surface and on the concomitant controlled change in the strength of chemisorptive bonds[4,5,7]. They also reveal a surprisingly simple relationship between the catalytic activity and the catalyst work function, measured *in situ* and, for the first time, varied at constant reactant composition. This relationship quantifies the importance of the electronic factor in heterogeneous catalysis.

The continuous-flow, atmospheric-pressure experimental apparatus using on-line gas chromatography, mass spectrometry and infrared spectroscopy for reactant and product analysis has been described in previous papers[1-5] where catalyst-film preparation and characterization details are also presented. The porous catalyst films that we use have thickness of ~5 μm, surface areas of 100–1,500 cm^2 and are supported on a solid electrolyte of area 2 cm^2. The three-electrode system (Fig. 1) used with the current-interruption technique permits accurate measurement of the ohmic-drop-free catalyst potential V_{WR} relative to a standard reference air electrode, and of the catalyst overpotential ΔV_{WR} (refs 4, 5) which has[1,5] a key role in the NEMCA effect. The catalyst work function was measured using a Kelvin probe (Besocke/Delta-Phi-Elektronik) with a 2.5-mm-diameter gold-grid vibrating electrode placed ~500 μm from the catalyst surface (Fig. 1). We used two types of solid electrolytes—fully stabilized zirconia (8 mol% Y_2O_3 in ZrO_2), an O^{2-} conductor, and β″-Al_2O_3, a Na^+ conductor.

Figure 2 shows that the change in the work function of the gas-exposed (that is, catalytically active) surface of the catalyst electrode is $e\Delta V_{WR}$, both under closed- and open-circuit conditions. In the former case V_{WR} was varied by changing the polarizing current with the catalyst exposed to air, whereas in the latter the catalyst was exposed to NH_3/O_2/He and CO/O_2/He mixtures. This result has been predicted theoretically[1,3-5] and stems from the spatial uniformity of the Fermi level throughout the conductive catalyst film, including the catalyst–gas and the catalyst–electrolyte interfaces. Thus the e.m.f. of solid-electrolyte cells with electrodes made of the same material provides a direct measure of the difference in work function between the working (catalyst) and reference gas-exposed electrode surfaces.

Figure 3 shows the effect of catalyst work function change on the rate of the platinum-catalysed ethylene oxidation to carbon dioxide and on the corresponding activation energy. Above a threshold work function value $e\Phi^*$, the catalytic rate increases exponentially with $e\Phi$. We have also observed threshold $e\Phi^*$ values in some other studies[1,4,5]. Their physical origin is not clear and could be related to the form of the distribution of the density of states around the Fermi level. Lateral interactions have been invoked to explain similar abrupt variations of the heat of adsorption with $e\Phi$ in ultra-high-vacuum studies[13]. Increasing $e\Phi$ weakens the platinum-chemisorbed oxygen bond, the cleavage of which is rate limiting[4], and causes a decrease in activation energy comparable to $e\Delta\Phi$. We note that the observed $e\Delta\Phi$ changes, which are due to spillover (spreading) of oxygen anions (very probably O^-; refs 1, 4, 14) at the catalyst surface, require only a small coverage of anions (<5% of a monolayer, as calculated using the Helmholtz equation with an ion radius of 0.17 nm) which does not affect significantly the coverages of covalently bonded species[4]. When β″-Al_2O_3 is used as the solid electrolyte a qualitatively similar behaviour is observed, that is, the rate of carbon dioxide formation decreases exponentially with the decrease in the work function resulting from the spillover of Na^+ onto the catalyst surface. Thus at 290 °C, and oxygen and ethylene partial pressures of 5 kPa and 0.02 kPa respectively, a 70% reversible decrease in reaction rate is observed when the catalyst potential is decreased by 400 mV. This rate decrease is 48,000 times higher than the rate of supply of Na^+.

The catalytic reactions studied so far (Table 1) fall into two groups depending on whether their rate increases or decreases exponentially with increasing $e\Phi$. In the former case of 'electrophobic' reactions[5] the rate-limiting step of the catalytic process involves cleavage of a metal/electron-acceptor adsorbate bond. In the latter case of 'electrophilic' reactions[5] cleavage of an intra-adsorbate bond of an electron-acceptor adsorbate is rate limiting. The observed dependence of catalytic rates (exponential) and activation energies (linear) on catalyst work function provides strong evidence that, as previously proposed[1-5], NEMCA is a long-range electronic effect. Long-range effects have been predicted theoretically for some adsorbates on metal surfaces[15] and have been invoked to explain the dependence of the sticking coefficient of oxygen on alkali-doped germanium, which was found to depend exponentially on the alkali-induced $e\Phi$ change, regardless of alkali type[16]. 'Short-range' explanations cannot yet, however, be entirely ruled out. The use of temperature-programmed desorption[17] and of scanning tunnelling microscopy[18] as an atomic-scale $e\Phi$ probe could further elucidate this point.

These results show that the NEMCA effect[1-6] is not limited to a particular metal catalyst or solid electrolyte and underline the importance of the electronic factor in heterogeneous catalysis by directly establishing the relationship between catalyst work function and catalytic activity. This exponential relationship seems to apply to all metal-catalysed reactions. Metal crystallites on supports may behave similarly and scanning tunneling microscopy[18] could be useful here also. Our results also show that solid-electrolyte cells can be used to conveniently control catalyst work function and to influence catalytic activity and selectivity in desirable directions. □

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Estimates of Antarctic precipitation

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PRECIPITATION fluctuations over Antarctica are a potentially important contributor to variations in global sea level[1,2]. Direct measurement of precipitation is, however, fraught with practical difficulties[3]. Two methods may be used to calculate indirectly the net flux of water (precipitation minus sublimation rate) to the surface of Antarctica: the first uses values of poleward atmospheric moisture transport obtained from climatological studies, and the second uses glaciological measurements of the accumulation rate. Here I show that the two estimates so derived are in marked disagreement for the entire continent but concur for the interior area between 80° S and the pole. I conclude that the large discrepancy near the coast is due to a calculated poleward moisture transport that is smaller than the actual value, as a result of

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TABLE 1 Annual zonal averages of meridional moisture transport and its convergence

Transport ($kg\ m^{-1}\ s^{-1}$)			Convergence ($kg\ m^{-2}\ yr^{-1}$) $[\bar{P}-\bar{E}]$			
Latitude °S	PO	HR	Latitude Belt °S	PO	HR	BR
50	−17	−10.5	50–60	290	160	452
60	−10	−6.7	60–70	270	133	322
70	−3	−3.7	70–80	90	97	183
80	−1	−1.6	80–90	60	77	64
90	0	0	70–90	82	92	153

Negative meridional transports are directed poleward. Square brackets denote a zonal average. $1\ kg\ m^{-2}\ yr^{-1}$ is equivalent to $1\ mm\ yr^{-1}$. PO, 10-year atmospheric averages from Peixoto and Oort[4]; HR, 9-year atmospheric averages from Howarth[5] and Howarth and Rayner[6]; BR, somewhat outdated climatological surface-based averages from Baumgartner and Reichel[8].

deficiencies in evaluating the effects of cyclones and surface winds at the coast. Improvements in the climatological atmospheric database should therefore make possible reliable estimates of Antarctic precipitation variations.

The budget equations used in the calculations based on atmospheric water balance and on glaciological accumulation measurements are, respectively[3],

$$\langle \bar{P}-\bar{E}\rangle = -\langle \nabla \cdot \mathbf{Q}\rangle - \left\langle \frac{\partial \bar{W}}{\partial t}\right\rangle \quad (1)$$

$$\langle \bar{P}-\bar{E}\rangle = \langle \bar{B}\rangle + \text{drift snow loss} + \text{run-off} \quad (2)$$

The angle brackets represent a spatial average, the bar denotes a time average, P precipitation, E evaporation/sublimation, B the accumulation rate and $\bar{W}$ the precipitable water. $\mathbf{Q}$ is the horizontal moisture-transport vector and is defined as

$$\mathbf{Q} = \int_0^{p_s} (q\mathbf{V})/g \ \mathrm{d}p$$

where q is specific humidity, $\mathbf{V}$ the horizontal wind vector, g the acceleration due to gravity and p the pressure. The integration is carried over the depth of the atmosphere from the surface ($p = p_s$) to the top ($p = 0$). W is given by $\int_0^{p_s} (q/g)\ \mathrm{d}p$. Because climatological conditions are of interest, results are averaged over a decade or more. For annual averages the second term on the right-hand side of equation (1) is negligible[4].

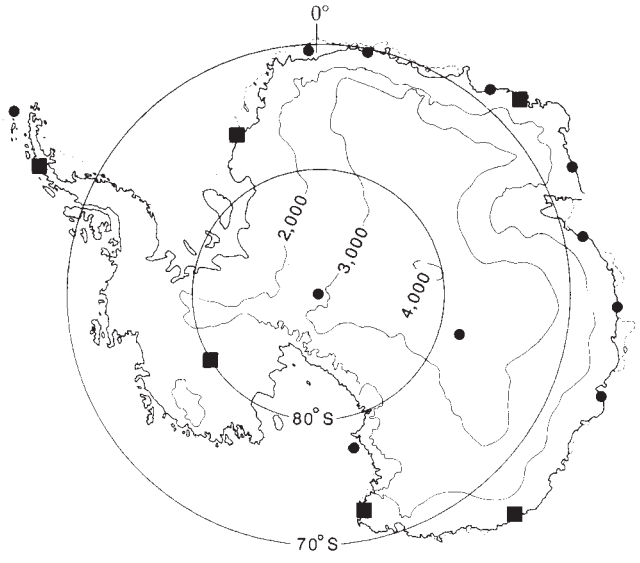

FIG. 1 Antarctic radiosonde stations, the data from which primarily determined the high-latitude atmospheric moisture fluxes obtained in ref. 4 and in refs 5, 6. Filled circles denote sites contributing to both studies and filled squares to only one. Notice the measurement gap along the West Antarctic coast (to the left); no upper-air observations have been collected at Byrd Station (80° S) since the early 1970s. Thin continuous lines are elevation contours in metres, starting at 2,000 m.

Multiannual estimates of the poleward atmospheric moisture transport in high southern latitudes (which allow the first term on the right side of equation (1) to be evaluated) are available from the global analysis of Peixoto and Oort[4] (1963–1973) and the composited hemispheric analyses of Howarth[5] (1973–1978) and Howarth and Rayner[6] (1980–1984)—see Fig. 1. The data in ref. 4 were based on radiosonde observations and the data in refs 5 and 6 were based on numerical syntheses by the Australian Bureau of Meteorology of all available observations, such as data from radiosondes, aircraft and satellites. Each data set contains systematic errors and has particular strengths and weaknesses[7].

Table 1 compares the north–south (meridional) components of the moisture transports given in refs 4–6. Out over the Southern Ocean (50°–72° S) where the radiosonde network is extremely sparse, the transports differ substantially. Close to and over Antarctica (~72°–90° S), the two sets of values are very similar. The $\bar{P}-\bar{E}$ values calculated from equation (1) also illustrate the large atmospheric discrepancies over the Southern Ocean and much better agreement over Antarctica. There are large differences between the atmospheric $\bar{P}-\bar{E}$ estimates and the obsolete surface-based values of ref. 8, except for the 80°–90° S latitudinal belt.

As will be discussed below, the accumulation contribution is by far the largest term on the right-hand side of equation (2). The recent comprehensive accumulation analysis of Giovinetto and Bentley[9] has been chosen for this term. By careful selection among existing data sets[10], they obtained slightly smaller rates over 90% of the continent (interior parts) and larger rates over the coastal margins. Overall their values for Antarctica are ~8% smaller than most previous estimates. Because of the emphasis on mutually consistent observations and data obtained with improved measurement techniques, I regard this analysis as the best long-term-average description of the annual accumulation rate so far.

To complete the surface-based estimate of $\bar{P}-\bar{E}$ from equation (2) the drift snow transported across the coastline and the liquid run-off into the ocean must be evaluated. Loewe[11] has done a careful analysis of drift snow transport over both Greenland and Antarctica, and found that it becomes a progressively smaller component of the ice-sheet mass budget as the area increases. The liquid run-off is small, and I have used the estimates in ref. 12.

In Table 2 I compare the annual average $\bar{P}-\bar{E}$ values derived from surface-based and climatological atmospheric observations for the entire continent and for the latitudinal belt 80°–90° S. The drift snow loss and run-off for Antarctica were obtained as described above. The values for 80°–90° S were calculated as follows. Because this area is entirely contained within the continent (Fig. 1) and spans regions with generally low accumulation rates (almost everywhere $<15\ mm\ yr^{-1}$), the drift snow loss should be small and is approximated by zero. As the summer air temperatures are almost everywhere continuously below the freezing point, the run-off must be zero[13]. Table 2 shows for the entire continent that the atmospheric estimates of $\bar{P}-\bar{E}$ are only one-third to one-half the size of the surface-based estimation. The somewhat dated[8] (surface) $\bar{P}-\bar{E}$ value for Antarctica is $141\ mm\ yr^{-1}$, slightly smaller than the surface-based estimate in Table 2. For 80°–90° S the atmospheric and terrestrial approaches give similar results. Because the accumulation values are well determined and larger estimates of drift snow loss and run-off would only add to the huge discrepancy between surface-based and atmospheric estimates of $\bar{P}-\bar{E}$ ($155-(80\text{ or }50)=75$ or $105\ mm\ yr^{-1}$), the poleward atmospheric moisture transport

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TABLE 2 Surface-based and atmospheric estimates of $\bar{P}-\bar{E}$ (mm yr^{-1})

Area	$\langle\bar{B}\rangle$	Drift snow loss	Surface run-off	$\langle\bar{P}-\bar{E}\rangle$ from accumulation data	$\langle\bar{P}-\bar{E}\rangle$ from atmospheric data of PO, HR	
Antarctica	143*	8†	0–5‡	151–156	44, 49§	76, 85‖
80°–90° S	82	~0	0	82	60, 77	

PO, Peixoto and Oort, ref. 4; HR, Howarth and Rayner, refs 5, 6; BR, Baumgartner and Reichel, ref. 8.
* ref. 9.
† ref. 11.
‡ ref. 12.
§ Method (1): Value for PO taken directly from ref. 22. Value for HR calculated from PO value by multiplying by ratio of HR meridional moisture transport convergence for 70°–90° S and PO value (from Table 1).
‖ Method (2): Calculated from $\bar{P}-\bar{E}$ for 70°–90° S in Table 1 by multiplying by BR ratio of $\bar{P}-\bar{E}$ for Antarctica and $\bar{P}-\bar{E}$ for 70°–90° S (141 mm yr^{-1}/153 mm yr^{-1} = 0.922).

at the coast must be responsible for the difference.

Possible factors are systematically low water-vapour values and grossly underestimated transports. Flight tests[14] of two types of radiosonde humidity elements showed that relative humidity measurements during night-time were systematically lower than the actual values by fractional amounts of 0.10 to 0.15. With most Antarctic precipitation falling during and around the polar night[3], this systematic error is approximately representative for Antarctica, and cannot account for the discrepancy.

There are two studies that demonstrate that atmospheric and surface-based estimates of $\bar{P}-\bar{E}$ can be in close agreement. First, Masuda[15] calculated the moisture transported across 70° S from 1979 atmospheric analyses by the European Centre for Medium-Range Weather Forecasts; for that year the atmospheric circulation over the Southern Ocean was monitored substantially better than either before or, to a lesser extent, since[16]. His 1979 $\bar{P}-\bar{E}$ value for Antarctica (using method (2) in Table 2) was 136 mm yr^{-1}, only 15–20 mm yr^{-1} less than the new long-term-average surface-based estimate. Second, I have derived[3] the 1972 atmospheric water balance for a part of East Antarctica chosen so that the available radiosonde observations accurately monitored the poleward moisture transport across the coast. In Table 3 the atmospheric values are compared with the modern surface synthesis in ref. 9. Even though interannual variability is not included, the two sets of estimates are seen to agree within the limits of error.

The probable causes of the anomalously small calculated poleward moisture transports at the Antarctic coast can be identified. As noted by Masuda[15], zonal averages of the poleward transport can be broken down into transport contributions from the transient eddies, the stationary eddies and the mean north–south air motions; it is the convergence of the poleward transport that yields $\bar{P}-\bar{E}$ values in equation (1). He found that the apparently reliable 1979 poleward transport across 70° S (discussed above) was dominated by the transient eddies (92% of the total), with the other two components nearly cancelling (+21% and −13%, respectively). Masuda compared transport components for the climatological analysis of Nakamura and Oort[17] (closely related to that in ref. 4) with those for 1979. The biggest differences were that both the transient eddy and mean meridional transports increased in his study by about the same amount, such that $\bar{P}-\bar{E}$ for 70°–90° S was four times larger.

Masuda's results are consistent with the present work. First, underestimating transient-eddy transports leads to an underestimate of the poleward transport at the coast but would have little impact in the interior, because the transient-eddy transport is a large fraction of the total at the coast but decreases to small values at high elevations[3,18]. Second, the characteristics of the dominant low-level part of the mean north–south air motions, namely the surface-wind regime[19], lead me to suspect that the inability to diagnose correctly this shallow and spatially variable feature[20] is important for mean transport determination at the coast[21] but negligible in the interior. Detailed exploration of this topic is, however, beyond the scope of this report.

Although recent climatological atmospheric analyses cannot be used to infer precipitation changes over Antarctica, and thus determine their impact on global sea level, results from studies for restricted areas and limited times indicate that improvements to the database and analysis methodology[15] would make this monitoring possible. An effective enhancement would be to eliminate the upper-air data gap along the coast of West Antarctica. □

TABLE 3 East Antarctic $\bar{P}-\bar{E}$ values

Source	$\langle\bar{P}-\bar{E}\rangle$ (mm yr^{-1}) 0°–110° E 68.4°–78.2° S	0°–55° E 69.3°–76.8° S	55°–110° E 67.2–79.8° S
Moisture budget, ref. 3 (value ±1 standard error)	105 ± 23	131 ± 43	105 ± 23
ref. 9	108	109	108
ref. 23	144	133	151

Moisture budget, 1972 atmospheric water balance. The data in refs 9 and 23 are multiannual accumulation analyses. The values inferred from the outdated accumulation analysis in ref. 23 are presented for comparison with previous work in ref. 3. Results are given for the entire domain and two subsections.

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