Gibbs function gives

$$X_C = G_{TM} - \sum_{i=1}^{I} \mu_{io} \sum_{j=1}^{J} \left(v_{ij}/v_j \right) N_{jTM} - \sum_{k=1}^{K} \mu_{koDS} N_{koDS} - \sum_{k=1}^{K} \mu_{koDS} N_{kDS}$$

The last two terms can be combined to give

$$X_C = G_{TM} - \sum_{i=1}^{I} \mu_{io} \sum_{j=1}^{J} \left(v_{ij}/v_j \right) N_{jTM} - \sum_{k=1}^{K} \mu_{koDS} \left(N_{koDS} + N_{kDS} \right)$$

The sum at the end is the total amount of species k left over at the end of the process, regardless of whether it is found inside the system boundary or in the environment. Since the only way to generate nonenvironmental species is from chemical transformation, this may be written as

$$N_{koDS} + N_{kDS} = \sum_{j=1}^{J} \left(v_{kj}/v_j \right) N_{jTM}$$

yielding the more-symmetric expression

$$X_C = G_{TM} - \sum_{i=1}^{I} \mu_{io} \sum_{j=1}^{J} \left(v_{ij}/v_j \right) N_{jTM} - \sum_{k=1}^{K} \mu_{koDS} \sum_{j=1}^{J} \left(v_{kj}/v_j \right) N_{jTM}$$

Recognizing that the resource composition is unchanged from the original state to the *TM* state means $N_{jTM} = N_j$, the final expression reads

$$X_C = G_{TM} - \sum_{i=1}^{I} \mu_{io} \sum_{j=1}^{J} \left(v_{ij}/v_j \right) N_j - \sum_{k=1}^{K} \mu_{koDS} \sum_{j=1}^{J} \left(v_{kj}/v_j \right) N_j$$

This differs from our previous expression in two ways: The first is that it includes a term for nonenvironmental species. The second is that, in that term, the chemical potential of the species involved is not known a priori—it can only be found by knowing how much is generated and the size (mole number) of our large-but-finite environmental reservoir.

Given the likely magnitudes for amount of nonenvironmental species released and what might be viewed as reasonable choices for the size of the environmental reservoir, the values of chemical potential for nonenvironmental species, while finite, are likely to be large, negative numbers. As such, they may overshadow the contributions from the resource and environmental species and in doing so call the utility of exergy analysis under such conditions into question.[11]

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[11] We will see an example of this when we calculate the effect of ambient relative humidity on the chemical exergy of fuels that produce water as a product. The point to take away from this is that unrealistic choices about the dead state will lead to results that are more confusing than useful.

A final observation is that summed together, the last two terms in the expression represent the chemical potential of the species left behind following our reversible equilibration process. In other words they confirm that

$$X_C = G_{TM} - \mathcal{G}_o$$

with $\mathcal{G}_o$ now given by

$$\mathcal{G}_o = \sum_{i=1}^{I} \mu_{io} \sum_{j=1}^{J} \left(v_{ij} / v_j \right) N_j - \sum_{k=1}^{K} \mu_{koDS} \sum_{j=1}^{J} \left(v_{kj} / v_j \right) N_j$$

still conveys the essence of chemical exergy: It is the difference between the chemical potential of the resource as it currently exists and what it will become once equilibrated with, and incorporated into, the environment.