



A simple thermodynamic model for evaluating the ecological restoration effect on a manganese tailing wasteland



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ABSTRACT

A simple model was established for calculating the Gibbs free energy G , enthalpy H and entropy S of a restored plant community on a manganese mine tailing wasteland. The experimental area was 4.4 ha including plots I (contaminated site amended with organic manure), II (contaminated site amended with chemical fertilizer) and III (uncontaminated site in the vicinity). Wood species *Paulownia fortunei* and *Koelreuteria bipinnata* were transplanted as dominant tree species. Results obtained from the experimental period (2010–2015) showed that the applied phyto-remediation method had not only effectively enhanced the biomass growth and metal uptake but also greatly enriched the biodiversity of the plant community. The estimated G , H and S values were significantly higher in plot I than in plot II. The values of G , H , S and their increments (ΔG , ΔH and ΔS) all increased with time, showing that the restored plant community possessed high growth and development potentials. A shift in distribution of the internal energy components was observed from the ΔG , ΔH and ΔS curves, showing that the energy conserved by the plant community was more transformed to S than to G in later years. In accordance with the thermodynamic theories, the observed increase in S associated with increasing number of naturally germinated native plant species in the experimental plots indicated that the plant community possessed a natural trend towards increase in its biodiversity. Compared with those commonly used ecological indices, G , H and S were shown to be adequate indicators for, respectively, ecosystem development capacity, primary productivity, and species richness. Use of G , H and S offered more information regarding the internal energy state and distribution of the plant community.

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1. Introduction

Matter and energy exchanges constitute the basis of ecological processes. Therefore, ecosystems can be regarded as open thermodynamic systems with bio-species as key components, while the state of an ecosystem and its changes can be determined and thus monitored using basic stationary and non-stationary state functions (Rodríguez et al., 2016). A plant community is a sub-ecosystem and the growth of a plant community is essentially an energy transformation process in which the plant species obtain energy from their surroundings. Due to variations in environmental conditions, plant communities in different regions may have different energy states. Apart from the solar energy input that determines the availability of energy to be used by plant species for their growth, other site conditions (temperature, pressure, O_2 , CO_2 ,

H_2O , nutrients, metal toxicity, etc.) are also essential factors affecting the growth rate or energy transformation efficiency of the plant species. For analysis of the environmental impact on a plant community, it should be useful to establish a quantitative relationship between the energy state of the plant community and its related site conditions.

Thermodynamics of ecosystems has become one of the foundational columns supporting the rapid and continuous development of systems ecology (Jørgensen et al., 2016; Patten, 2016). The contribution to thermodynamics of ecosystems that should be mentioned is the systematic work done by Jørgensen and his co-workers on establishment of eco-exergy models (Jørgensen, 1992; Jørgensen et al., 1995, 2005; Marques and Jørgensen, 2002; Marchi et al., 2011). According to its definition (Jørgensen, 2000; Jørgensen and Marques, 2001), exergy of an ecosystem is the amount of work that the system can perform when it is brought into thermodynamic equilibrium with its environment. In comparison with other functions and ecological indices, eco-exergy has been successfully applied as a thermodynamic variable (Jørgensen, 2010; Jørgensen

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and Nielsen, 2007; Draganovic et al., 2013; Molozzi et al., 2013; Puzachenko et al., 2016) for description of various types of ecosystems (Jørgensen, 2007; Perryman and Schramski, 2015; Lu et al., 2011) and assessment of ecosystem health (Jørgensen, 1995; Tang et al., 2015; Xu et al., 2011; Zhang et al., 2010).

The internal energy state of a thermodynamic system involves three basic and interrelated components, Gibbs free energy G , enthalpy H and entropy S (Engel and Reid, 2006). Unlike exergy, which, according to Jørgensen (2007), is not a state variable because it is dependent on both the system and environment, G , H and S are state functions. Analysis of G , H and S of an ecosystem based on conventional thermodynamic theories should be expected to offer valuable information concerning ecosystem growth and development. It is likely the complexity of ecosystem constitution and ecological process that gives rise to difficulties to accurately quantify the components of ecosystems and determine the impacts of related factors. Direct uses of the functional relationship among G , H and S for description of ecosystems have not been found reported in available literatures. As a primary step to look into ecosystems from a different angle, the present study was conducted to establish a simple thermodynamic model for determination of G , H and S of ecosystems. The presented model was tested using the data obtained from an ecological restoration project implemented on a manganese tailing contaminated wasteland.

2. Theoretical

2.1. Gibbs free energy, enthalpy and entropy of a thermodynamic system

Thermodynamics (including the ideal gas theory) is the branch of science that describes the behavior of matter and the transformation between different forms of energy on a macroscopic scale (Engel and Reid, 2006). The Gibbs free energy of a thermodynamic system at a given state is given as

$$G = \sum G_i = \sum C_i \mu_i \quad i = 1, 2, 3, \dots, N \quad (1)$$

where μ_i and C_i are, respectively, the chemical potential and the molar mass quantity of component i , and N is the number of system components. The chemical potential of component i is related to its activity a_i , activity coefficient γ_i and mole fraction x_i by

$$\mu_i = \mu_i^0 + RT \ln(a_i) = \mu_i^0 + RT \ln(\gamma_i x_i) \approx \mu_i^0 + RT \ln(x_i) \quad (2)$$

where μ_i^0 stands for the standard chemical potential of component i given temperature T and standard pressure P^0 , and R is the gas constant. The mole fraction x_i is the ratio of C_i to the total molar quantity of the system, C_T ,

$$x_i = C_i / C_T = C_i / \sum C_i \leq 1 \quad (3)$$

It is noted from Eqs. (2) and (3) that x_i is a factor relating the chemical potential of a component to its system composition. Though Eq. (2) was initially derived from ideal gas systems, the equation has been developed into a general expression for chemical potential and widely applied to determine the behaviors of different substances involved in various reactions occurring in gas, liquid, solid and mixed systems. On substitution, using x_i to replace a_i , we obtain

$$G = \sum C_i \mu_i = \sum C_i [\mu_i^0 + RT \ln(x_i)] = \sum C_i \mu_i^0 + RT \sum C_i \ln(x_i) \quad (4)$$

Relating the Gibbs free energy to enthalpy H and entropy S , we have

$$G = H - TS = \sum C_i \mu_i^0 + T \sum RC_i \ln(x_i) \quad (5)$$

Introducing two factors, h and s ,

$$h = \sum C_i \mu_i^0 \quad (6)$$

$$s = \sum RC_i \ln(1/x_i) \quad (7)$$

Eq. (5) can be rewritten as

$$G = H - TS = h - Ts = \sum C_i \mu_i^0 - T \sum RC_i \ln(1/x_i) \quad (8)$$

which shows that h and s correspond, respectively, to H and S . Taking the partial derivative of G with respect to T gives

$\partial G / \partial T = -S = -s = -\sum RC_i \ln(1/x_i)$ which confirms the essential connection between s and S and thus that between h and H . Using the conventional expression of H , we have

$$H = U + PV = G + TS \propto h + Ts = \sum C_i \mu_i^0 + \sum C_i \mu_i + T[\sum RC_i \ln(1/x_i)] \quad (9)$$

which shows that given system volume V and pressure P , H and h are both proportional to the total internal energy U . As seen in Eq. (2), μ_i^0 is the highest μ_i value for species i since $x_i \leq 1$ and $\ln(x_i) \leq 0$. The term $\sum C_i \mu_i^0$ thus stands for the total internal energy of the system, namely,

$$h = \sum C_i \mu_i^0 = U = G + Ts = H - PV \quad (10)$$

which shows that the total internal energy U consists of G and Ts . Since

$$H - TS = h - Ts = H - PV - (TS - PV)$$

$$Ts = T \sum RC_i \ln(1/x_i) = TS - PV$$

We obtain the connection between s and S ,

$$s = \sum RC_i \ln(1/x_i) = S - PV/T \quad (11)$$

If V and P are kept unchanged, an infinitesimal change in H will be equal to that in h ,

$$dH = dU - PdV = dU = dh$$

If T is also kept constant,

$$dS = ds + (P/T)dV = ds$$

Since H , S , h , s and G are all system properties, their changes from state I to state II can be uniquely determined by their differences between states,

$$\Delta H = (H_2 - H_1) = \Delta U - P\Delta V = \Delta U = \Delta h \quad (12)$$

$$\Delta S = (S_2 - S_1) = \Delta s + (P/T)\Delta V = \Delta s \quad (13)$$

Eqs. (12) and (13) shows that the changes in h and s are equal, respectively, to the changes in H and S under given T , V and P conditions. It follows that given the same P , V and T for systems I and II, we have

$$\Delta H_{I-II} = (H_I - H_{II}) = \Delta h_{I-II} = \sum C_{II} \mu_{II}^0 - \sum C_{III} \mu_{III}^0 \quad (14)$$

$$\Delta S_{I-II} = \Delta s_{I-II} = R \sum C_{II} \ln(1/x_{II}) - R \sum C_{III} \ln(1/x_{III}) \quad (15)$$

$$\Delta G_{I-II} = \Delta H_{I-II} - T\Delta S_{I-II} = \Delta h_{I-II} - T\Delta s_{I-II} \quad (16)$$

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